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Extended Abstracts

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MINERALOGIA POLONICA – SPECIAL PAPERS
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Igor BROSKA[1], Pavel UHER[2]

THE ROLE OF TYPOMORPHIC ACCESSORY MINERALS IN THE VARISCAN GRANITIC SUITES OF THE WESTERN CARPATHIANS

Abstract: Acessory minerals giving principal information to the granite typology and important for the granite discrimination can be named as „typomorphic". In the Western Carpathians, I-, S- and A-type granite discrimination is significantly covered by zircon, monazite, allanite, apatite, xenotime, Fe-Ti oxides and tourmaline distribution as well as their compositional and morphological characteristics. The presence of garnet (almandine-spessartine), monazite, xenotime, low-S/L-type zircon locally Mn-bearing apatite and Nb-Ta-Ti phases (columbite-tantalite, Nb-Ta rutile) are typical for the S-type granite suite. On the contrary, abundant apatite, allanite, magnetite, and titanite is characteristic for the I-type granite. Increasing Fe content in apatite, Fe^{3+}-rich allanite, Hf-poor D,P_5-subtype zircon are typical for the hypersolvus A-type granites, whereas subsolvus A-type granite contains monazite, zircon with higher Zr and Y concentrations and P_1, P_2 subtype morphology. Locally, Y-Nb-(Ti) phases (mainly fergusonite) are present in the A-type granites. Tourmaline (schorl to foitite), locally cassiterite, topaz and Nb-Ta-W phases (columbite, wolframite) are characteristic mainly for the specialized S-type granites, less for the derivates of S-type granites.

INTRODUCTION

The investigation of granitic rocks s.s. attracts attention of geoscientists for their close connection with tectonic and geodynamics of any orogenesis and geological evolution of given area. Granitic rocks are window to the interior of the Earth crust giving chance to understand the PTX conditions in time and space for many possibilities of their petrogenetic investigations and geochronological datings. They are important tool for the reconstruction of the main stages in the development of lithosphere.

Although granitic rocks in the Western Carpathians cover relatively small area, their compositional and age variability is widely used for the research of pre-Alpine crystalline basement formation and, of course, also its magmatic and post-magmatic evolution. This contribution offers the short overview on granite typology of the Western Carpathians and points to the importance of selected (typomorphic) accessory minerals for their discrimination.

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GRANITIC SUITES IN THE WESTERN CARPATHIANS

Variscan granites in the Western Carpathians (mainly Slovakia) form a heteregoneous assemblage of rocks differing in their age, source and tectonic position. There is also variability in their post-Variscan metamorphic history; the granites of Veporic unit have been overprinted during Alpine orogenesis, others shows significantly lower level of the metamorphic overprint. The Variscan plutonic rocks of Western Carpathians can be divided into several suites originated from orogenic to post-orogenic stage dated back in relation to the main Upper-Devonian/Lower Carboniferous Variscan collision and Middle/Upper Carboniferous post-collisional phases. All events took place within time span around 150 Ma (Petrík, Kohút 1997; Petrík et al. 2006).

Each granitoid suite is composed of several types of granitic rocks, geochemically and mineralogically reflecting the character of the source rock and physico-chemical condititions of home geotectonic environments, where individual suite originated. In the Meso-Variscan stage the S-, I- and S/I- type orogenic suites has been defined with dominancy of S-type, in the Neo-Variscan stage with dominancy of I-type granites. Post-orogenic granite suites has been developed as the Permian A-type granite (in sense Whalen et al. 1987) and specialized S-type granites (Uher, Broska 1996, Broska, Uher 2001). The primary discrimination of the plutonic Variscan rocks into several genetic granitic suites has been significantly realised using the accessory mineral paragenesis controlled by geochemistry of the main and trace elements (Tab. 1, Fig. 1).

Table 1. General scheme of granite typology in the West-Carpathians crystalline basement

Orogenic granites		
collisional	**post-collisional granites**	**Post-orogenic granites**
S-type	I-type	A-type
I-type	S-type	specialized S-type
	I/S type	

THE ROLE OF TYPOMORPHIC ACCESSORY MINERALS FOR GRANITE DISCRIMINATION

Zircon morphology is very important factor for the recognition of granite suites mainly due the Pupin morphological classification. Zircon from the S-type granites form low S subtypes (S_7, S_{11}, S_{12}, S_{13}) with mean point I.A = 294, I.T = 282, the I-type zircons typically represent forms S_{12}, S_{13}, S_{17} a S_{18}, the hypersolvus A-type granite posses zircons of D and P_5 subtypes and zircons from subsolvus A-type granites characterise G_1, P_1, P_3 subtypes. Zircon composition, especially Zr/Hf ratio, Y, REE, U and Th contents are tracers of magmatic to post-magmatic evolution, mainly fractionation of the parental rocks. High Zr/Hf (50 to 70) and low Y, REE, U and Th concentrations of zircon in high-temperature hypersolvus A-type granites are in contrast to subsolvus A-, I- and especially S-type granites with lower the Zr/Hf (35 to 50). Highly fractionated specialized S-type leucogranites and granitic pegmatites show Zr/Hf <30 and Y+REE and U+Th in zircon ≥0.5 wt.% (Uher, Broska unpubl. data). REE distribution in granitic rocks is linked with accessory minerals, such as monazite and allanite but significantly the disttribution of LREEs is controlled also by apatite, titanite and HREE by xenotime, garnet and zircon. The allanite - monazite stability relationship in granites is important for the recognition of the S/I-type granite suites and is very distinctly developed in the West-Carpathian granites (Broska, Uher 1991). The presence of monazite or allanite is explained by different solubilities of these minerals in relation to the aluminium saturation index of the host granite, as well as to its fO_2. Allanite crystallize preferentially in metaluminous (or slightly peraluminous), rather than in peraluminous granitic rocks with higher fO_2 or primary water contents (Petrík, Broska 1995). A higher concentration of allanite is typical for the early magmatic differentiated I-type granites but these fractionated granites contain also monazite. On the other hand, high concentrations of monazite are present in early differentiations of the S-type granite suite, locally accompanied by primary allanite.

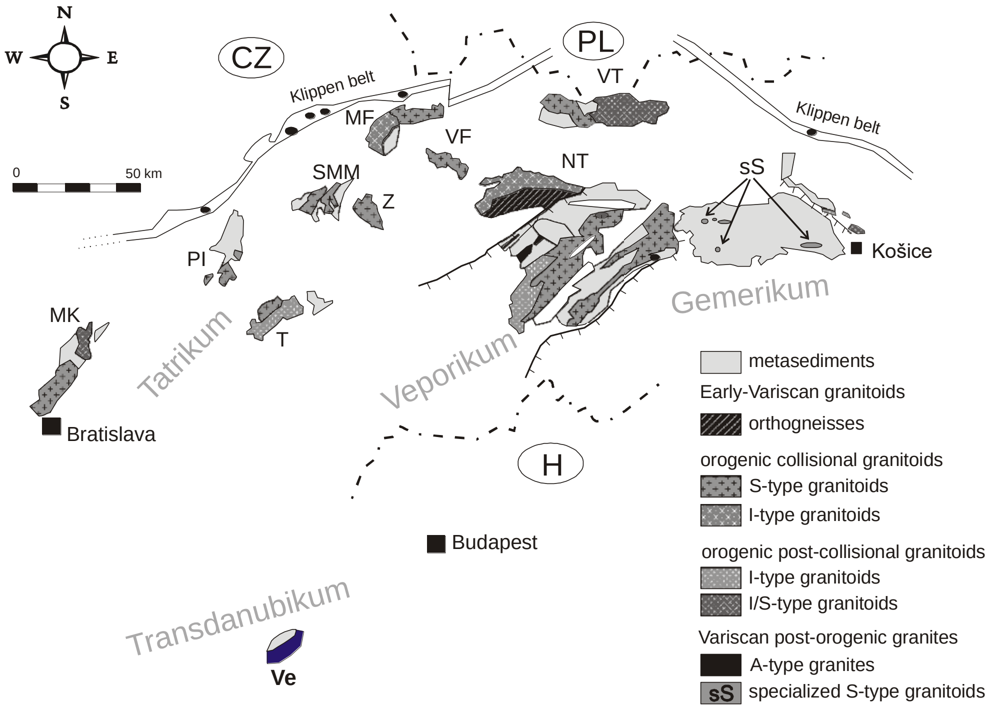

Fig. 1. Distribution of principal granite suites in the Western Carpathians. Explanation: MK-Malé Karpaty; PI- Považský Inovec; T – Tribeč; SMM- Suchý a Malá Magura; MF- Malá Fatra; VF-Veľká Fatra; NT- Nízke Tatry; VT-Vysoké Tatry

Strong differences in composition of accessory minerals during differentiation of silicic magmas in time and space were described by Wark & Miller (1993) can be expected everywhere, also in the Western Carpathians. Early magmatic monazite shows higher content of huttonite molecule, on the other hand, later monazite decrease of huttonite component. Cheralite component in monazite increases in strongly peraluminous evolved granites. Specific subsolidus influx of As-bearing fluids caused formation of monazite-gasparite and xenotime-chernovite s.s. in A-type rhyolites (Ondrejka et al. 2007). Allanite composition show also some variability. In comparison to allanite from the S-type granites, allanite from the I-type granites contains lower ferric contents (Broska et al. 2000). Secondary allanite is usually enriched in iron.

Other important hosts for the REEs include apatite, titanite, xenotime and zircon. Apatite from S-type granitoids posses slightly increased Mn in comparison to I-type because of enhanced entering of divalent Mn for Ca in low oxygen fugacity melts (Belousova et al. 2001; Sha, Chappell 2003, Broska et al. 2004). Also sulphur is typically increased in apatite from the I-type granitic rocks but apatite in the A-type granitic rocks has higher total Fe concentrations. Differences are also in REE concentrations in the anion site of apatite composition. In the granitic rocks of the Western Carpathians, xenotime-(Y) is present both as a late-stage magmatic mineral, and as a secondary post-magmatic phase. Magmatic xenotime occurs with monazite mostly in the S- and A-type granites and displays minor compositional zonation involving Si, Th and U. The source of elements for the formation of secondary xenotime-(Y) in the granitic rocks results from leaching of P and (Y + REE), mainly from zircon (Michalik et al. 2000) and apatite (Broska et al. 2004). Monazite is present in subsolvus A-type granite, whereas it is rare in hypersolvus A-type granite.

Primary titanite occurs only in the early differentiates of the I-type suite as a late magmatic mineral. It precipitates at increase of oxygen fugacity (log $fO_2 \sim -13$). The REE content in titanite is similar to apatite very low and show similar chondrite-normalized pattern.

A specific accessory Y-Be-silicates (gadolinite – hingganite s.s.) were recently determined in the hypersolvus to transsolvus A-type granites (Turčok and Upohlav granites; Uher and Ondrejka, unpubl. data). They probably originated during a late-magmatic to subsolidus stage of the Y, HREE-rich A-type granite evolution.

Special importance shows the presence of tourmaline (schorl to foitite) in granites indicating the increase of B-rich volatiles in magmas. Tourmaline is typical in the specialized S-type granite suites in the Gemeric unit, localy occurs in leucogranites (Gaweda et al. 2002) of S or I/S affinity . Such granites in the most differentiates varietes are often able accumulates some rare metals (Sn, W, Nb, Ta, Li). Tourmaline is in the specialized granite suites in the Gemeric Unit.

Rare Nb-Ta oxide minerals occur usually in highly fractionated leucogranites of the S- and A-type and as well as in the granitic pegmatites (S- and I-type) of the Western Carpathians (Uher 2005). Nb-Ta rutile, Ti-rich ixiolite and ferrocolumbite locally occur in the S-type leucogranites (Tribeč Mountains, Uher and Broska 1992; Považský Inovec Mountains, Chudík et al. in prep.), whereas Nb-Ta-Ti-W assemblage (mainly ferrocolumbite to manganocolumbite, qitianlingite?, Nb-rich ferberite, Nb-Ta rutile) are typical for the specialized tin-bearing S-type granites in the Gemeric Unit (Uher 1995). A specific Y-Nb-(Ti) mineral assemblage (fergusonite, euxenite?) was determined in hypersolvus and subsolvus A-type granites; it reflects high Y, REE and Nb abundance and relatively high fractionation level of the A-type post-orogenic granitic suite in the Western Carpathians (Turčok and Hrončok granites; Uher & Ondrejka, unpubl. data). Nb-Ta oxide minerals (columbite-tantalite, ferrotapiolite, pyrochlore-group minerals etc. are typomorphic accessory phases also for S- and I-type granite-related pegmatites (Uher, Broska 1995; Uher et al. 1998a, b).

The comparative data with the main features of typomorphic REE-bearing accessory minerals, zircon and Nb-Ta mineral phases for the discrimination of granites is presented in Tab. 2.

Table 2 Characteristics of accessory minerals in the S- I- and A-type granite suites

	S-type		I-type		A-type	
mineral /stage	Ortho-magmatic stage	late-magmatic/ post-magmatic stage	Ortho-magmatic stage	late-magmatic/ post-magmatic stage	Ortho-magmatic stage (hypersolvus granites)	late-magmatic/ post-magmatic stage
apatite	high Mn and Fe	not common	low Mn, high S, more Cl	low Mn	high Fe	rare
allanite -(Ce)	low Fe^{3+}	absent	high Fe^{3+}	absent	high Fe^{3+}, high REE	(?)
magne-tite	rare	absent	high Ti	stoichiometric pure	rare	stoichiometric pure
monazite-(Ce)	high huttonite	more cheralite (?)	absent	cheralite type	present in subsolvus granites	rare
xenotime-(Y)	present	present?	rare	absent	present	present
titanite	absent	absent	absent	high Fe^{3+}	absent	absent
zircon	L and low S subtypes	G_1 subtype, lower Zr/Hf ratio, more metamict	high S subtypes	G_1 subtype	low Hf; D, P5 subtypes	high Hf; P1, G_1 subtype
Nb-Ta phases	absent	rare Nb-Ta rutile, ferrocolumbite, Ti ixiolite	absent	absent	absent(?)	ferguso-nite-(Y)

CONCLUDING REMARKS

Our knowledge on accessory mineral character in granitic rocks gives a benefit to the recognition of the process forming the granites both in orogenic belts and in the anorogenic positions (Kohút 2002). Basically the development of plasma source mass spectrometric techniques and further development of laser Raman and infrared spectroscopy, high-resolution transmission electron microscopy, special X-ray techniques will give a new impuls for the further discoveries in accessory mineral (Poitrasson et al. 2002). Recently the development of different geochronological investigations including along conventional also chemical in situ datings illustrate the great potential of geochronological information locked in different accessory minerals. The geodynamic research will in the future strongly benefit from improved understanding of internal mineral textures, and mechanisms of element mobility within crystals (Poitrasson et al. 2002). Acessory minerals giving principal information to the granite typology and discrimination of the environment can be named as „typomorphic".

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REAL OUTCROPS, PRECISE MACHINE DATA AND MODELS FOR GRANITE GENESIS: WHERE DOES CERTAINTY COME INTO IT?

Abstract: The origin and the emplacement of granitic rocks remains the focus of intense research. That research seems to increasingly rely on machine-based studies as support for field work lessens and granite histories are encapsulated in, e.g., zoned minerals. Petrography and other whole-rock data are more than just a means of classification; they have key roles to play in the understanding of granites. Future certainty probably lies where it always did – on the outcrops, on the maps relating those outcrops to one another and in truly representative samples.
Keywords: Granite, whole-rock, Karkonosze granite, Thorr granite, Strzegom granite

INTRODUCTION

In this age of ion microprobes, laser ICP-MS and the in-context, precise measurement of O and Hf in the smallest granite zircons, granite itself somehow eludes precision. How did a particular granite magma originate, what did it happen to mix with and when did it crystallise? Lasting certainty comes only grudgingly. Is the way in which samples are collected, and data used, part of the reason?

At first sight, many granite outcrops appear uniform. However, enclaves with compositional reaction halos, banding more or less cryptic and ghostly schlieren are everywhere. The weather-bleached outcrop should be, in the mind's eye, the rock as polished cladding or paving stone - in the rain. If not, the chain of evidence linking the field geologist, the petrographer and the micro-chemist will not always be intact as zoned minerals replace whole-rocks?

Where a granite intrusion as a whole is the focus, how should the rock variety characterising all scales be better addressed – at reasonable cost? Should replication be more common? How often, for instance, are adjacent rock samples analysed to test the geological worth of analytical decimal places? The sample itself, in its varying mineralogy, size and unmapped place, may be compromising any precise laboratory derivative down the line - far more than does a bit of weathering.

Whole-rock granite studies lead to imprecise results – recognised as such most obviously in isotope dating. The modern dating of individual zircons can be very precise – but what does that precision mean in the context of a large heterogeneous granite body cooling and crystallising heterogeneously? The analytical methods, ever more sophisticated, rely on everyday geological skills the appreciation of which is, perhaps, tending to be lost – and expensive data undervalued. This paper is an attempt, using a few Polish and Irish examples, to show why.

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PETROGRAPHY – CRUCIAL STARTING POINT

The sample collected, analysis starts with petrography commonly involving the counting of a mode. For some time, modal analysis has been a cheap, effective, if time consuming way to classify granite compositions - and to provide a compositional framework within which to place selected samples. However, the common porphyritic granite has never proved easy. In published point-counted modes, numbers of points counted are typically given - but usually without mention of the area over which counting took place. As an adequate sample of a structure-less rock should be 100 times the area of the largest grain at least (Larsen, Miller 1935; see also Chayes 1956), accurate modes of porphyritic granites strictly require large slabs or photographs. Could it be that the mode-based classification of granites (LeMaitre 2002) suffers a bias driven by tedium? However, modal analysis remains appropriate for granite and is a method which automation, in some inventive way or another (e.g., Hill et al. 1993), could make less onerous.

Modes do more than classify. Whitten (1957 and later) long ago demonstrated the potential of modal analysis in a study of the Thorr Pluton in Ireland. In this granite, Pitcher (1953) had mapped a ghost stratigraphy defied by country-rock enclaves. Whitten using raw modal data, and derivative trend surfaces, revealed a cryptic mineralogical stratigraphy reflecting the mapped ghost stratigraphy extending into apparently homogeneous rock. Though controversial questions surround any fundamental country rock role in the granite petrogenesis at the present level, this study did show that modal analysis keyed to field geology can provide challenging insights – and provide a reference for future sampling.

CHEMICAL AND ISOTOPE ANALYSIS OF GRANITES

To completely reflect granite variability in terms of chemistry would require some geographic strategy involving more than a sample or two – perhaps, as in Whitten's work, a sampling grid. Intuitively, the sample adequately reflecting the texture and the grain size of a coarse porphyritic granite could be the cubed analogue of that required for modal analysis - ca 20-25 cm^3. How often is anything like such used? The payback from countless granite XRF analyses may not always have been all that it could have been. Of course, large samples may not reveal the detail.

Similar questions arise even more often in the case of whole-rock isotope analyses, especially whole-rock isotope analyses. The unique value of granite whole-rock Rb-Sr data lies in the fact that they describe mapped rock, the essential granite components and, as the data reflect time, the samples may be definably linked. Analysis of ca 25 kg granite samples was commonly recommended - to balance daughter-isotope migrations in and out. Such a sample would compare with the 20-25 cm^3 sample appropriate for XRF analysis of porphyritic granite. However, though it has been demonstrated many times that small samples may yield younger Rb-Sr ages, many studies do not explicitly acknowledge using such. So-called whole-rock ages may not always compare. With adequate samples, patterns of Rb-Sr whole-rock data could also act as a guiding template for the evaluation of XRF and other data.

Rb-Sr whole-rock data from two quarries in the Karkonosze Granite support two ca 328 Ma ages (Duthou et al.1991 and Fig. 1). Initial ratios discriminate between porphyritic granite (0.7056) and granite with biotite schlieren (0.7064) – but not within error. Some additional data from between 200-1000 metres in core (opus cit) suggest compositional changes at depth; some falls below both quarry isochrons on Figure 1. Horizontal contacts separating granite varieties have been noted on outcrop (Mierzejewski 1982). How might a variable granite body such as this, layered perhaps on every scale, best be sampled? The few data involved here are from just three sites that lie only 5 km apart along an east-west traverse. Because they can be spatially related, these data begin to characterise the components of a large intrusion. A template for further study is partially revealed that would give added value to other types of data if obtained from the same samples.

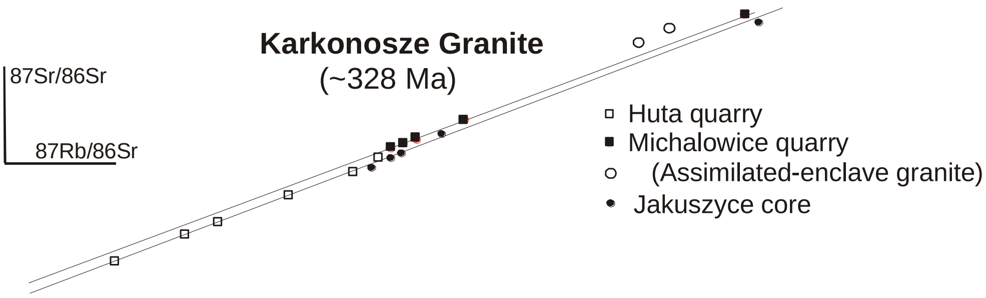

Fig. 1. Rb-Sr data for the Karkonosze granite, Sudetes, Poland (based on the figure in Duthou et al. 1991).

Sample size and rock chemistry are not always independent. A ca 480 Ma whole-rock Rb-Sr isochron age (Pankhurst et al.1976), long deemed to date crystallisation in the Caledonian Ox Mtns Granodiorite, Ireland, has only recently been replaced by a much younger U-Pb zircon age of 412 Ma more appropriate to the geological context (Chew, Schaltegger 2005). The Rb-Sr age, based on large samples, involved only low Rb/Sr samples. In this case, the age is wrong – or is it? The older isochron may actually date the source. The Thorr Pluton, Ireland provides a comparable example; a poor whole-rock errorchron (O'Connor et al. 1982) is much 'improved' by omitting low Rb/Sr samples (Fig 2). Here is a pattern concerning the role of mantle components that merits more precise examination. In passing, the Thorr example also highlights the importance of data from aplites.

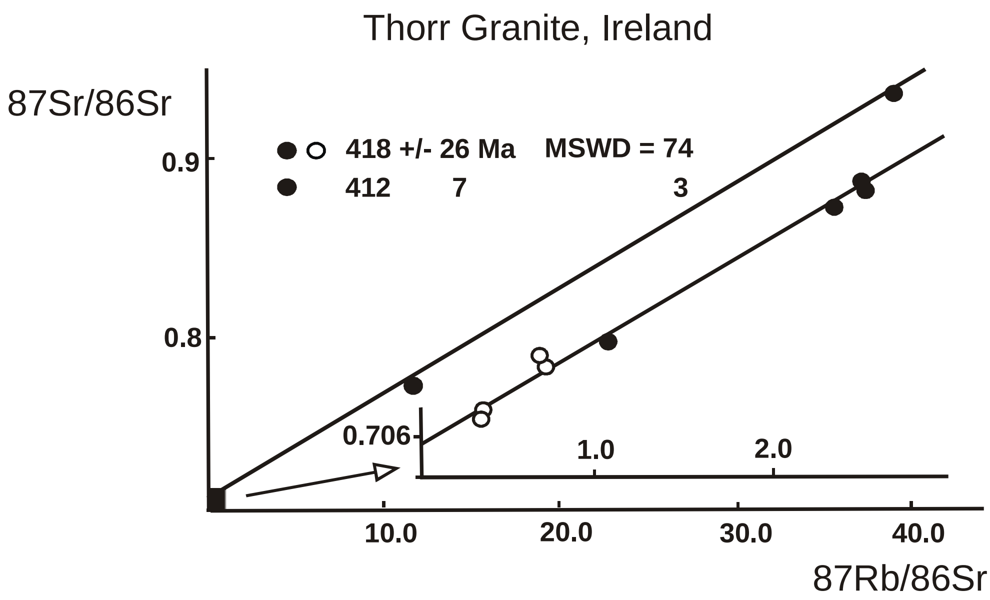

Fig. 2. Rb-Sr data for the Thorr granite, Donegal, Ireland (data from O'Connor et al. 1982).

It is challenging and interesting, and cautionary, that sample size can conspire with chemistry to yield Rb-Sr isochron ages that accurately date intrusion and crystallisation – and both older and younger isochron ages that do not – and that zircon U-Pb ages from the same pluton may be younger or older than apparent Rb-Sr isochron ages. Every age clearly requires petrographic and/or outcrop corroboration. Sampling large areas in multi-component intrusions can also lead to scatter on isochron diagrams or even spurious ages – the Murrumbidgee Paradox (Roddick, Compston 1977) comes to mind. Sampling at varying depths, even within a single granite variety, can do likewise (Mohr 1991) – as in the Karkonosze intrusion (above). In the Murumbidgee intrusion, NSW, the explanation may also be understood in terms of scales of isotope homogenisation (Roddick, Compston 1977) or of protracted cooling (McCarthy 1980) – but there likely other options in this pluton (see Chappell 2003) as in many others.

Though sample size may not be significant in the U-Pb dating of zircons or other minerals, these data too require support from a clearly understood contextual framework. A good example is the composite Strzegom-Sobótka Massif, Silesia, from which a two-mica granite component has given a 326±22 Ma whole-rock Rb-Sr age buttressed by a 324±7 Ma biotite-whole rock cooling age (Pin et al. 1989). Recently, a precise 309 Ma monazite U-Pb age, and a similar 306 Ma xenotime age, were deemed best estimates for time of emplacement (Turniak, Bröcker 2002) of the two-mica rock. The intrusion, at about that time, of a later component of the massif provides a more satisfactory context (Turniak et al. 2005). Exact sample location may also be crucial to understanding the ca 324 Ma cooling (ca 350^{o}C) age; individual intrusions cool at different rates in different places.

The few examples introduced here show that secure analytical answers to the questions granites pose are not easily and quickly found. In the Rb-Sr context, fewer whole-rock samples, but adequately large, might provide secure ages or help to support others. In others, smaller samples taken along defined horizons may do so. In every case, field context and petrography will underpin any certainty – with accurate modal analysis having an initial strategic role to play. Single-mineral studies are, of course, more easily constrained and the data more precise. Might they best contribute detail to a larger-scale whole-rock pattern?

SOME CONCLUDING COMMENTS

- As analytical methods become ever more sophisticated, will focussed granite sample-collection practices inevitably become small-scale only?
- Large type-specimens from major granite body could prove invaluable as long-term sources of equivalent replicate material for multiple/future studies.
- Accessible archives of data would focus future research, avoid wasteful duplication and revalue old data; little of the latter is useless.
- Unprocessed chemical data related to some spatial or other framework may actually be more powerful than initial ratios and other model derivatives.
- The outcrop, in its spatial context, and the thin section, will continue to underpin geological certainty.

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Urs KLÖTZLI [1]

THE SOUTH BOHEMIAN PLUTON: A REVIEW ON A MULTICOMPOSITE BATHOLITH WITHIN THE CENTRAL EUROPEAN VARISCAN BELT

In Central Europe the Variscan orogen is characterized by the presence of large volumes of mostly peraluminous granitoids. The surface exposure can reach more than 30%. Probably the largest plutonic complex is the South Bohemian Pluton (SBP) in N Austria and the S Czech Republic. It covers more than 10'000 km^2 and thus forms the most prominent tectonic unit of the Moldanubian part of the southern Bohemian Massif (Klötzli et al. 1999).

A number of different models for the generation of these huge masses of granitoid rocks have been put forward in the last decades. Evidently the rocks intruded during an episode of late-orogenic HT-LP metamorphism in the Carboniferous. But in contrast to traditional thinking, there is no evidence for the significant addition of mantle melts (for instance by means of crustal under plating) to the crust. Instead the South Bohemian Pluton was probably formed by the increased contribution of radiogenic heat in the thickened crust during the post-collisional stage of the Variscan orogenesis (Gerdes et al. 2000a).

PETROLOGICAL, GEOCHEMICAL AND GEOCHRONOLOGICAL CHARACTERISTICS

This contribution reviews and summarizes the main petrological, geochemical and geochronological characteristics of the three main granitoid suites which are traditionally distinguished and presents a two-stage evolution model:

A) Potassium-rich peraluminous biotite and two-mica granites often showing megacrystic potassium-feldspar crystals constitute the major part of the batholith. These are collectively deciphered as Weinsberg granites (WBG) and Eisgarner granites (EG), respectively. Geochronological data point to intrusion ages of several large magma batches spanning some 15 Ma from 335 to 320 Ma (Klötzli et al. 1999). The geochemical characteristics can best be explained by 30 to 50 vol.-% partial melting of psammitic to pelitic graywackes. There is no evidence for magma mixing or abundant wall rock assimilation in the peraluminous granites (Gerdes et al. 2000). Instead, the geochemical and isotopic data of the WBG suggest individual granite intrusions with internally rather homogenous compositions, for instance each magma

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batch has a different initial $^{86}Sr/^{87}Sr$ ratio (0.7080, 0.7093, 0.7106) but a more or less identical age (Gerdes 2001).

B) Durbachitic to ultrapotassic rocks and minor amounts of granodiorites are termed Rastenberg granodiorite (RGD) and Trebic granite (TG). They form separate and minor intrusions to the E of the WBG and EG. These rocks are hybrid in nature stemming from a mixture of enriched mantle melts and crustal derived melts. They exhibit abundant magma mingling and mixing features. In this respect RBG and TG are not comparable to the rocks of the WBG and EG suites, respectively (Gerdes et al. 2000b, Rene, Stelling 2007). They are somewhat older than the former ones with intrusion ages ranging from 345 to 335 Ma (Klötzli, Parrish 1996). Abundant inherited zircons ages (ca. 620 Ma) point to the reworking of a Cadomian protolith.

C) Fine-grained biotite granites to two-mica granites of the Mauthausen (MGG) and Freistadt (FGG) suites, respectively, form high-level plutons, stocks and dikes. Contacts to the WBG and EG granitoids are sharp and discordant. They form a calk-alkaline and metaluminous suite (Finger, Büttner 1994; Liew et al. 1989). Published intrusion ages are in the range of 320 to 300 Ma (Klötzli et al. 1999).

Basic plutonic rocks are rare and not well investigated.

Additional geochronological information: Throughout the pluton another zircon forming event around 355 to 350 Ma can be detected occasionally (Klötzli et al. 2001). This is interpreted as a widespread early magmatic stage, probably occurring during the compressional phase of the Variscan orogenesis.

CONCLUSIONS

Based on the available petrological, geochemical and geochronological data, a two-stage model can tentatively be invoked to explain the generation of the South Bohemian Pluton:

a) at 355 to 350 Ma: widespread melt generation in the lower crust during collisional tectonics i.e. during nappe emplacement. The melts probably stayed in-situ, as no large igneous bodies were formed;

b) from 345 to 300 Ma: formation of huge masses of granitoid magma and intrusion of the South Bohemian Pluton due to melting by radiogenic heat production in the thickened continental crust. No significant mantle contribution can be detected.

The durbachitic and ultrapotassic rocks of the RGD and TG form an independent intrusion event which does not seem to be directly related to the formation of the other two granitoid suites.

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Milan KOHÚT[1]

OROGENIC GRANITIC MAGMATISM IN THE WESTERN CARPATHIANS – 500 Ma HISTORY: A REVIEW

Abstract: The genesis of the Paleozoic, Mesozoic and Cenozoic granitic rocks from the Western Carpathian is discussed in the frame of European tectonic evolution from the pan-African Gondwana margin to Neo-Alpine back-arc extension within the Carpathians arc. Different granite types well mirrored changing tectonic processes from rifting, subduction and amalgamation of an oceanic lithosphere, through collision with lithospheric thickening, followed by delamination or break-off and finished in extensional tectonic during three orogenic cycles. The recycled continental crust with a contribution from lithospheric mantle plays crucial role at their genesis and compositions, indeed of repeated intrusions of Andean-type calc-alkaline and Himalayan-type peraluminous and/or scarce A-type alkaline granitic magmatism.
Keywords: granitic rocks, tectonics, geochemistry, Western Carpathians

INTRODUCTION

The distribution of various types granitic and associated mafic rocks within the European orogenic belts is associated with distinct thermal and tectonic environments. The Phanerozoic orogenic evolution in Europe is generally related to the pan-African break-up of the Gondwana northern continental margin (Pin, Marini 1993; Matte 2001), followed by the Hercynian continent-continent collision processes (Matte 1986; Franke et al. 1995) connecting with major strike-slip faults, and finished by the Alpine evolution what is connected with Tethys Ocean and/or convergence of the African and Arabian plates and their collision with Eurasia, mainly from the Cretaceous to the recent (Ziegler 1990; Stampfli, Borel 2002). There were recognised following principal stages of the orogenic development within European basement areas: an Early Paleozoic cycle of Gondwana rifting – pan-African stage, followed by subduction and amalgamation of oceanic lithosphere and/or convergence of microcontinents during Eo-Hercynian period; proper collisional tectonics marked by lithospheric thickening with the formation of crustal scale nappe structures and large transcurrent faults – Meso-Hercynian stage; lithosphere delamination (slab breakoff) resulting in rapid post-collisional uplift and/or extensional tectonics – Neo-Hercynian stage. The Alpine orogeny in contrast to previous evolution is generally granite-poor period in Europe, although Late Cretaceous – banatite magmatism originated due to continuous subduction/collision processes forms an important constituent of the Carpathians chain. The Oligocene –

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Miocene magmatism-volcanism as a consequence of back-arc extension associated with the asthenosphere uplift similarly played a significant role in evolution of our territory. Changing tectonic processes produced in the Western Carpathians following orogenic granites: *i)* Late Cambrian – Ordovician felsic magmatites/volcanites now – Older Orthogneisses; *ii)* Devonian – Older S-type high-K peraluminous granites (later transformed into Younger Orthogneisses); *iii)* Lower Carboniferous – Younger S-type peraluminous granites; *iv)* Upper Carboniferous calk-alkaline I-type granites; *v)* Permian post-orogenic subalkaline A and S_s-type granites; *vi)* Late Cretaceous calk-alkaline "banatitic" granites, and *vii)* Miocene calk-alkaline granites.

RESULTS

The Cambrian – Ordovician felsic magmatites/volcanites so called Older Orthogneisses were distinguished from Younger Orthogneisses only recently by means of modern dating methods (CLC TIMS, SIMS, SHRIMP). This type of orogenic magmatic rocks was identified mainly within the polymetamorphosed basement rocks in the Veporicum and Tatricum units. They are felsic coarse-grained and porphyric to medium-grained rocks with K-feldspar, plagioclase, albite, quartz, biotite, phengitic white mica, minor monazite and garnet. Although partly share their geochemical characteristics with younger successors, some difference can be seen: SiO_2 vary in 70 – 77 wt. %, K_2O/Na_2O = 0.54 ~ 1.38; Rb/Sr = 0.8 ~ 2.3; contents of Ga, Y, Th, U, and Co have slightly enriched, whereas Sr and Zr have depleted. Generally, have peraluminous character (ASI = 1.0 – 1.4). REE's have low values and show slightly U-shaped pattern with a pronounced negative Eu-anomaly. Initial $^{87}Sr/^{86}Sr$ values range between 0.712 and 0.725 and $\varepsilon Nd_{(i)}$ between -2.6 and -5.0 are suggesting rather for their crustal source alike their whole rocks Pb/Pb isotopic characteristics ($^{206}Pb/^{204}Pb$ = 19.585 ~ 20.651, $^{207}Pb/^{204}Pb$ = 15.673 ~ 15.762 and $^{208}Pb/^{204}Pb$ = 38.950 ~ 40.104) indeed feedback from the lower crustal metaigneous source can be seen. Typical representative of these Western Carpathians earliest felsic magmatites are so called Murán orthogneisses with age 464 ± 35 Ma (Gaab et al. 2006) and granitic orthogneisses from the northern Veporic area 462 ± 10 Ma; 467 ± 8 Ma (Gaab et al. 2005). Comparable or slightly older results brought SHRIMP dating of Veporic orthogneisses with ages 485 ± 6 Ma; 496 ± 4 Ma and 507 4 ± 4 Ma (Putiš et al. in print). The Late Cambrian magmatic age (491 ± 11 and 495 ± 4 Ma respectively) were detected from detrital magmatic zircons of the Lower Unit metasediments in the Western Tatra Mts. that represents the last magmatic activity of the precursor rocks and/or it defines the maximum age for sedimentation of the present day metasediments (Kohút et al. in print).

The Devonian felsic granitic rocks sheared and/or dynamically transformed to "banded" and "augen" Younger Orthogneisses are common in Tatric and Veporic units. Their precursors were mostly biotite and muscovite-biotite monzogranites to granodiorites. Typical medium- to high-potassic magmatic rocks of the calk-alkaline series, with subaluminous to peraluminous character (ASI = 0.9 – 1.5) represent this type of rocks. Overall geochemistry shows that SiO_2 vary in

67 – 77 wt. %, K_2O/Na_2O = 1.04 ~ 2.03; Rb/Sr = 0.7 – 1.5; generally have low abundances of Ba, Sr, B and increased Rb, Li, and iron group elements (Cr, Ni, V, Sc) and W. The low to moderate REEs show typical fractionated pattern with distinct negative Eu anomaly and their contents are apparently controlled by presence of monazite and apatite. The increased initial Sr values (I_{Sr} = 0,709 ~ 0,722) indicate dominance of crustal source, whereas initial εNd values ($\varepsilon_{Nd(i)}$ = -5.03 ~ -7.87) suggest for slight influence by lower crustal source. The whole rocks Pb/Pb isotopic characteristics ($^{206}Pb/^{204}Pb$ = 17.9995 ~ 20.4876, $^{207}Pb/^{204}Pb$ = 15.6065 ~ 15.7470 and $^{208}Pb/^{204}Pb$ = 37.9630 ~ 40.7480) similarly suggest for crustal source of the former magmatic rocks with slight influence by less radiogenic Pb derived from enriched lithospheric mantle (EM II). The scarce oxygen isotope data indicate analogous dominance of the crustal source with $\delta^{18}O_{(SMOW)}$ = 11.0 ~ 11.7‰ (all data taken from Kohút 2004; 2007). Geochronological data – U/Pb dating of zircons provides informations its magmatic age between 406 ± 5 Ma and 381 ± 6 Ma (Poller et al. 2000; Putiš et al. 2003). However, the Meso-Hercynian HT-MP metamorphic/magmatic event is responsible their sheared pattern and/or metamorphic overprint at 360 – 340 Ma what recorded EMP monazite dating (Petrík et al. 2005) and zircon SHRIMP dating (Putiš et al. in print).

The Younger S-type granites are common in the Core Mountains of Tatric unit and within Veporic composite batholith. They are peraluminous (ASI = 1.1 – 1.5), dominated by two-mica granites and granodiorites while biotite granodiorites to tonalites are less common. The accessory mineral association monazite + ilmenite, and the presence of host (metamorphic) rock xenoliths is typical for these rocks. From a geochemical point of view, Ba, Sr and Rb range widely (up to 1600, 600 and 200 ppm respectively) with Rb/Sr = 0.2 – 0.8; rarely up to 1.8. SiO_2 varies from 66 to 77 wt.% and K_2O/Na_2O = 0.7 – 1.4. The contents of CaO, TiO_2 and P_2O_5 are generally low (<2.5; <0.7 and <0.3 wt.%.). The REE content is moderate, with a fractionated pattern and a small, negative, Eu anomaly. Initial Sr ratios are between 0.706 – 0.708; $\varepsilon Nd_{(350)}$ = -0.62 to -4.24; the $^{206}Pb/^{204}Pb$ ratios of the whole rock samples range from 18.39 to 19.28 and the $^{207}Pb/^{204}Pb$ ratios from 15.59 to 15.74, and the stable isotope (O and S) values range between $\delta^{18}O_{(SMOW)}$ = 8.8 to 11.3‰ and $\delta^{34}S_{(CDT)}$ from -0.9 to +5.7‰ (all data are from Kohút et al. 1999; Poller et al. 2001; Kohút et al., 2001; Kohút, Recio 2002). Magmatic intrusion ages of these granites are between 350 – 330 Ma, with most values around 340 Ma (Bibikova et al. 1988; Michalko et al. 1998; Poller et al. 2000, 2001, 2005; Poller, Todt 2000; Putiš et al. 2003; Gaab et al. 2005).

The Upper Carboniferous calk-alkaline I-type granites spatially come with previous type of granites but in less volume. Generally, they are rather metaluminous to subaluminous (ASI = 0.8 – 1.1), dominated by biotite tonalite to granodiorite with scarce hornblende. Muscovite-biotite granodiorite to granite are less frequent. The accessory mineral association magnetite + allanite, and the occurrence of mafic microgranular enclaves (MME), are characteristic of this group. Lower SiO_2 concentrations, from 60 to 68 wt.%, coincide with higher trace elements Zr, Ba, Sr (up to 380, 1350, and 800 ppm), higher LREE and Fe group element contents. REE patterns are typically steeper, with higher LREE and without Eu anomaly. The initial Sr = 0.704 – 0.707 with Rb/Sr = 0.05 – 0.7, are consistent with a Rb-poor crustal source and/or mixed lower crustal or mantle component. These rocks are clearly richer in CaO, TiO_2 and P_2O_5 than previous granites, whereas K_2O/Na_2O = 0.5 – 0.9. Few Nd data fall within the S-type group with $\varepsilon Nd_{(310)}$ = -1.7 to -3.5, although mafic dioritic enclaves with $\varepsilon Nd_{(310)}$ = 1.8 to 0.5 clearly indicate interaction with a basic or intermediate, dioritic, lower crustal melt. The $^{206}Pb/^{204}Pb$ ratios of tonalitic whole rock samples range from 17.99 to 18.85, and the $^{207}Pb/^{204}Pb$ ratios from 15.53 to 15.70 suggest heterogeneous continental crustal source with recycled oceanic crust. The stable isotopic (O and S) ratios, with $\delta^{18}O_{(SMOW)}$ = 7.8 – 9.9‰ and $\delta^{34}S_{(CDT)}$ from -2.9 to +2.3‰ support melting of a more basic lower crustal protolith. Magmatic intrusion ages of this I-type granite group vary between 310 – 300 Ma (Broska et al. 1990; Bibikova et al. 1990; Michalko et al. 1998; Poller, Todt 2000; Poller et al. 2005).

The Permian mildly alkalic A-type group of granites with distinctive mineralogical and geochemical signature is found within the Veporic unit and/or its border zone with Gemeric unit. Various petrographic types include porphyritic to megacrystic (up to 6 cm), aplitic to microaplitic varieties and granite porphyries were observed. Typical representatives of this type are so called Hrončok granite (Petrík et al. 1995), Turčok granite (Uher, Gregor 1992) and also as pebbles in Cretaceous flysch in the Outer Carpathian Klippen belt – Upohlav type (Uher, Marschalko 1993). The Velence granite from Hungary also belongs to this group according to Uher & Broska (1996). Although the A-type granites do not form a homogenous group they exhibit some common characteristics: high Si, K, F, REE, Ga/Al, sometimes Na, Rb, Zr, Nb, Y and W; low Ti, Mg, Ca, P, Ba, Sr, and V contents (SiO_2 values (70 – 77 wt. %), peraluminous character (ASI = 1.0 – 1.3), K_2O = 4 – 5 wt. %, Rb = 66 – 280 ppm with average 185 ppm, high Ga = 17 – 35 ppm, F = 350 – 500 ppm, Th = 10 – 52 ppm (av. 19 ppm), low Sr = 30 – 110 ppm (av. 75 ppm), Ba = 50 – 500 (av. 479 ppm), in Upohlav type up to 1300 ppm (Uher, Broska 1996; Broska, Uher 2001). Particularly distinct are REE´s, which show characteristic weakly fractionated patterns with pronounced negative Eu-anomaly. Scarce, depleted stable isotopes values $\delta^{18}O_{(VSMOW)}$ = 7.8 ‰, and $\delta^{34}S_{(CDT)}$ = -0.69 ‰ indicate a lower crustal meta-igneous protolith (Kohút et al. 2001). The age of the A-type granites is known from conventional zircon datings: 274 ± 13 Ma for the Upohlav type (Uher, Pushkarev, 1994); 239 ± 1.4 Ma for the Hrončok granite, and 278 ± 11 Ma for its fine-grained microaplitic equivalent (Putiš et al., 2000) Recent SHRIMP zircon data suggest for 256 ± 6 Ma magmatic event for Turčok granite (Putiš et al. in print).

The Gemeric granites are represented by several petrographic types e.g. coarse-grained and/or porphyric biotite granite variety occurs in the deeper part, whereas medium-grained muscovite-biotite granite and fine-grained two-mica granite often greisenized are found in upper part of body. Geochemically, the Gemeric granites are unique compared to other Western Carpathians Hercynian granitic rocks. Their overall characteristics place them among specialised tin-bearing S_s-type granites.

They have elevated SiO_2 values (73 – 78 wt. %), a strongly peraluminous character (ASI = 1.2 – 1.6), the high concentrations of F, B, Rb, Li, Cs, Sn, Mo, Be and low concentrations of Sr, Ba, Zr and V (Petrík, Kohút 1997; Broska, Uher 2001). The high initial Sr isotope ratios (I_{Sr} = 0.711 – 0.715) together with higher $\varepsilon_{Nd(i)}$ = -4.6 and elevated stable isotopes values $\delta^{18}O_{(VSMOW)}$ = 10‰, $\delta^{34}S_{(CDT)}$ = 4.48‰, indicate a mature continental metasedimentary feldspar and muscovite-rich protolith (Kovách et al. 1986; Kohút et al. 1999; Kohút et al. 2001; Kohút, Recio 2002). The opinions concerning the magmatic age of the Gemeric granites were changed several times. Kantor (1957) did first isotopic determination of this granite by K-Ar method on K-feldspar from Betliar locality with an age 98 Ma, although later presented cooling ages on micas from 241 ± 5 to 222 ± 5 Ma (Kantor, Rybár, 1979). However, recent EMP chemical isochrone method of monazite dating confirmed older Hercynian age of Gemeric granites with a 276 ± 13 Ma to 263 ± 28 Ma age (Finger, Broska 1999; Finger et al. 2003). These data are in accordance with the present-day precise single-grain U-Pb zircon dating, which suggests a Permian (273 ± 30 – 246 ± 5 Ma) crystallisation age for the Gemeric granites (Poller et al. 2002). The Permian age (263 ± 0.8 Ma) was confirmed by recent Re-Os molybdenite dating from exocontact greisen (Kohút, Stein 2005).

The Late Cretaceous – Rochovce hidden magmatic body was discovered by geophysics and drilling in the contact zone between Veporic and Gemeric units. This type is formed by two intrusive phases. *The first phase* comprises two petrographic varieties: coarse-grained biotite monzogranites with the pink K-feldspars phenocrysts, locally with mafic microgranular enclaves, and granite porphyries. *The second phase* is more evolved type representing by medium- to fine-grained biotite leucogranites and leucogranitic porphyries. The Rochovce granites have normal to elevated SiO_2 values (66 – 77 wt. %), a typical calc-alkaline, subaluminous to peraluminous character (ASI = 0.9 – 1.4), high concentrations of Ba, Rb, Li, Cs, Mo, Nb, Y, V, W, Cr, F, Th, U and low concentrations of Sr, Zr and Be (Határ et al., 1989). The low initial Sr isotope ratios (I_{Sr} = 0.7083 – 0.7126), together with negative $\varepsilon_{Nd(i)}$ = -3.0 and depleted stable isotopes values $\delta^{18}O_{(VSMOW)}$ = 8.0‰, $\delta^{34}S_{(CDT)}$ = -2.1‰ indicate a lower crustal meta-igneous protolith (Hraško et al. 1998; Kohút et al. 2001). Their Cretaceous magmatic age was proved by U-Pb zircon dating – conventional method 82 ± 1 Ma (Hraško et al. 1999) and cathodoluminescence controlled single zircon method 75.6 ± 1.1 Ma (Poller et al. 2001b), and/or recent Re-Os dating from disseminated molybdenite – 80 Ma (Kohút et al. in print).

Miocene calk-alkaline granites form an integral component of volcanic and hypabyssal rocks in the Central Slovakian Neovolcanic field exposed in the Banská Štiavnica and Hodruša tract of its central zone (Hodruša – Štiavnica Intrusive Complex). The massive granodiorite consist of intermediate plagioclase, quartz, K-feldspar, biotite, amphibole, and accessory magnetite, titanite, pyroxene, apatite and zircon. The rock's texture is evengrained and porphyric in marginal parts, locally with mafic microgranular enclaves. The granitic rocks are often altered – sericitized, chloritized and propylitized. These granodiorites have standard values of SiO_2 (59 –

66 wt. %) higher contents of CaO (3.7 – 7.0 wt. %) FeO (1.5 – 4.0 wt. %) MgO (1.2 – 3.8 wt. %) and lower content of TiO2 (0.5 – 1.0 wt. %). Generally have enriched Ba (400 – 900 ppm), Cr (10 – 45 ppm), V (60 – 155 ppm), and F (220 – 800 ppm), whereas values of Sr = 320 – 540 ppm, Rb = 80 - 180 ppm, and Zr = 103 – 188 ppm are standard compared to other Western Carpathians granites (Marsina et al. 1999). Its initial Sr value 0.706 (Kumar 1991) suggests for lower crustal source affected by lithospheric mantle and/or its I-type character. The age of this granitic rock was determined by K/Ar dating with ages between 19.5 ± 0.8 Ma and 10.5 ± 0.5 Ma (Konečný et al. 1983) respectively 16.9 ± 3 Ma (Rozložník et al. 1991); FT method – 17.2 ±1.5 Ma (Repčok 1981) and Rb/Sr isochrone 19.6 ± 8 Ma (Rozložník et al. 1991) whereas U/Pb zircon dating indicate its homogenisation before 24 – 21 Ma (Rozložník et al. l.c.).

DISCUSSION & CONCLUSIONS

The Western Carpathians form a part of an extensive, equatorial, orogenic belt extending from the Atlas Mountains in Morocco, through the Alps, Dinarides, Pontides, Zagros, and Hindukush to the Himalayas and to China. They are the northernmost, E–W trending branch of this Alpine belt, linked to the Eastern Alps in the west and to the Eastern Carpathians in the east**.** Generally, granitic rocks are good medium that recorded various orogenic processes through their mineral and chemical (isotopic) composition, linking not only chronometric informations, but achieve progress in understanding the dynamics of mountain building processes. Presented review throughout the time show that granites mirrored orogenic evolution within the Western Carpathians since the Cambrian to Miocene. Various types of granitic rocks and their chemistry document change of tectonic processes from rifting, subduction and amalgamation of an oceanic lithosphere, through collision with lithospheric thickening, followed by delamination or break-off and finished in extensional tectonic during three orogenic cycles. Many similarities in compositions of these granites indicate repeating origin of calc-alkaline I-types, peraluminous S-types and scarce alkaline A-type granites in our realm, while M-type granites were not prove yet, indeed some indications of plagiogranites exist there mainly within LAC complexes. Taking in account granite typology their ages, associated mafic rocks and P-T conditions of host metamorphic rocks it is obvious the Carpathians granites originated during several convergent orogeny mainly at an active Andean-type arc or a Himalayan continental collisional processes in time of Phanerozoic orogenic cycles.

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CONTRIBUTIONS

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CHEMISTRY OF CASSITERITE IN RARE METAL BEARING-GRANITOIDS AND THEIR ASSOCIATING ROCKS, EASTERN DESERT, EGYPT

Abstract: Syngenetic cassiterite is associated with the Li-albite granite of G. Abu Dabbab and the leucogranite segments of Igla Ahmar area (i.e. magmatically specialized granites). Post-magmatic stage of tin mineralization is commonly confined to the metasomatized zones of the alkali feldspar granites of G. Mueilha and G. Homr Akarem. The cassiterite of the specialized granites has deep orange to reddish brown pleochroic core that are alternately rimmed with lighter bands and shows low Nb/Ta ratio. Whereas, The cassiterite of the albitized granites is characterized by development of deep brown to dark brown pleochroic color zones, which are progressively alternating with lighter ones and has high Nb/Ta contents.
Keywords: cassiterite, specialized and metasomatized granitoids, Arabian-Nubian Shield

INTRODUCTION

Tin is chiefly found in the form of cassiterite (SnO_2), which is the main source of such metal. Specialized granitoids are those genetically and spatially associated with cassiterite mineralization (Tischendorf, 1977). In the Arabian-Nubian Shield, the granitoids associated with Sn-W deposits are considered to be fractionated product of calc-alkaline I-type magmatism at destructive plate margins (Roger and Greenberg, 1977) and within plate A-type granites (Harris, 1982). In the metasomatized granites, Sn mineralization is associated with the granites through metasomatism (i.e. apogranite). Accordingly, two different rare-metal bearing granitoids varieties are investigated through four granite plutons spread in the central and southern Eastern Desert of Egypt. These include: G. Abu Dabbab (Li-albite granite) and the leucocratic granite segment of G. Igla Ahmar Ahmar, which represent the specialized granitoids. On the other hand, the albitized granite parts of G. Homr Akarem and G. Mueilha depict as metasomatized granitoid ones. The present study concerns with the typomorphic characters and mineral chemistry of cassiterite confined to some rare-metal bearing granitoids at the Eastern Desert of Egypt, which related to the specialized and metasomatized granitoid varieties.

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SAMPLING AND ANATICAL TECHNIQUES

Electron-microprobe (Jeol JXA-50A, situated in Hokkaido University, Japan) microanalyser has been used for analyzing cassiterite in thin polished sections of the studied granitoids, greisen and quartz veins well as in thin polished grain mounts prepared for cassiterite fractions separated from the placer samples (Tab. 1).

RESULTS

Cassiterite is commonly displaying three styles of zoning namely; progressive, oscillatory, and sector. In the progressive zoning, the crystals show smooth color (and compositional) variation rim-wards. The core is yellowish brown to black is grading outward into faintly yellow to colorless rim. In the oscillatory-zoned crystals, successively alternating zones of colorless, white, yellow, orange, red and deep reddish brown zones are extending parallel to the c-axis. For simple treatment of the present investigation, the colored zones were discriminated into three variants namely: i) light (i.e. colorless, white, yellow); ii) intermediate (i.e. yellowish-orange); and dark (i.e. red, deep reddish brown to even opaque). Cassiterite crystals disseminated in stanniferous granites commonly exhibit gentle progressive zoning characterized by small-scale variations in Nb, Ta, and Fe.

Table (1): Selected EPMA analyses of the investigated cassiterite from the rare metal bearing-granitoids of the different studied areas, Eastern Desert of Egypt.

Granitoid types	Specialized granitoids							Metasomatized granitoids			
	Leucogranite				Li-albite granite			Albitized granites (Apogranites)			
Area	Igla Ahmar				Abu Dabbab			Mueilha		Homr Akarem	
No.*	1	2	3	4	5	6	7	8	9	10	11
Nb_2O_5	0.18	0.20	0.36	0.80	0.36	0.28	0.82	0.46	1.22	0.14	0.43
Ta_2O_5	0.87	0.29	0.94	1.02	0.51	0.76	1.30	---	0.15	0.04	0.08
SnO_2	96.10	97.30	95.31	94.21	96.31	96.71	93.51	96.70	95.41	99.51	98.52
TiO_2	0.72	1.10	0.67	1.51	0.63	0.45	1.40	1.49	1.45	0.11	0.22
WO_3	0.12	0.08	0.14	0.16	0.11	0.14	0.14	0.08	0.14	0.03	0.08
Ga_2O_3	0.01	0.01	0.02	0.04	0.01	0.02	0.03	---	0.01	---	---
Fe*O	1.52	0.21	1.78	2.10	0.75	1.30	1.82	0.81	0.74	0.19	0.55
MnO	0.14	0.01	0.16	0.23	0.08	0.12	0.19	0.02	0.01	0.10	0.11
Total	100.66	99.20	99.38	100.07	98.76	99.78	99.21	99.56	99.13	100.12	99.99
Number of cations based on 2 oxygens.											
Nb	0.002	0.002	0.004	0.009	0.004	0.003	0.009	0.005	0.014	0.002	0.005
Ta	0.006	0.002	0.006	0.007	0.003	0.005	0.009	0.000	0.001	0.000	0.001
Sn	0.958	0.971	0.952	0.926	0.969	0.965	0.929	0.956	0.945	0.992	0.981
Ti	0.014	0.021	0.013	0.028	0.012	0.008	0.026	0.028	0.027	0.002	0.004
W	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.000	0.001	0.000	0.001
Ga	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Fe*	0.032	0.004	0.037	0.043	0.016	0.027	0.038	0.017	0.015	0.004	0.012
Mn	0.003	0.000	0.003	0.005	0.002	0.003	0.004	0.000	0.000	0.002	0.002
Nb/Ta	0.33	1.00	0.67	1.28	1.33	0.60	1.00	>5.0	14.00	>5.0	5.00

Analysis No.*.: 1, 2, 5,8 and 10 refer to light-colored zones; 3 = yellowish orange (intermediate-colored) zone; 4, 6, 7, 9 and 11 refer to dark-coloured zones in the investigated cassiterite.

Total iron as FeO*.

--- below detection limit.

CONCLUSIONS

The high Nb/Ta ratios in the hosting apogranites as well as the associated columbite mineral and cassiterite may suggest that the predominance of Nb over Ta is initially attributed to igneous fractionation (i.e. crystal/melt or fluid partitioning) characterizing such granitic association. The conspicuous variation in colors, pleochroism and chemistry of cassiterite from albite granites and metasomatized apogranites can be considered as a valuable exploration tool when prospecting for primary cassiterite mineralization. In other words, during the panning survey, which is largely applied for rare metal mineralizations in general and cassiterite deposits in particular, the pleochroism of any cassiterite present indicates the nature of the primary mineralizations (i.e. magmatically specialized versus metasomatically host granites).

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MINERALOGIA POLONICA – SPECIAL PAPERS
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PROVENANCE OF DETRITIC GARNETS IN THE MIDDLE JURASSIC CLASTIC SEDIMENTS OF THE CRACOW REGION.

Abstract: Detritic garnets from the Upper Bathonian/Lower Callovian sands of the Cracow-Wieluń Upland show high proportion of the almandine-pyrope and even pyrope garnets. Their source rocks were most likely granulites, eclogites and ultrabasics. Their source area is unknown. Similar compositions of the detrital garnets were also recorded in the Outer Western Carpathians (Flysch Zone, Pieniny Klippen Belt), i.e. the crustal segments which formed Silesian and Magura cordilleras and the Czorsztyn Swell were not necessarily derived from Moldanubian Zone of the Hercynides as was thought before.
Keywords: heavy minerals, Jurassic, Kraków-Wieluń Upland, provenance analysis, garnet

INTRODUCTION

Detritic heavy mineral analysis of the Middle Jurassic sands and sandstones in the southern part of the Kraków-Wieluń Upland was performed to compare the heavy-mineral assemblages with those published from the Tethyan Jurassic of the Western Carpathians (Łoziński 1956, 1957, 1966; Aubrecht 1993, 2001), Eastern Alps (Faupl 1975) or from the Tethyan margin of the Bohemian Massif (Štelcl et al. 1972, 1977). The results from the Tethyan regions show big differences in the heavy mineral spectra between the internides and externides. The externides are dominated by garnet, accompanied by zircon, rutile and tourmaline, with subordinate amounts of other minerals. The internides are characterized by predominance of tourmaline and apatite, accompanied with zircon and rutile. The results from the margin of the Bohemian Massif correlate well with the results from the externides. Analyses of detritic garnet in the samples from the externides (Jurassic to Paleogene of the Pieniny Klippen Belt and Flysch Zone) display big portion of pyrope-almandine garnets coming from granulites and eclogites (Otava et al., 1997, 1998; Aubrecht, Méres 1999, 2000; Salata 2004, Grzebyk, Leszczyński 2006). Wieser (1985) reports about numerous granulitic pebbles from the Silesian Unit of the Flysch Zone. Pyrope-almandine garnets were also reported from the Carboniferous of the Moravo-Silesian Culm basin (Čopjaková et al. 2001; Hartley, Otava 2001). Most of the authors derived this exotic garnet material from Moldanubian zone of the Bohemian Massif. Except of this zone, there are only two other known occurrences of granulites

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and eclogites - Góry Sowie Block and the Śnieźnik area complex in the Western Sudetes (Oberc 1972; Smulikowski 1967; Kryza et al. 1996). These are, however, too small to be a regionally important source of clastic material.

GEOLOGICAL SETTING

Middle Jurassic deposits of the Kraków region (Kraków-Wieluń Upland, Poland) represent the transgressive sequence. They were laid down on the erosional surface, which is developed on the older, Palaeozoic and Mesozoic rocks. In some places the lower or early middle Jurassic continental clays (mainly lacustrine) are preserved.

The sequence of Middle Jurassic deposits commences with quartz sand and sandstone, which comprises conglomeratic horizons. These deposits are devoid of any fossils excluding silicified fragments of tree trunks. They are of shallow marine origin, however their basal part might be deposited in fluvial environment. The transgression caused the filling of the uneven basement topography. It is reflected by variable thickness of clastic deposits, which varies from zero up to 10 m. The sands gradually pass upwards into sandy limestone of Calloviense zone which is about 3 m in thickness. The underlying clastics are then of uppermost Bathonian and lowermost Callovian age. Percentual amounts of heavy minerals in this formation were previously published by Krysowska (1960, 1962). She reported about the heavy mineral spectra dominated by garnet, accompanied by zircon and rutile, with subordinate amount of turmaline and staurolite. We studied heavy minerals at the following localities: quarry at the road between Dębnik and Czatkowice (N 50°13'16.5", E 19°47'41.3"), Dębnik Quarry (N 50°09'52.1", E 19°40'17.4"), Paczółtowice (N 50°10'33", E 19°39'22.9") and Racławice (N 50°11'7.8", E 19°40'34.5").

METHODS USED

The heavy minerals were separated from the sands in heavy liquids (bromoform, density cca 2.8 g/cm^3). To check the ratios of various heavy minerals in the samples, the fraction 0.08-0.25 mm was studied in transmitting polarized light. The amounts of heavy minerals were determined by ribbon point counting. Detrital garnets were separated manually under binocular lens. The composition of garnets was determined using a CAMECA SX-100 electron microprobe at the State Geological Institute of Dionýz Štúr in Bratislava. The analytical conditions were 15 kV accelerating voltage and 20 nA beam current, with a peak counting time of 20 seconds and a beam diameter of 2—10 μm. Raw counts were corrected using a PAP routine.

RESULTS AND INTERPRETATIONS

The studied heavy mineral spectra were slightly dominated by garnet but the contents of zircon, rutile and turmaline were also high which is in contradiction with previous results of Krysowska (1960, 1962). These four minerals were accompanied by lesser amounts of staurolite and apatite. The microprobe analyses of detrital garnet grains show that they can be divided into 5 groups, according to their composition (Fig. 1):

1) Garnets coming from garnet peridotites. These have high contents of pyrope molecule (~ 70 mol %), relatively low contents of almandine (~ 15 mol %), grossular (~ 12 mol %) and very low spessartine molecule(< 1 mol %).

2) Garnets coming from granulites. They have relatively lower contents of pyrope (30-50 mol %) than the previous ones, but have higher contents of almandine (50-60 mol %), low proportion of grossular (~ 5 mol %) and very low contents of spessartine (~ 2 mol %).

3) Garnets coming from eclogites. These have pyrope contents about 30-56 mol %, almandine contents of 35-45 mol % and that of spessartine less than 1 mol %. They differ from the group No. 2 by higher proportion of the grossular molecule (20-30 mol %).

4) Garnets coming from gneisses. They have high almandine contents (~ 60 mol %), low pyrope contents (~ 10 mol %) and higher contents of spessartine (10-27 mol %) than granulitic garnets. Contents of grossular were less than 6 mol %.

5) Garnets coming from amphibolites (for better overview, in the diagram they are grouped together with garnets from gneisses). They are characteristic by pyrope contents of about 15-25 mol %, low spessartine contents (< 10 mol%), higher grossular contents (20-30 mol %) and relatively high contents of almandine (~ 75 mol %).

All the garnets from the **Dębnik** locality are characterized by high pyrope contents (> 30 mol %). Such garnets are typical for granulites, eclogites and garnet peridotites. In the samples from the quarry **between Dębnik and Czatkowice**, garnets from garnet peridotites, granulites and eclogites were distinguished. Garnets from gneisses were in minority. The source rocks of the garnets from **Racławice Locality** were granulites, eclogites, gneisses and amphibolites. Garnets from the **Paczółtowice Locality** were derived from garnet peridotites, granulites and eclogites.

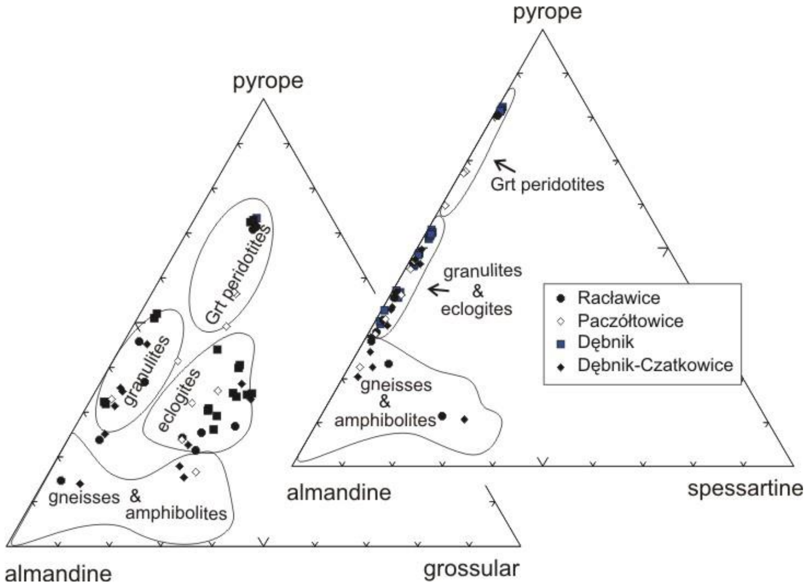

Fig.1. Composition of the detrital garnets from the Bathonian-Callovian sands from the Cracow Region and their source rocks (for source rocks - see Aubrecht and Méres, 2000).

DISCUSSION AND CONCLUSIONS

All the examined samples yielded surprisingly high portion of pyrope-almandine to pyrope garnets. The heavy mineral percentages and the garnet chemistry are very similar to the data from the West Carpathian externides. In this part of the Hercynides, however, it is difficult to estimate the source area. As mentioned in the introduction, there are only small terrains with granulites and eclogites in Poland (Góry Sowie and Śnieźnik). Granulitic rocks are generally considered as exotic in the area of Cracow. Some granulitic pebbles were found in the Carboniferous sediments of the Upper Silesia Coal Basin (Paszkowski et al. 1995). In the Carboniferous clastics of the Moravo-Silesian Zone, the authors invariably derive the clastic material from the Moldanubian Zone of the Bohemian Massif (Paszkowski et al. 1995; Hartley, Otava 2001). Similarly, the crustal segments of the Pieniny Klippen Belt were interpreted to be derived from the Moldanubian Zone (Aubrecht, Méres 1999, 2000). However, the new data presented in this paper indicate that the source area should be more proximal to the recent Polish Platform. The detrital garnet chemistry shows that the source area was predominantly formed by granulites, eclogites and peridotites. Any river draining recently known crystalline areas in the Moravo-Silesian Zone would bring a big portion of almandine-rich garnets coming from phyllites, mica-schists and gneisses, because they form majority of these terrains. Góry Sowie and Śnieźnik cannot solely represent a source area. The only possible interpretation is to admit an existence of yet unknown terrane with granulites, eclogites and peridotites that was situated near the Moravian-Silesian area before the Jurassic rifting.

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MINERALOGIA POLONICA – SPECIAL PAPERS
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POST-MAGMATIC GARNET, PREHNITE AND PUMPELLYITE IN MAFIC DYKES OF THE KARKONOSZE MASSIF – PRELIMINARY DATA

Abstract: Mafic hypabyssal rocks of the Karkonosze massif (lamprophyres, monzo-diorites) show evidence of post-magmatic alteration. Apart from previously recognized minerals (e.g. chlorite, clinozoisite-epidote, sericite) there are also newly identified Ca-Al-Fe silicates, including grossularite-andradite, prehnite and pumpellyite. The post-magmatic processes spanned a relatively wide range of P-T conditions and the resulting mineral assemblages were also dependent on bulk-rock modal compositions and textures.
Keywords: lamprophyre, monzodiorite, dyke, alteration, Karkonosze, Sudetes

INTRODUCTION

The eastern part of the Carboniferous Karkonosze granitic pluton (Sudetes, SW Poland) is cut by a NNE-trending swarm of mafic to felsic dykes. The mafic rocks comprise various lamprophyres and monzodiorites to micromonzodiorites (Awdankiewicz et al. 2005) which often show extensive post-magmatic alteration, including albitization and/or sericitization of plagioclase as well as the replacement of ferromagnesian minerals by chlorite, actinolite, epidote-group minerals, carbonates and clay minerals (e.g. Borkowska 1966). However, recent studies reveal also the presence of such Ca-Al-Fe silicates, as grandite garnets, prehnite and pumpellyite, which were not noted previously in these rocks. This paper provides (i) preliminary data on the occurrence of the newly identified minerals, including their chemical composition, and (ii) a brief discussion of the post-magmatic alteration processes in the mafic dykes of the Karkonosze massif.

PETROGRAPHY AND MINERAL CHEMISTRY OF THE MAFIC ROCKS

The post-magmatic garnets, prehnite and pumpellyite were identified in 7 samples of mafic hypabyssal rocks collected from dykes near the villages of Bukowiec and Trzcińsko, SE of Jelenia Góra. These minerals occur in various combinations with other post-magmatic phases, like chlorites, carbonates or clino-zoisite/epidote. Selected examples, which illustrate the most typical mineral associations and textures, are characterised below.

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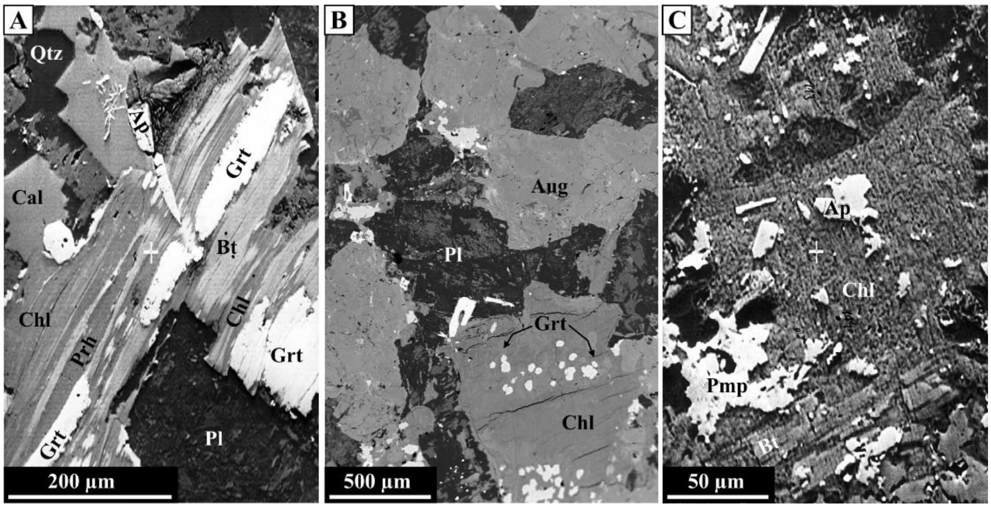

Fig. 1. Back-scattered electron images showing Ca-Al-Fe silicates in mafic hypabyssal rocks of the Karkonosze massif. A – biotite intergrown with chlorite, garnet and prehnite in a fine-grained monzodiorite. B – chlorite pseudomorph with oval garnet inclusions in a cognate enclave in micromonzodiorite. C – anhedral aggregate of pumpellyite and chlorite in a groundmass of minette. Minerals: Ap – apatite, Aug – augite, Bt – biotite, Cal – calcite, Chl – chlorite, Grt – garnet, Pl – plagioclase (strongly replaced by serictite and other post-magmatic minerals), Prh – prehnite, Qtz – quartz.

Garnets associated with prehnite were identified in fine-grained monzodiorites and micromonzodiorites. The fine-grained monzodiorites are mainly composed of strongly sericitized plagioclase with relics of andesine-oligoclase composition, partly overgrown by K-feldspar and granophyric intergrowths of quartz and K-feldspar. Intersticies are filled with anhedral quartz and calcite, and locally with chlorite and titanite. Other minerals comprise biotite, augite and minor brown amphibole, ilmenite and apatite. Augite is partly replaced by actinolite, and biotite by chlorite. However, most biotite plates contain also characteristics intergrowths of garnet and prehnite aligned parallel to cleavage planes (Fig. 1A).

The microcrystalline monzodiorites contain phenocrysts of augite, altered plagioclase and chlorite pseudomorphs (after olivine?), often forming glomerocrystals grading into small cognate enclaves. Augite is partly replaced by actinolite, and plagioclase is strongly sericitized, with relics of labradorite to oligoclase-albite composition. The groundmass consists mainly of altered plagioclase and augite with minor K-feldspar, quartz, ilmenite, titanite, chlorite, calcite, epidotes and, rarely, brown amphiboles. Post-magmatic garnets occur in the groundmass, and form also small round inclusions in some chlorite pseudomorphs (Fig. 1B). In addition, small prehnite intergrowths were identified in a strongly altered plagioclase.

Table 1. Selected chemical analyses of garnet (Grt), prehnite (Prh) and pumpellyite (Pmp) from fine-grained monzodiorite (MD), micromonzodiorite (MMD), minette (MIN) and spessartite (SPT). Normalization: Grt – 12 O, total Fe=Fe^{3+}; Prh – 11 O, total Fe=Fe^{3+}; Pmp – 24.5 O, 16 total cations. Analyses were carried out using the CAMECA SX100 electron microprobes at Warsaw University and Ruhr Universität Bochum.

Rock Mineral	MD Grt	MMD Grt	Rock Mineral	MD Prh	MMD Prh	Rock Mineral	MIN Pmp	SPT Pmp
SiO_2	34.865	36.504	SiO_2	42.308	43.771	SiO_2	35.753	37.114
TiO_2	0.124	0.635	TiO_2	0.304	0.076	TiO_2	0.502	0.108
Al_2O_3	6.471	9.988	Al_2O_3	21.236	23.086	Al_2O_3	20.193	20.797
Cr_2O_3	0.031	0.050	Cr_2O_3	0.000	0.012	Fe_2O_3	6.461	7.792
Fe_2O_3	23.273	18.107	Fe_2O_3	5.119	2.165	FeO	8.865	7.577
MnO	0.058	0.224	MnO	0.000	0.000	MnO	0.200	0.194
MgO	0.028	0.108	MgO	0.013	0.000	MgO	0.073	0.035
CaO	34.821	34.599	CaO	27.191	26.468	CaO	20.875	22.714
Total	99.671	100.215	Na_2O	0.003	0.065	Na_2O	0.000	0.038
#Si	2.884	2.929	K_2O	0.023	0.000	K_2O	0.055	0.000
#Al IV	0.116	0.071	Total	96.197	95.643	Total	92.977	96.369
Z site	3.000	3.000	#Si	2.954	3.022	#Si	6.027	6.027
#Al VI	0.515	0.874	#Al IV	1.047	0.979	#Ti	0.064	0.013
#Ti	0.008	0.038	T site	4.000	4.000	#Al	4.012	3.980
#Cr	0.002	0.003	#Al VI	0.700	0.898	#Fe+3	0.820	0.952
#Fe+3	1.449	1.093	#Fe+3	0.269	0.113	#Fe+2	1.250	1.029
Y site	1.974	2.009	O site	0.968	1.011	#Mn+2	0.029	0.027
#Mn	0.004	0.015	#Ti	0.016	0.004	#Mg	0.018	0.008
#Mg	0.003	0.013	#Cr	0.000	0.001	#Ca	3.770	3.952
#Ca	3.086	2.975	#Mn	0.000	0.000	#Na	0.000	0.012
X site	3.094	3.003	#Mg	0.002	0.000	#K	0.012	0.000
#Total	8.067	8.012	#Ca	2.034	1.958	#Total	16.000	16.000
Prp	0.11	0.43	#Na	0.001	0.009			
Alm	0.00	0.00	#K	0.002	0.000			
Sps	0.13	0.51	A site	2.054	1.971			
Adr	73.41	54.43	#Total	7.022	6.981			
Uv	0.10	0.16						
Grs	26.25	44.48						

Pumpellyite occurs in some spessartites and minettes. The spessartites consist mainly of deep brown amphiboles (kaersutite), clinopyroxenes (augite to diopside) and strongly albitised and sericitised plagioclase, whereas the minettes are mainly composed of dark mica (phlogopite to biotite), diopside and variable K- to Na-feldspars. The ferromagnesian minerals form phenocrysts and groundmass crystals, and feldspars are confined to the groundmass. In the samples studied the groundmass contains abundant chlorite associated with pumpellyite, the latter forming anhedral aggregates (Fig. 1C).

The garnets (Tab. 1) represent members of grossularite-andradite solid solution, dominated with andradite (50 – 85% mol.) and with a very low content of the end-members other than andradite and grossularite (below c. 1%). Prehnite analyses indicate compositions close to the ideal formula of this mineral, but with relatively high content of Fe^{+3} substituting Al in ocathedral sites. Pumpellyite represents an iron-rich variety with a very low Mg content.

FINAL REMARKS

Prehnite, pumpellyite and clinozoisite-epidote are typical minerals in mafic igneous rocks affected by very low- to low-grade metamorphism at sub-greenschist facies conditions. These minerals, together with grossularite-andradite garnets, are also common alteration products in plutonic rocks of granitic or syenitic to dioritic composition. Their formation is linked with autometasomatic processes that affect rocks during the subsolidus cooling of plutonic bodies (e.g. Freiberger et al. 2001).

The post-magmatic mineral assemblages in the mafic rocks of the Karkonosze massif include minerals typical of the greenschist facies (albite, chlorite, actinolite, epidote) as well as the newly recognized sub-greenschist-facies minerals (grossularite-andradite, prehnite and pumpellyite). This may suggest that the alteration processes spanned relatively wide range of P-T conditions. However, the post-magmatic mineral assemblages were also dependent on the modal composition of the protoliths (e.g. garnets occur in samples with abundant decomposed plagioclase which probably supplied Ca for garnet formation) and their textural heterogeneity (e.g. actinolite preferentially developed on clinopyroxene, and prehnite crystallized within biotite). Further studies will possibly enable some quantification of the P-T and other controls involved in post-magmatic alteration processes in the discussed dykes.

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PRELIMINARY SHRIMP ZIRCON AGE OF THE MICROMONZODIORITE DYKE FROM BUKOWIEC: AGE CONSTRAINT FOR THE KARKONOSZE GRANITE (POLISH SUDETES)

Abstract: The late Variscan Karkonosze Granite in the West Sudetes is cut by locally numerous lamprophyre and other rock-type dykes. Preliminary results of SHRIMP zircon geochronology in a micromonzodiorite dyke indicate an important admixture of inherited zircons of c. 2.0, 1.4 Ga, and c. 570 (and 500?) Ma. The most likely age of the main magmatic population of the zircons is estimated at c. 318 Ma and this age would constrain the minimum age of host Karkonosze Granite.
Keywords: zircon, SHRIMP geochronology, Variscan magmatism, hypabyssal dykes, Karkonosze Granite, Sudetes

INTRODUCTION

The late Variscan Karkonosze Granite is a large pluton emplaced within the metamorphic complexes of the Karkonosze-Izera Block in the West Sudetes, at the NE margin of the Bohemian Massif (Mierzejewski, Oberc-Dziedzic 1990). The pluton comprises several granite types, with two dominating varieties: porphyritic and even-grained (aphyric) granites (Borkowska 1966). The eastern part of the pluton is cut by a NNE-trending swarm of mafic to felsic dykes, including lamprophyres, monzodiorites and porphyrytic microgranites (Awdankiewicz et al. 2005).

The main porphyritic type of the Karkonosze Granite was dated at 329±17 Ma using the Rb-Sr whole-rock isochrone, whereas the even-grained variety (the ridge type) yielded the date of 310±17 Ma (the same method, Duthou et al. 1991). ^{40}Ar-^{39}Ar dating of a single biotite from the porphyritic type (Liberec-type granite) gave an age plateau at 320±2 Ma, with two last high temperature steps at 315 and 314 Ma (Marheine et al. 2002). The dykes cutting the Karkonosze intrusion, thus generally younger than the granites, have not been dated so far.

This study provides preliminary results of SHRIMP zircon dating of a micromonzodiorite from a dyke in the eastern part of the Karkonosze pluton. Micromonzodiorites are widespread there and represent relatively evolved members

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of the hypabyssal igneous suite. Individual dykes are up to 10-20 m thick, several hundred meters long and they cut the porphyrytic granites. Sharp contacts with the host granite, local cataclasis of the granite along the contacts, and chilled margins of the dykes (observed in blocks) show that the micromonzodiorite dykes postdate the consolidation of the host granite. Thus, dating of dykes (i) gives information on the age of the hypabyssal magmatism in the Karkonosze Massif, and (ii) can help to better constrain the age of the Karkonosze Granite.

METHODS OF INVESTIGATION

The samples for this study were collected in several old quarries near Bukowiec, c. 12 km SE of Jelenia Góra. Our observations are based on 25 thin sections, EMP results from two samples, and SHRIMP data from 1 sample. The sample selected for zircon geochronology, c. 3 kg in weight, was crushed, sieved, and the heavy fraction 0.06–0.25 mm separated using the conventional heavy liquid (sodium polytungstate) procedure. Hand-picked zircons representing various morphological types were mounted in epoxy resin, and a polished section was used for optical microscopy, CL imaging, and SHRIMP analysis at VSEGEI in St. Petersburg.

RESULTS

Petrography

The micromonzodiorites represent porphyrytic rocks with phenocrysts of altered plagioclase, relatively fresh augite and rare chlorite pseudomorphs (after olivine ?). Plagioclase is strongly replaced by sericite and other post-magmatic minerals, but relics of labradorite to oligoclase-albite composition are also found. Augite shows normal zoning (Fs increases rimwards) and sieve-textured, altered cores and contains small intergrowths of Mg-hornblende, actinolite and ferroactinolite. The microcrystalline groundmass consists mainly of altered plagioclase and augite with minor K-feldspar, quartz, ilmenite, titanite, chlorite, calcite, epidotes and, rarely, brown amphiboles. In some specimens post-magmatic garnet, prehnite and pumpellyite are also found (Awdankiewicz M., Awdankiewicz H. 2007).

Zircon characteristics

The zircons are diversified in morphology and many crystals are broken. Some of the euhedral crystals are strongly structured, with CL bright and dark oscillatory zoning. A few grains have rather irregular forms. Common Pb is rather low, between 0 and 0.68 %, whereas the Th/U ratio is mostly moderate to fairly high (c. 0.2 – 0.6), typical of magmatic zircons.

SHRIMP ages

Sixteen points in fourteen zircon crystals have been analysed. Four analytical points are significantly negatively discordant (two of them having ^{207}Pb-^{206}Pb minimum ages of c. 500 Ma) and these have been excluded from our interpretation.

Two points in irregular zircon grains gave positively discordant ^{207}Pb-^{206}Pb minimum ages of c. 1.4 and 2.0 Ga. Two other euhedral and zoned crystals (apparently magmatic in origin) yielded Neoproterozoic, fairly concordant ^{206}Pb-^{238}U ages: 565±5 and 578±6 Ma. Evidently, all these represent inherited materials.

The main population of zircons displays ^{206}Pb-^{238}U ages dispersed within the range of 298 – 318 Ma. The average Concordia age for seven points is 313±3 Ma. However, all the points are slightly- to significantly positively discordant which makes this average age problematic. The discordance indicates either Pb loss or mixing domains with variable proportion of inheritance.

Based on the data available, it is difficult to precise the true age of the micromonzodiorite dyke. Four positively discordant points oscillate around 307 and 311 Ma. However, most likely, the moderately discordant and relatively old ages of c. 318 Ma, representing the main population of the zircons, may approximate the magmatic event of the dyke.

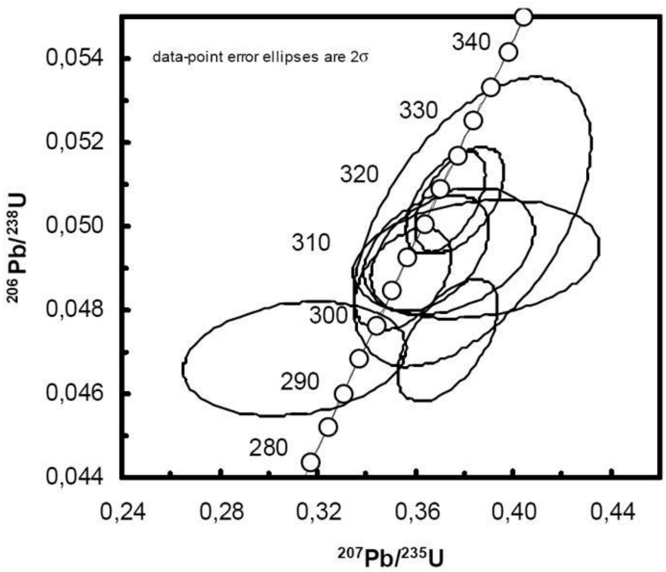

Fig. 1. Concordia diagram showing part of the SHRIMP zircon data from micromonzodiorite.

CONCLUSION

The preliminary SHRIMP data of zircon grains from the micromonzodiorite dyke in Bukowiec indicate a significant admixture of inherited materials of c. 2.0, 1.4 Ga, and c. 570 and, tentatively, 500 Ma. This information helps to define the older crustal materials, either in the source of the magma, and/or contributing to its contamination.

The SHRIMP data obtained suggest that the likely minimum age of the dyke is c. 318 Ma, and this would constrain the minimum age of the Karkonosze granite in that part of the pluton.

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MINERALOGIA POLONICA – SPECIAL PAPERS
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Wojciech BARTZ[1],Tomasz FILAR[2]

MINERALOGY OF BAROQUE RENDERINGS FROM THE HISTORICAL MONUMENT IN KOŻUCHÓW (LUBUSKIE VOIVODSHIP)

Abstract: This research focuses on the characteristics of the seventeenth century renderings of the façade of a building in Kożuchów (lubuskie voivodship), used in decorating details (figures of Saints). Petrographical, XRD and chemical analyses have been used to characterize these materials. Based on this study, two separate renderings have been distinguished, differing in composition of their filler. The first one is dominated by coarser grained siliceous sand, whereas the second one has a much finer grained filler, composed of a mixture of siliceous sand and numerous, non-transparent particles (charcoal and presumably metallurgical slag). Both renderings have similar, microcrystalline binder mass, composed of calcite and gypsum. Clay minerals, as well as carrion were also detected, as additives. The binder/filler proportion is found around 1:1.
Key words: baroque renderings, petrography, X-ray diffraction

INTRODUCTION

One of the main problems in the conservation of monuments is the knowledge of original technology. Typical masonry mortars between bricks and stones, mortars used as wall finishing materials internally (plaster) or externally (render), are composed of a mixture of water, binding material, filling material and sometimes additives, which modify their properties. Within this context the presented analysis of the renderings employed in the decorating details of the façade of a building located in the Klasztorna street no. 6, in Kożuchów (lubuskie voivodship, 21 km southwards the Zielona Góra) was made to determine their composition. The upper storey of the building is decorated with two figures of Saints, situated between windows. The figure on the northern side represents Saint Peter, whereas the one on the opposite side represents Saint Paul. Both of them are composed of brick core, covered with three renderings, of which only two are fully preserved. They are 1) the inner, creamy rendering and 2) the outer, greyish one. The third and the outermost rendering exists only fragmentarily.

Until now, no detailed data of the characteristics of the building's original masonry were known. According to Kowalski (1976) the building is baroque, and presumably was erected in the beginning of the XVIII century. However, records of the Office of the Protection of the National Heritage, Department in Zielona Góra date this building from the XVII century (Evidence Card Green: Kożuchów, Klasztorna 6, 1959). Across centuries several repairs and reconstructions were conducted for renderings, plasters and stuccowork, leaving only figures of the Saints

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unchanged. After a period of neglect, in 1960 the construction was pulled down, except for its façade, which is intentionally preserved due to the specific nature of its architecture. Both figures were in poor condition, particularly that of Saint Peter, which lost almost 80% of its primary form. In 2006 a renovation project has started, aiming at restoration of the building's original splendour.

SAMPLES AND METHODS

Due to the importance of the monument, four small, representative samples of the inner and the outer rendering were taken with the use of hammer and chisel. Two samples were collected from the figure of Saint Peter and the other two from the figure of Saint Paul. The choice of the appropriate analytical technique depended mainly on the available quantity of samples. The description of renderings was made with the application of optical microscopy and X-ray diffraction. The utilized preparation and methodology were described by Bartz and Wanad (2006). Two samples representing outer rendering from both figures were additionally digested with diluted hydrochloric acid, following the procedure depicted by Alvarez et al. (1999), to determine the acid insoluble residue. On the basis of this estimation, the binder/filler ratio was calculated, assuming that these constituents correspond to soluble fraction and insoluble residue, respectively (op. cit.). According to Alvarez et al. (1999) this assumption is valid, excluding materials with limestone filler.

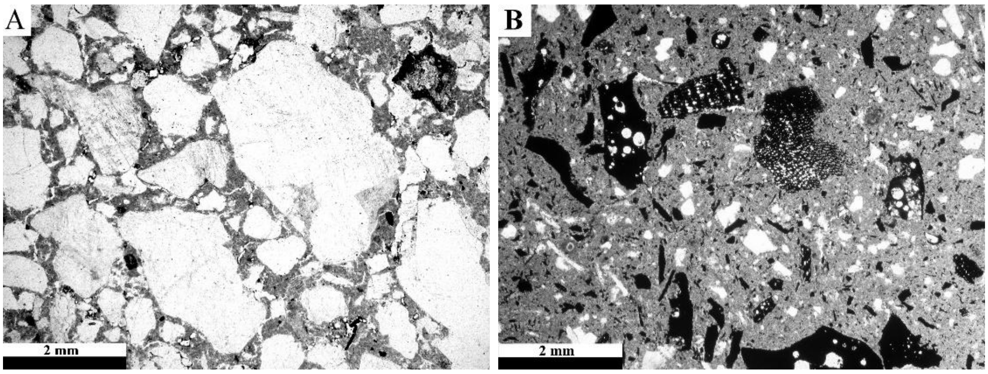

Fig. 1. Photomicrograph of a thin section cut from: a) inner rendering b) outer rendering, taken in plane polarized light.

RESULTS AND DISCUSSION

Optical microscopy shows that the filler of the inner rendering is coarse grained (0.2 to 2.0 mm), composed mainly of angular quartz and sparse rock-pieces grains (Tab. 1), disseminated in homogenous and microcrystalline binder mass (Fig. 1A). The filler of the outer rendering is finer grained and made up of numerous black coloured, elongated particles as main compound with subordinate angular, siliceous grains (Tab. 1, Fig. 1B). The latter ones typically reach up to 0.5 mm, whereas the former ones vary from very fine-grained, abundant dust, up to large, sparse 2.5 mm long pieces. Part of these black particles are regularly porous, with fuzzy edges and are recognized as charcoal. According to Brochwicz (1973) regularly arranged pores within charcoal particles suggest these were burnt from coniferous trees. The remainig black particles are amorphous, irregularly porous. Sparse larger grains are partly crystalline, enclosing some small inclusions of unidentified, medium birefringent phases (calc-silicates ?). According to Elsen (2006) the presence of these inclusions suggests they presumably represent grains of metallurgical slag, rather than scale forge. Charcoal, as well as scale forge and metallurgical slag, were previously widely used for preparation of mortars, plasters and renderings (Brochwicz 1973, Rogal 2002, Bartz, Wanad 2006, Elsen 2006). This kind of mortars was described by Furtenbach in 1628 (vide: Brochwicz 1973 pp. 84) for the first time. The addition of these components increases durability of mortars, maintaining desired moisture content, in addition giving them grey colour (Brochwicz 1973).

Tab. 1. Main mineralogical phases revealed by microscopic observations of analysed renderings.

	Quartz	Rock grains	Clay minerals	Opaque particles	Calcite	Gypsum	Organic fibres
Inner rendering	+++	++	+	-	+++	++	-
Outer rendering	++	-	+	+++	+++	++	++

+++ dominantly present + traces
++ present - not present

The volume of insoluble residue is high, ranging from 51% to 56% in the outer rendering. On the basis of these estimations, the filler/binder ratio was found around 1:1. Sparse organic fibres (wood, coat) and clayey particles were identified within the insoluble residue of outer rendering (Tab. 1) added to improve the tensile strength of the material (Elsen 2006).

The XRD analysis of both kind of renderings shows the predominant presence of calcite and gypsum, which constitute microcrystalline binder mass. The relative strong gypsum peaks on the XRD pattern suggest that this phase could not have resulted from sulfation by atmospheric deterioration (Sabbioni 2001), but represents intentionally added constituent. Quartz has also been identified as the main constituent of the filler. Through the XRD analysis of the outer rendering it is possible to detect the presence of peaks which might be assigned to lipscombite ($Fe_3(PO_4)_2(OH)_2$). This mineral supposedly could be attributed to the reaction of metallurgical slag, rich in iron, with organic additives (carrion) rich in phosphorus. The latter one was usually added to slaking pits (Brochwicz 1973). The increase of intensities at very low 2θ angles on XRD pattern could be attributed to the presence of clay minerals and organic matter, observed within insoluble residue of the outer rendering. The lime lumps (*sensu* Elsen 2006) have not been found within renderings, thus wet slaking of properly burnt lime is assumed rather than dry slaking (op. cit.).

SUMMARY

Two different renderings of the seventeenth century façade of a building located in Kożuchów have been recognized to be used in decorating details (figures of Saints). The outer rendering was prepared with a 1:1 mixture of a filler composed of siliceous sand with a heavy addition of additives (charcoal + presumably metallurgical slag) and a lime – gypsum based binder. The inner rendering consists of calcite and gypsum as a binder and siliceous sand as a filler.

The mineralogical characteristics of these renderings is similar to the XVII mortars found among the monuments of Toruń (Brochwicz 1973) and Henryków (Bartz, Wanad 2006). The absence of Portland cement compounds is the evidence of the originality of the renderings.

Those renderings prove to be older than restorations, that occurred at the turn of the XIX and the XX century. The examined renderings represent the unique technique of the XVII century masonry. The specific nature of the building has no equivalents in Kożuchów, as well as within the southern area of lubuskie voivodship, thus it requires an intensive protection.

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MINERALOGIA POLONICA – SPECIAL PAPERS
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Jakub BAZARNIK[1]

THE SULPHIDES AND SULPHATES IN SPHAEROSIDERITES FROM THE LUBLIN FORMATION (LUBLIN COAL BASIN; WESTPHALIAN B)

Abstract: Large sphaerosiderites from the Lublin Coal Basin (LCB) exhibit septarian structure with radial cracks filled by secondary minerals. Sulphides and sulphates from this paragenesis were examined. Nearly stoichiometric formulas of sulphides may suggest their origin in low-temperature solutions during late diagenesis. Analyses of Ni-Fe solution showed high content of Ni in sulphides from septarian cracks. The source of Ni is probably organic matter. The results of isotopic analyses of S suggest its origin in coal forming processes (Smith and Batts 1974). Sulphides were formed as a result of bacteria activity, and organic matter was a source of H_2S. Differentation of sulphur isotopes come in close system of H_2S source by the way of microbial activity. Sulphides formed during methanogenesis with high microbial activity while sulphates formed in late methanogenesis stage. Characteristic diffrences beetwen coexisting pyrite and barite confirm possibility of biogenic fractionation effect.
Keywords: sulphides, sulphates, sulphur isotopes, sphaerosiderites, Lublin Coal Basin

INTRODUCTION

Large sphaerosiderites from the Lublin Coal Basin (LCB) exhibit septarian structure with radial cracks filled by secondary minerals. Sphaerosiderites were collected from claystones and mudstones from the Bogdanka Coal Mine (LCB). Beside the presence of carbonates (siderite, calcite, dolomite), apatite, quartz, kaolinite (Bazarnik 2005) sulphides and sulphates are also present in septarian structures. Pyrite, nickelian pyrite ("bravoite"), millerite, sphalerite, chalcopyrite, barite and celestobarite were examined.

METHODS OF INVESTIGATION

Scanning electron microscope (SEM) observations and microphotographs were performed using FEI QUANTA 200 FEG microscope at the Department of Mineralogy, Petrography and Geochemistry, AGH-University of Science and Technology in Kraków.

Chemical compositions of minerals were obtain using Cameca SX-100 electron microprobe at the State Geological Institute of Dionýz Štur in Bratislava.

Sulphur isotope compositions were examined at the State Geological Institute of Dionýz Štur in Bratislava. Sulphides were converted to SO_2 for isotopic analyses by combustion with CuO at 770°C. The measurements were performed using Mat

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Finingan 200 mass spectrometer. Barite was converted to ZnS and then analysed as sulphides below. The $\delta^{34}S$ results are reported using the standard relative to the Canyon Diablo Troilite (CDT).

RESULTS

Pyrite is present as primary mineral in sphaerosiderite bodies, and as secondary one in septarian cracks. Primary pyrite forms small, allomorphous crystals with pure chemical composition: $FeS_{1.94-1.99}As_{0-0.01}$. Pyrite present in septaria forms large automorphous crystals (up to 2-3 cm) and framboidal aggregates. Framboidal pyrites are very pure: $FeS_{1.92}$ (low value of sulphur is caused by very small sizes of analysed crystals), while automorphous pyrites exhibit isomorphic substitution of Ni. Two varieties of large pyrites were determined: first one with higher Ni content: $Fe_{0.95}Ni_{0.04}Co_{0.01}S_{1.95-1.96}$ (Fig. 1; Secondary pyrite I) and the second one with lower Ni content: $Fe_{0.98-0.99}Ni_{0.01}S_{1.97-2}$ (Fig. 1; Secondary pyrite II).

Nickelian pyrite ("bravoite") forms small (up to tens of μm), single, automorphous crystals (Fig. 2a) with septarian cracks. The variable empirical formula of this mineral was constrained to $Fe_{0.64-0.79}Ni_{0.19-0.35}Co_{0.01-0.03}S_{1.95-1.99}As_{0-0.01}$.

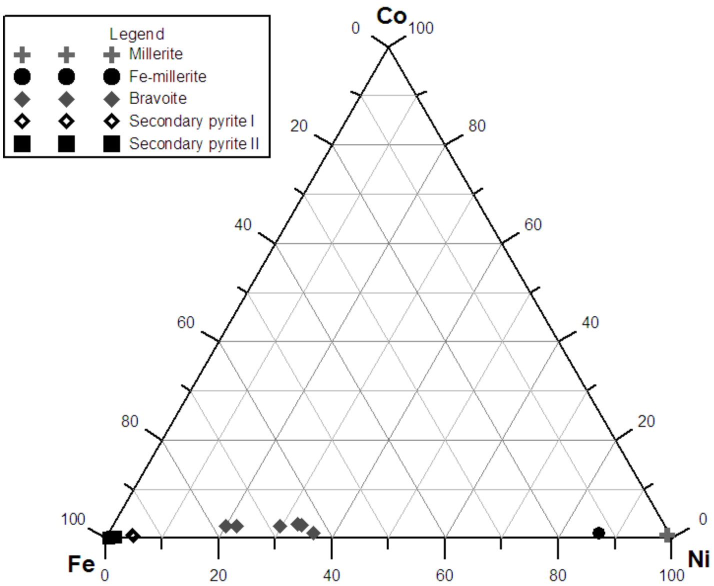

Fig. 1. Fe-Co-Ni plot of secondary sulphides with chemical compositions of analysed minerals.

Millerite forms aggregates of brass-yellow, needle-like crystals, up to 1cm long. The empirical formula was constrained to $Ni_{0.99}Co_{0.01}S$, except one crystal of millerite $Ni_{0.86}Fe_{0.13}Co_{0.01}S_{0.92}$.

Sphalerite and chalcopiryte are uncommon and form small (up to hundreds of μm), single crystals (Fig 2b and d). The formula of sphalerite is $Zn_{0.94-0.99}Fe_{0-0.01}Cd_{0-0.01}S_{1.01-1.05}$ and chalcopyrite - $Cu_{0.97-1}Fe_{0.96-1.01}Zn_{0-0.07}S_{1.99-2}$. Similar Fe-poor sphalerite from the Kladno coal district (Zacek and Fryda, 1995) is interpreted to be diagenetic.

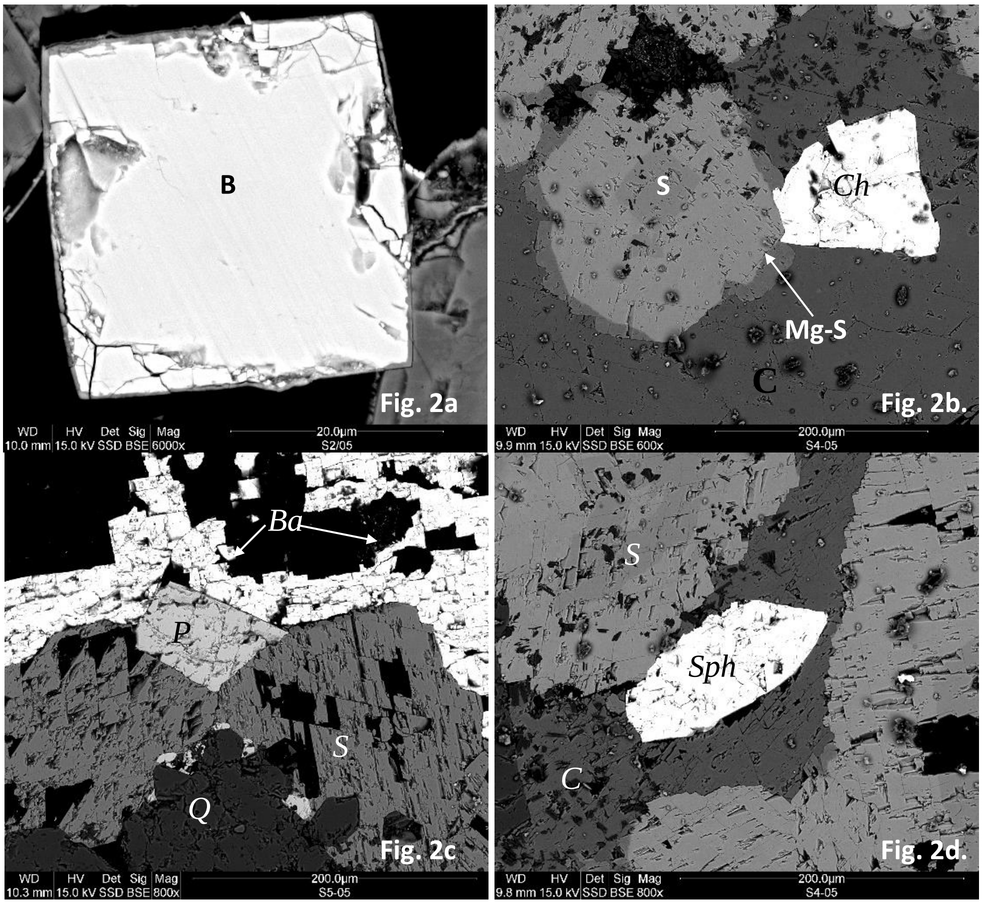

Fig 2a-d. Microphotographs of sulphides and sulphates from septarian cracks. B – nickelian pyrite (“bravoite”), Ch – chalcopiryte, C – calcite, S – siderite, Mg-S – Mg-siderite, P – pyrite, Ba – barite, Sph – sphalerite, Q – quartz.

Beside sulphides crystals of barite and strontium-bearing barite were observed in septarian cracks. Barite ($Ba_{0.92\text{-}1}Sr_{0\text{-}0.07}Fe_{0\text{-}0.01}Ca_{0\text{-}0.01}(SO_3)_{0.98\text{-}1}$) forms large aggregates of crystals (up to few cm; Fig. 2c), whereas strontium-bearing barite ($Ba_{0.67}Sr_{0.31}Fe_{0.01}Ca_{0.01}SO_3$) is present as very small (up to 20 µm), single crystals.

Stable isotope analyses of minerals provided high diversity of results (Tab. 1). Isotope composition of sulphur in sulphides varies between –3.794 and 37.391‰. Isotope compositions of sulphur in barite is very high: 75.432‰. It could be a result of isotope fractionation. Difference between coexisting pyrite and barite is ca. 28‰. It may suggest effect of biogenic fractionations of SO_2 (Kaplan, Rittenberg 1964).

Table 1. Sulphur isotope composition of some minerals from spaerosiderites.

Mineral	Millerite	Sphalerite	Pyrite	Barite
$\delta^{34}S$ (CDT) ‰	-3.794	14.611	37.391	75.432

CONCLUSIONS

Nearly stoichiometric formulas of sulphides suggest their origin in low-temperature solutions during late diagenesis. Analysis of Ni-Fe solution showed high content of Ni in sulphides from septarian cracks. The source of Ni is probably an organic matter. Similar paragenesis from the Kladno coal district desribed by Zacek and Fryda (1995) is interpreted to be diagenetic also. The results of isotopic analyses of sulphur are typical for coal forming processes (Smith and Batts 1974). Forming of sulphides was a result of bacteria activity and organic matter was a source of H_2S. Differentation of sulphur isotopes come in close system of H_2S source by the way of microbial activity. Sulphides were formed during methanogenesis under high microbial activity, while sulphates formed in late methanogenesis stage. Characteristic diffrences beetwen coexisting pyrite and barite confirm possible biogenic fractionation effect.

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Dawid BIAŁEK[1]

CHEMICAL COMPOSITION OF MONAZITES FROM THE JAWORNICKIE GRANITOIDS, WESTERN SUDETES

Abstract: The paper presents results of a comprehensive electron microprobe study of monazites from the Jawornickie granitoids, Western Sudetes. The monazites appeared chemically fairly uniform in all analyzed samples with ThO_2 contents of ca. 4,99-11,9, wt.%, UO_2 0,33-1,02 wt.%, La_2O_3 12,4-15,43 wt.%, Nd_2O_3 8,9-10,6 wt.%, Y_2O_3 1,12 to 1,91 wt.%. Some grains displayed weak zoning in the BSE image with increasing darkness near the rims. It was found that U and Y contents were somewhat lower in the outer growth shell. Chemical composition indicates monazite formation during a single stage and probably at constant P-T-X_{fluid} conditions.
Keywords: monazite, geochemistry, granitoids, Sudetes

INTRODUCTION

In acidic magmas the REE typically form minerals of their own: monazite, allanite and xenotime. The main REE-phosphate minerals in the Jawornickie granitoids are allanite and monazite, however they do not occur together in a rock samples.

The Jawornickie granitoids are dyke-like, elongated plutons of small size which occur within the multiply deformed rocks of the Złoty Stok – Skrzynka shear zone. The Jawornickie granitoids may be grouped into five groups according to mineralogical and geochemical criteria: type A - most typical, biotite is the only mafic silicate; type B – amphibole-bearing; biotite occurs as a primary mineral phase and as a reaction product associated with the margins of many amphibole grains; type C- with primary muscovite; Or_{96-99}, An_{27-1}; Bt – Fe/(Fe+Mg) - 0.4-0.43, Ti – 0.21-0.23; Msc – Na/(Na+K) – 0.10-0.13, Si – 7.18-7.39 (for O=22); type D- leucogranite; type E- pegmatite. The monazite compositions discussed here occur in granites of group C.

Geochemically Jawornickie granitoids of group C are broadly calc-alkaline with relatively high alkali (Na_2O+K_2O) content, ranging from 6.8 to 8.3 wt. %, Na_2O/ K_2O ratios of 2.5 to 3.6 and A/CNK ratios of 1.08 to 1.17. The average La_N/Lu_N is 20.87. Varieties with allanite as main REE phase are generally metaluminous to weakly peraluminous (A/CNK ratios of 0.8 to 1.07), high-K calc-alkaline rocks with higher concentrations of TiO_2, CaO, K_2O, MgO, Ba, Zr, and lower concentrations of Al_2O_3, Na_2O and La_N/Lu_N ratio (average -14.07) comparing to granitoids from group C.

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METHODS OF INVESTIGATION

Mineral analyses were performed in Clermont-Ferrand using CAMECA SX-100 electron microprobe, employing ZAF correction procedure. Analyses were conducted at 15 kV, and 20 nA. The counting times on the peak were 300 s for Pb, 75 s for Th and 225 s for U. For The REE and other elements, counting times were 60 s and 40 s on peak, respectively.

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RESULTS

Monazite typically forms euhedral to anhedral grains of stable size (100 μm to 150 μm) and mostly devoid of inclusions. Grains may be homogeneous or compositionally zoned, and are most commonly included within biotite. In the BSE image some grains displayed weak zoning with increasing darkness near the rims (Fig.1).

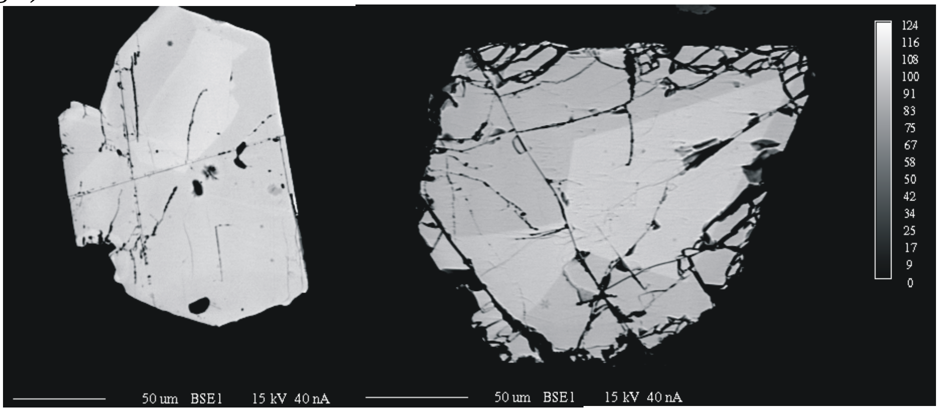

Fig.1. BSE images of monazites from the Jawornickie granitoids.

Concentrations of ThO_2 in monazites from the Jawornickie granitoids range from 4.99 to 11.9 wt%, which is typical for S- and I-type granites (Watt, Harley 1993; Förster 1996).

Typical reported concentrations of UO_2 in monazite-(Ce) from granitic rocks rarely exceed 1 wt% (Cuney, Friedrich 1987) similar to those studied here (from 0.33 to 1.02 wt.%). Th/U ratio range from 5.9 to 18.6. Such values of UO_2 and ThO_2 are characteristic for primary monazites (Bea 1996). Secondary monazites have very low Th and U contents, and often high Y contents. Y concentrations observed at Jawornickie granitoids are of the same order (from 1.12 to 1.91 wt% Y_2O_3) as those reported for monazite from common granitic rocks.

Concentration of Ce_2O_3 ranging from 24.76 to 30.04 wt.%. Ce/La and Ce/Nd ratios are grater than 1.8 and 2.7 respectively. Following the proposal of the IMA in distinguishing the members monazite-(La), monazite-(Ce) and monazite-(Nd) monazites from the Jawornickie granitoids are monazite-(Ce).

Concentration of Nd_2O_3 ranging from 8.7 to 10.6 wt.%, which is typical for monazites from granitic rocks, is generally accompanied by enhanced contents of Sm_2O_3 up to 1.93 wt.%.

Considering the number of atoms p.f.u., the following order of REE abundances emerges: Ce→ La → Nd →Gd →Pr → Sm → Er →Ho → Tb →Yb.

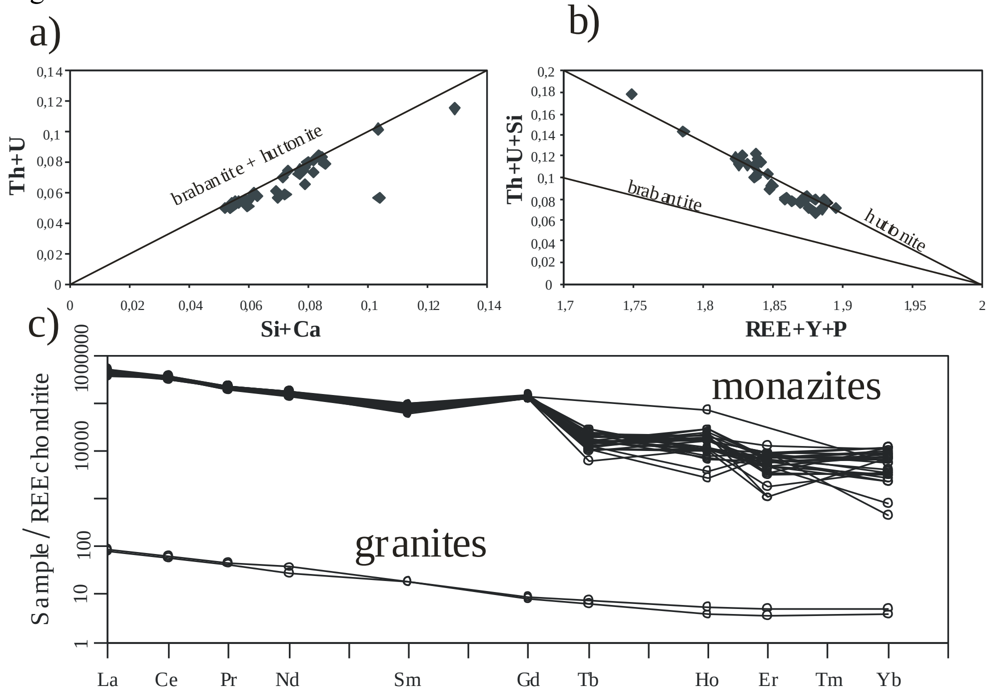

Fig.2. Chemical variations of investigated monazites: a) a plot of formula proportions Si+Ca vs. Th+U calculated on the basis of 4 O atoms; b) a plot of formula proportions REE+Y+P vs. Th+U+Si calculated on the basis of 4 O atoms; c) chondrite-normalized REE plots of analyzed monazites and their host rocks (normalized values are from Boynton, 1984).

Compositional variations of the analyzed monazites can be described in terms of the substitutions of the isostructural end-members brabantite, huttonite and monazite, and hypothetical tetragonal end-member xenotime. The influence of these substitutions on the compositional variations of the monazites is illustrated in a Si+Ca vs. Th+U diagram (Fig.2a), which shows that most analyses follow the linear trend defined by the huttonite [(Th,U)SiREE$_{-1}$P$_{-1}$] and brabantite [Ca(Th,U)$_{REE-2}$] exchange. In the (Th+U+Si) vs. (REE+Y+P) monazite analyses plot almost perfectly along the vector representing huttonite substitution (Fig. 2b).

Chondrite normalized REE concentrations are fairly homogenous (Fig. 2c) which suggests that monazite growth was a single-stage process which took place under constant conditions. A positive anomaly of Gd can be explained as a consequence of huttonite substitution. Förster et al. (2000) the predominance of Gd in chondrite-normalized patterns of huttonite explained in terms of charge and ionic radius of substituting elements.

CONCLUSIONS

Monazites from the Jawornickie granitoids are primary, magmatic monazite-(Ce). They do not show any evidence of inherited component. The chemical composition of monazites from Jawornickie granitoids can be described by simple substitutions, since all analyses plot uniformly along the same exchange vector. This indicates monazite formation during a single stage and probably at constant P-T-X_{fluid} conditions.

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MINERALOGIA POLONICA – SPECIAL PAPERS
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ORIGIN OF OCELLAR TEXTURE IN MAFIC INTRUSIVE ROCK FROM THE MARGIN OF THE EAST EUROPEAN PLATFORM

Abstract: Unusual ocellar texture from a compound diabasic-basaltic dyke from the margin of the East European Platform is described. It is concluded that ocelli are of several different types that formed by different processes, such as magma mingling, segregation of late-stage melts and hydrothermal filling of vesicles.
Keywords: ocelli, alkali diabase, mafic dyke, Teisseyre-Tornquist Zone

INTRODUCTION

Ocelli are spherical or ellipsoidal felsic bodies, up to a few millimetres in diameter, that occur in some mafic rocks, such as lamprophyres or alkali basalts. They have been usually interpreted as globules of one immiscible liquid in the other (e.g. Philpotts 1976; Vichi et al. 2005), however, their origin from late stage segregation melts (e.g. Foley 1984) or even hydrothermal fluids filling vesicles (Azbej et al. 2006) has also been considered.

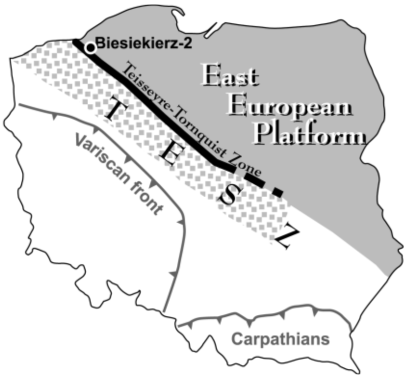

Fig. 1. Location of Biesiekierz-2 borehole on the background of main geological units in Poland.

A set of mafic dykes was recognized in the subsurface of Western Pomerania, at the margin of the East European Platform (e.g. Muszyński, Protas 2004). All the dykes exhibit similar chemical composition corresponding to alkali basalts, but differ in texture. A characteristic feature of one of the dykes, classified as a diabase (Muszyński, Protas 2004), is the presence of small spherical structures. The aim of the present contribution is to describe the spherical bodies and briefly discuss their magmatic vs. hydrothermal origin.

The study is based on macro- and microscopic observations, and on results from an electron microprobe. In the latter case, measurements were performed on five rock samples using the Cameca SX 100 electron microprobe in the Inter-Institution Laboratory of Microanalysis, Warsaw University.

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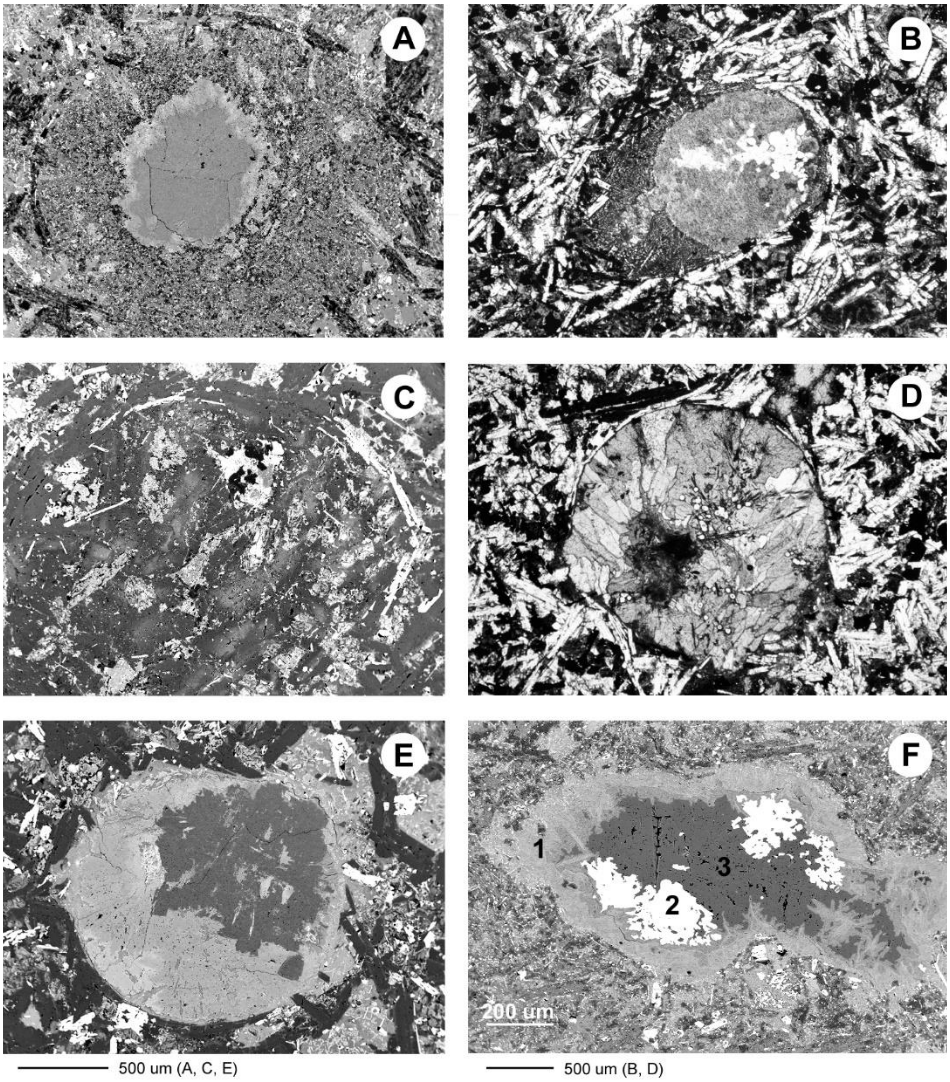

Fig. 2. Examples of "ocellar" texture in mafic dyke from Western Pomerania. **A** — BSE image of ocellus composed of two distinct zones: inner chlorite and outer multi-mineral fine grained zone; **B** — Photomicrograph of globule with carbonate (-quartz) core and alkali feldspar rim; **C** — BSE image of spherical microstructure composed of alkali feldpar with patches of chlorite and carbonates. Ilmenite and plagioclase crystals are arranged tangentially around the structure; **D** — Photomicrograph of carbonate spherical microstructure with minor chlorite and small quartz spheres; **E** — BSE image of carbonate sphere; light colour – magnesian siderite, dull colour – ankerite; **F** — Irregular-shape amygdale filled with chlorite (1), barite (2) and dolomite (3).

PETROGRAPHY

The Biesiekierz dyke was drilled by the Piła Petroleum Company at the depth of 3280-3300 m (Fig. 1). It cross-cuts Upper Devonian limestones. Generally, the dyke is composed of two parts which differ in texture. An eight-meter thick (apparent thickness) inner zone consists of a basaltic rock with porphyritic, intersertal, and amygdaloidal textures. Outer zones, of which the upper one is 9 m thick and only 4 m of the lower one was pierced, exhibit a subophytic texture, i.e. they consist of a diabase. Both rock types differ also in chemical composition: the basaltic rock contains more iron and magnesium, and less silica and alkalis in comparison to the diabase (average content of $Fe_2O_{3\,(tot)}$: 17.9 wt.% and 15.1 wt.%, respectively, MgO: 9.1% and 5.2%, (Na_2O+K_2O): 3.3% and 4.3%, SiO_2: 41.5% and 44.0%, LOI free basis). Chemically, the basalt is of subalkaline type and the diabase is an alkaline variety.

The diabase consists of plagioclase laths (andesine and labradorite), diopside relics, ilmenite, apatite, biotite and alkali feldspar. The latter fulfils interstices and amounts to 15 vol.% of the rock. Secondary minerals include abundant chlorite and calcite. The basaltic rock is more altered, phenocrysts of plagioclase and mafic minerals are replaced by albite, chlorite, calcite, quartz and K-feldspar. The groundmass is brown in colour and contains tiny crystals of chlorite, albite, anatase, K-feldspar, quartz, and needles of apatite.

Contact between both rock types is sharp; a distinct feature of the contact zone is the presence of several millimetre-centimetre sized fragments of the basaltic rock in the diabase. This suggests that the dyke was formed in at least two intrusive pulses, and the subsequent magma of higher temperature and density was delivered before the earlier magma was completely crystallized and cooled.

Ocelli-like microstructures occur in the diabase and are of several types. All of them have a sharp contact with the groundmass.

(1) 2-3 mm ovoid bodies composed of two distinct zones, a core filled with chlorite and a very fine grained multi-mineral rim (Fig. 2A). The rim consists of a mixture of chlorite, albite, anatase, K-feldspar, quartz, apatite and zircon. The average crystal size equals 10-20 μm. Apatite needles are of similar shape and composition as in the groundmass. This type of ocelli occur 10-30 cm below the contact zone with the basaltic rock.

(2) 2-3 mm globules composed of a spherical core and alkali feldspar rim (Fig. 2B) or 2-3 mm spherical structures filled largely with alkali feldspars (Fig. 2C). The compositional range of alkali feldspars in the ocelli and in the groundmass is almost identical (Fig. 3).

(3) 2-3 mm spheres filled with carbonate minerals (magnesian siderite or ankerite, or both, Fig. 2E), or spherical bodies with a complex microstructure with chlorite, carbonates, 10 μm silica spheres (Fig. 2D).

Plagioclase laths, ilmenite needles and chlorite flakes are arranged tangentially around the (2) and (3) structures.

In addition, the basaltic rock contains abundant spherical to irregular amygdales. The amygdale sizes vary from 0.05 to 1 mm. An upward size increase toward the top can be observed in many hand-specimens. The amygdales are

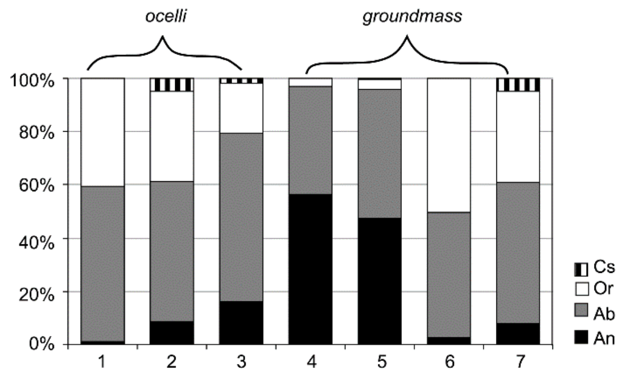

Fig. 3. Compositional range of feldspars in ocelli and in the diabase groundmass. Alkali feldspars filling ocelli (1-3) are almost identical in composition to late-stage feldspars from the host rock (6-7).

filled with chlorite, or with chlorite and calcite. Rarely, there are more minerals formed in subsequent episodes (e.g. chlorite, barite, dolomite – Fig. 2F).

PRELIMINARY CONCLUSIONS

Several lines of evidence suggest that the spherical microstructures observed in the diabase formed by several different processes.

The type **(1)** ocelli are an effect of magma mingling, i.e. the ocelli are solidified droplets of a basaltic magma in a diabasic one. This conclusion is supported by their limited occurrence below the contact zone and the textural and compositional similarity between the ocelli rim and the basalt groundmass. The chlorite core represents a former gas bubble and suggests that the basaltic magma was fluid-rich.

The type **(2)** ocelli formed as a result of segregation of a late-stage melt into vesicles which is shown by the similar compositional range of alkali feldspars in the spherical microstructures and the diabase groundmass.

The type **(3)** spherical microstructures probably represent hydrothermally filled vesicles. Common tangential arrangement of crystals around these structures points to bubble expansion with decreasing pressure.

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MINERALOGIA POLONICA – SPECIAL PAPERS
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Michał BOROWSKI[1]

SERPENTINITE STRUCTURES FROM THE EASTERN PART OF THE GOGOŁÓW-JORDANÓW SERPENTINITE MASSIF AS A KEY TO PETROARCHAEOLOGICAL ANALYSIS OF NEOLITHIC STONE TOOLS

Abstract: Results of comperative study of serpentinite structures from eastern part of the Gogołów-Jordanów serpentinite massif (the Ślęża ophiolite) and from neolithic artifacts are presented. Partly pseudomorphic structures with numerous bastites in lepidoblastic antigorite background that prevail in analysed serpentinite stone tools are typical for the area of the investigation. However, the presence of mesh structure with good preserved relics of primary minerals sugests, that some artifacts must have come from other sources.
Keywords: serpentinite, Ślęża ophiolite, petroarchaeology, the Neolithic, stone tool

INTRODUCTION

The Neolithic (also called the Younger Stone Age), lasting on the Lower Silesia approximately since 5500 till 2000 B.C., brought dissemination of permanent settlement, rise of farming and caused a brilliant development of material culture. Significant progress in neolithic stone tools manufacturing is manifested not only in careful forming and polishing of their surfaces but also in widespread using, apart from flint, other stone raw-materials.

Serpentinite was in Lower Silesia, especially in the late Neolithic, the most popular local raw material for production of various polished stone tools. Hitherto petrographic analysis and archaeological investigations suggest that the most important source of this rock was located in the Gogołów-Jordanów Serpentinite Masiff (GJSM).

The GJSM is a large ultramafic body, situated in the northern margin of the Góry Sowie Gneissic Block, composed of serpentinized mantle tectonites and ultramafic cumulates. These rocks were described by Majerowicz (1979) as the lowest member of the larger ophiolitic sequence (the Ślęża ophiolite). Together with similar, smaller outcrops of serpentinites (the Szklary Massif and the Grochowa-Braszowice Masiff) the GJSM is a part of the Central Sudetic Ophiolite.

The aim of this study is petrographic characteristic of serpentinite structures from the E part of GJSM and their comparison with structures observed in serpentinites from Neolithic artifacts.

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SERPENTINITE AS A RAW MATERIAL FOR PRODUCTION OF NEOLITHIC STONE TOOLS

Serpentinite is the most popular raw-material in the colection of 670 stone tools from the Lower Silesia. About 100 artifacts (18,5 % of the assemblage) was made of this rock. Interestingly, 3,3% of artifacts in the collection was produced of nephrite, which occurs together within serpentinite in the vicinity of the Jordanów Śląski village (the E part of the GJSM) (Cholewa 2004).

Such widespread use of ultramafic rocks was relevant to their suitable technical properties: high specific gravity, substantial compactivity and low porousity. This advantages, in conjunction with good decorative peculiarities, caused the great popularity of serpentinite. Neolithic tool-makers preferred dense, unweathered, fine-blastic varieties of this rock. This sort of raw-material in the eastern part of the GJSM is widely exposed near the surface. It forms several, isolated outcrops on flat hills. Thus serpentinite could be easily found and exploited there by Neolithic people. (Cholewa 2004)

Petrographic analysis of serpentinite stone tools performed by Majerowicz et al. (2000) indicates that the main primary source of the raw-material was the GJSM. This results was supported by measurements of magnetic suscebility of serpentinites from artifacts (Prichystal & Gunia 2001). Furthermore, this conclusions are confirmed by results of archaeological excavation of Wojciechowski (1983), who described the Neolithic open pit-mine of serpentinite, situated on Jańska Góra – hill in the eastern part of the GJSM.

PETROGRAPHY

Several tens of serpentinite samples were taken from archaeological excavation area situated on the Jańska Góra hill (old Neolithic mine) as well as from four abandoned quarries of serpentinites near Jordanów Śląski, Glinica, Piotrówek and Trzebnik. For describing of petrographic features of serpentinites clasification of Wicks and Whittaker (1977) has been applied.

Investigated ultrabasites are aphanitic and exhibit massive texture. Macroscopically rocks from the eastern part of the GJSM show different tints of green, from pale yellow-green (Piotrówek) to deep green variety called “viper stone” (polish name: “żmijowiec” - Jordanów Śląski), brownish or grey to nearly black in some varieties (Jordanów Śląski). Serpentinites from Trzebnik quarry are generally olive-green and olive-beige. In all described outcrops serpentinites display small (usually up to 1 mm), scattered grains or thin veins of opaque minerals and differently coloured spots and patches usually occurs. Serpentinite from Janska Góra hill are characterized by presence of numerous parallel, thin (up to 3 mm) grey veins.

Under microscope serpentinites reveal lepidoblastic flame-structure (sensu Wicks and Whittaker 1977), usually partly pseudomorphic – with numerous bastites scattered in homogenuous antigorite background. Bastites are pseudomorphs of serpentine after primary minerals: commonly pyroxenes and rather seldom olivines. Opaque minerals, are represented mainly by magnetite, which forms scattered grains or (especially in serpentinites from Jordanów Śląski) replaces poligonal outlines of primary minerals. Magnetite forms also greater, irregular aggregates of opaque grains inside bastites or imitate cleavage in pseudomorphs after primary pyroxenes.

Short and thin (below 1mm) veins of talc and carbonates also not uncommonly occure in antigorite background or inside bastites.

Few better preserved grey, hypidiomorphic relics of diallag with characteristic cleavage were ascertained only in one sample from Trzebnik quarry. Completely nonpseudomorphic structure, that indicates advanced serpentinization and intensive recrystalization of serpentine minerals, was observed solely in several samples from Jordanów Śląski quarry. In serpentinites from the Jańska Góra hill, in addition to typical partly pseudomorphic structure, numerous, parallel, slightly folded, discontinuous chrisotile and carbonate veins were observed. They often display red-brownish colour caused by little amounts of dispersed Fe-hydroxides and contain also numerous irregular opaque minerals aggregates with some translucent, russet grains of chromite. Few, small, flaky aggregates of chlorite were also observed in serpentinites from this outcrop.

Macroscopically serpentinites from Neolithic artifacts display similar various tints of green or grey with scattered spots and dark grains of opaque minerals. They are aphanitic and usually exhibit massive texture. Oriented textures manifested by thin parallel veins or colour differentiation are uncommon. Surfaces of the stone tools are usually covered with thin layer of brown patina.

In thin sections two main structures can be observed in studied serpentinites from the artifacts: partly pseudomorphic structure with numerous scattered bastites in the predominant antigorite background and lepido-nematoblastic mesh structure with good preserved relics of primary minerals – mainly pyroxenes but also olivines and amphiboles.

Serpentinites with partly pseudomorphic and uncommon completely nonpseudomorphic structures are very similar to described rocks from the eastern part of the GJSM. Additionaly veined structures – very resembling to those observed in the serpentinite from the Jańska Góra hill - were ascertined in several cases. Serpentinites with numerous good preserved relics of primary minerals are significantly different from ultrabasites from the area of the investigation.

CONCLUDING REMARKS

Presented results confirm the thesis that the E part of the GJSM was in the Neolithic very important source of ultramafic rocks used for stone tool production. Observed in many serpentinite artifacts partly pseudomorphic, nonpseudomorphic and veined structures with predominant lepidoblastic antigorite background are typical for the area of the investigation. Especially the Janska Gora hill and the nearest vicinity of the Jordanów Śląski village (the Kamienny Grzbiet hills) seem to be very probable areas of exploatation.

Serpentinite with significant amounts of good preserved relics of primary minerals and mesh structure may come from the central part of the GJSM, where ultrmafic rocks are less serpentinized then in the E part of the unit. However the provenance from one of the other Lower Silesian ultramafic massifs cannot be excluded.

Accurate and certain identification of sources where raw materials for production of individual artifacts were obtained is very difficult. However future investigations of serpentinite structures from the GJSM and similar units, combined with comperative studies may support further regional specifications.

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INCREASED PRECISION IN MICROPROBE MONAZITE GEOCHRONOLOGY: IMPLICATIONS FOR EVOLUTION OF THE CRYSTALLINE ROCKS FROM THE SILESIAN RIDGE (WESTERN OUTER CARPATHIANS, POLAND)

Abstract: Total U-Th-Pb geochronology of monazite by electron probe microanalysis was used to study three metamorphic rock cobbles from ca. 60 Ma flysch rocks in the Silesian Unit. These cobbles were derived from the Silesian ridge, one of the source areas that supplied Carpathian basins with clastic material. Microtextural observations suggest that some monazite grew during igneous crystallisation and others grew during subsequent metamorphism and hydrothermal alteration. The age of these grains was determined to be ca. 592 Ma in gneiss from Gródek and ca. 370 Ma in gneiss from Izdebnik and granulite from Siekierczyna. Reaction textures involving growth of monazite during metamorphism in the latter two samples were constrained to ca. 336-315 Ma.
Keywords: monazite, gneiss, granulite, provenance, Silesian ridge, Western Outer Carpathians, Poland

INTRODUCTION

Monazite, a rare earth element orthophosphate, commonly occurs in gneiss and granulite cobbles from the Upper Istebna Beds (Silesian Unit, Western Outer Carpathians, southern Poland). These cobbles are considered to have been derived from the Silesian ridge, one of the internal source areas that supplied Carpathian basins with clastic material (Oszczypko 2006). These source areas are no longer exposed because of erosion in the Tertiary period followed by overthrusting of the Carpathian nappes. Therefore, studying the clastic material is the only way to improve knowledge of its geological structure and evolution. This methodological study provides increased precision on the age of important events during the evolution of some crystalline rocks from the Silesian ridge compared to previous results (e.g. Budzyn et al. 2006).

METHODOLOGY

Preliminary observations of microstructures and semi-quantitative analyses of polished thin sections were performed using a HITACHI S-4700 field emission scanning electron microscope (FESEM) equipped with a NORAN Vantage energy dispersive spectrometer (EDS) at the Institute of Geological Sciences of the Jagiellonian University in Kraków, Poland.

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All Electron Microprobe analyses were performed at the University of Massachusetts Amherst. X-ray maps were collected on the Cameca SX-50 operating in wave-length dispersive mode with 4 crystal spectrometers using a focused beam (~2-3µm spot size) with an accelerating voltage of 15kV, a 200nA beam current, 100ms dwell times, and 0.3-0.8µm steps. *In situ* quantitative analyses were made using the Cameca *Ultrachron* which is specially adapted for trace element analysis (Jercinovic, Williams 2005). Polished thin sections coated with an aluminum and carbon to reduce beam-damage effects during point analyses (cf. Jercinovic, Williams 2005; Williams et al. 2007) were studied using a focused beam (~1µm spot size) with a 15kV accelerating voltage and a 200nA beam current.

MONAZITE CHRONOLOGY

An analytical strategy based on *in situ* mapping (Williams and Jercinovic 2002) was used in this study. Grains were selected for analysis on the basis of FESEM microstructural observations and mapped for Y, Th, U and Ca to distinguish compositional domains prior to *in situ* analysis (Fig. 1). For each compositional domain identified in a monazite grain, wavelength scans of the Th, U, and Pb regions of the X-ray spectra were collected. Background intensities for each compositional domain were determined by regression with BKGII software (M. Williams personal communication) so as to minimise the effects of background curvature and background interferences caused by high-order REE X-ray lines. Individual spot analyses specific to each compositional domain were collected in a tight cluster around the background point (Fig. 1). An age and error for each domain were calculated using the DATCON III program (M. Williams personal communication).

ANALYZED SAMPLES

One gneiss cobble from Izdebnik (sample IZD5), and a granulite cobble from Siekierczyna (sample SE2) studied by Budzyn et al. (2006) using the methodology of Montel et al. (1996), and a previously unstudied gneiss cobble from Gródek (sample JR20A) are described in this contribution.

RESULTS AND DISCUSSION

Monazite in gneiss from Gródek (sample JR20A) exhibits concentric growth zoning interpreted to be related to igneous crystallization of the protolith. Monazite cores and rims yield a statistically identical age of 592±20 Ma.

A monazite inclusion in garnet from the granulite (sample SE2) yielded ages of 372±5 Ma for core and 336±5 Ma for rim (Fig. 1). Monazite core ages are interpreted to be related to primary crystallization in the granite protolith. From the relatively lower Y content in the monazite rim and its younger age, the monazite rim is interpreted to have grown during, or shortly after the crystallization of garnet and therefore dates the age of amphibolite- to granulite-facies metamorphism. Matrix monazite gives ages of ca. 315 Ma and most likely reflects the age of peak granulite-facies metamorphism (cf. Budzyn et al. 2006).

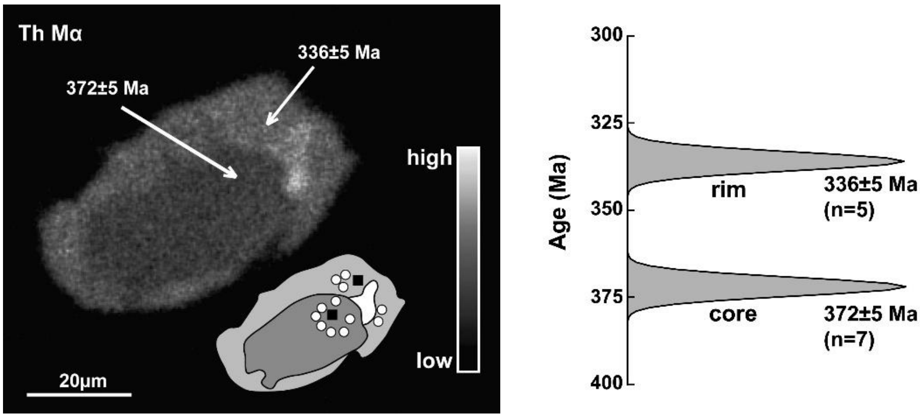

Fig. 1. Monazite inclusion in garnet from granulite (sample SE2). *Left image* – Th Mα X-ray map. Black squares on the sketch represent background collection points, and circles – quantitative analysis points. Analyses were obtained from two homogenous domains in core and rim. The highest Th domain was not analyzed because of its small size. *Right image* – normal distribution curves summarizing EMP ages for both domains in monazite grain. Zonation in monazite is interpreted as an igneous core overgrown by the metamorphic rim.

Monazite ages of 368±12 Ma and 333±8 Ma were obtained from monazite grains in gneiss from Izdebnik. The older age was determined in a ca. 180 μm monazite grain, and in a second monazite core with a younger rim. Two other grains (monazite intergrown with apatite and matrix monazite) display only younger ages of 333±8 Ma.

CONCLUSIONS

Monazite geochronology in metamorphic rock cobbles was significantly improved compared to a previous study (Budzyn et al. 2006). The methodology used in that study involved the collection of large datasets that were then subdivided according to user defined limits. Application of the CHIME method would also be unsuitable because although better suited to studying grains with a wide compositional variation, it is dependence on all compositional domains and grains being of one age. Moreover, the inconsistent analytical procedures and absence of reproducibility in the previous dataset arising from factors such as incorrect measurement of background intensities, as well as the failure to take into consideration the complex compositional zonation of monazite grains, give the new results greater reliability.

The results indicate two periods of monazite crystallization in the granitic protoliths, at ca. 592 Ma and ca. 370 Ma. Metamorphism in the Silesian ridge was constrained to ca. 336-315 Ma. These results are consistent with previously reported results, but they are significantly more tightly constrained (e.g. Budzyn et al. 2006; Poprawa et al. 2005). The increased precision obtained in this study is the result of treating each compositional domain as a unique Chrono-Chemical system that must be analytically investigated in isolation by multi-point analyses, providing a single age and uncertainty for those domains.

Acknowledgments: Paweł Poprawa and Tomasz Malata are greatly acknowledged for providing samples of gneiss (IZD5) and granulite (SE2). This work was partially suported by the Junior Fulbright Advanced Research Grant (to B.B.), the MNiSW research grant 2P04D04129 (to B.B.), the Jagiellonian University research funds DS811 and BW.

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MINERALOGIA POLONICA – SPECIAL PAPERS
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Jolanta BURDA[1]

U-Pb ZIRCON AGE OF LEUCOGRANITE FORMATION IN THE CRYSTALLINE BASEMENT OF THE WESTERN TATRA MTS.

Abstract: U-Pb LA-MC-ICP-MS geochronological analyses of zircons from leucogranites within the Western Tatra crystalline complex establish crystallization ages of 359.2±1.4 Ma (2 sigma). It implies that leucogranite bodies and dated earlier migmatitic leucosomes present in the metamorphic basement reflect the same stage of partial melting, that occurred during shearing and overthrusting related to the Upper Devonian/Lower Carboniferous continent-continent collision. The local occurrence of inherited, neo-Proterozoic magmatic zircon cores indicate the presence of a magmatic component (orthogneiss?) in the melted source.
Keywords: LA-MC-ICP-MS, zircon, leucogranites, Western Tatra Mts.

INTRODUCTION

Crystalline basement of the Western Tatra Mts. is formed by polygenetic granitoid intrusion and its metamorphic envelope. The metamorphic envelope is cut by two types of granites: older granite (at present orthogneiss - 405 Ma) and younger granite (350-360 Ma, Poller et al. 2000). The metamorphic complex is composed of two superimposed units, differing in petrographical and chemical character, P-T conditions of metamorphism and tectonic deformations (Kohut, Janak 1994; Gawęda, Burda 2004). In the shear zone dividing both units and in close association with migmatitic rocks from the upper unit small intrusions of leucogranites are present (Gawęda 2001).

The P-T conditions of both migmatites and leucogranite portions generation are P = 7.5 – 10 kbar and T = 690-800°C (Burda, Gawęda 1999, Gawęda, Burda 2004). Trace element modelling showed that leucogranites are 20-30% partial melts, squeezed from the surrounding metapelitic rocks during collision of tectonic microplates (Gawęda 2001). The investigations carried out in the last time revealed the age of migmatization in the Upper Unit complex around 360 Ma (Burda 2007). The aim of this paper is to establish the age of leucogranite melt formation using LA-MC-ICP-MS U–Pb zircon dating and cathodoluminescence (CL) image analysis and to compare them with the age of migmatization process.

SAMPLE DESCRIPTION

A sample of medium-grained leucogranite from Ornaczański Żleb was taken for the analyses. This rock is composed of K-feldspar (Or_{99-95} Ab_{1-5}), oligoclase-albite (An_{14-19} to An_{4-9}), quartz, with minor garnet, muscovite, biotite (*fm* = 0.58-0.66), monazite, and sporadically found zircon and apatite crystals. Leucogranite shows

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SiO_2 content 74% wt. and high A/CNK value (1.4) with $K_2O \geq Na_2O$, typical for peraluminous melts. Oriented fabric due to magmatic flow is a typical feature of the investigated leucogranite. Mineralogy and the geochemical characteristics of the leucogranites in the study area have been discussed by Gawęda (2001) in detail.

METHODS OF INVESTIGATION

Zircons were separated using standard techniques involving crushing, hydrofracturing, washing, Wilfley table, magnetic separator and final handpicking. The separation was carried out in the Institute of Geological Sciences, Polish Academy of Sciences, Kraków. Zircon grains were selected for morphological studies by scanning electron microscopy (SEM). Then they were mounted in epoxy in 2,5 cm-diameter circular grain mounts, polished and imaged by cathodoluminescence (CL) using a FET Philips XL 30 electron microscope (15 kV and 1 nA) at the University of Silesia, Sosnowiec.

Zircon $^{206}Pb/^{238}U$ and $^{207}Pb/^{206}Pb$ ages were determined using a 193nm solid state Nd-YAG laser (NewWave UP193-SS) coupled to a multi-collector ICP-MS (Nu Instruments HR) at the University of Vienna. Ablation in a He atmosphere was either spot- or raster-wise according to the CL zonation pattern of the zircons. Spot analyses were 15-25 µm in diameter, whereas rastering line widths were 10-15 µm with a rastering speed of 5 µm/sec. The calculated $^{206}Pb/^{238}U$ and $^{207}Pb/^{206}Pb$ intercept values were corrected for mass discrimination from analyses of standards 91500 (Wiedenbeck et al. 1995) and Plesovice (Slama et al. 2006) measured during the analytical session. The correction applies regression of standard measurements by a quadratic function. A common Pb correction was applied to the final data using the apparent $^{207}Pb/^{206}Pb$ age and the Stacey and Kramers (1975) Pb evolution model. The final U/Pb ages were calculated at 2σ standard deviation using the Isoplot/Ex program - version 3.00 (Ludwig 2003).

RESULTS

Zircons from leucogranite are mainly euhedral, clear, colourless crystals with aspect ratio < 4:1. For most grains, CL images reveal oscillatory zoning (single-phase crystals) that is characteristic of magmatic growth. One crystal shows an older inherited component surrounded by an oscillatory zoned rim (Fig.1).

The sample studied is exceptionally poor in zircon. The age determination is based on five measurements by LA-MC-ICP-MS only. All data points fit within error on the concordia. Five single-phase zircons give a concordia age of 359.2±1.4 Ma. One inner core was dated at about 590 Ma (Fig. 1 - JBAl04).

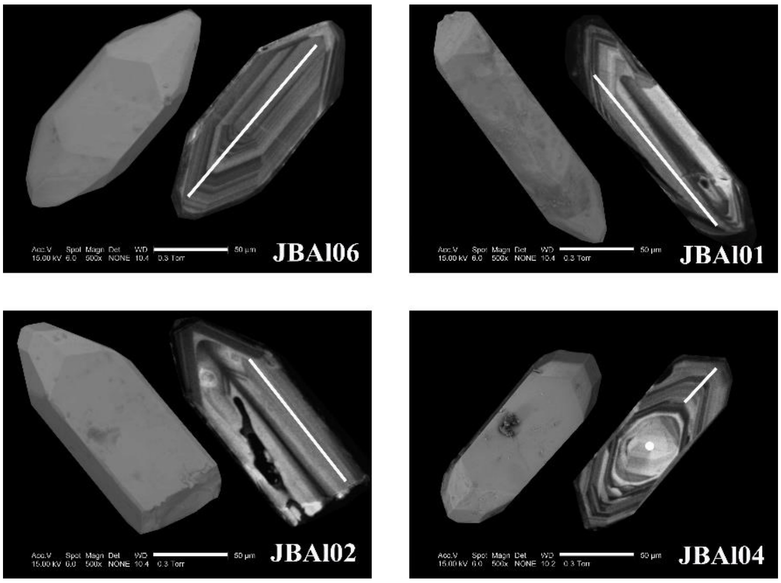

Fig. 1. Secondary electron (the left) and cathodoluminescence (the right) images of zircon from leucogranite. The lines and point show the approximate locations of laser ablation trenches and are not to scale.

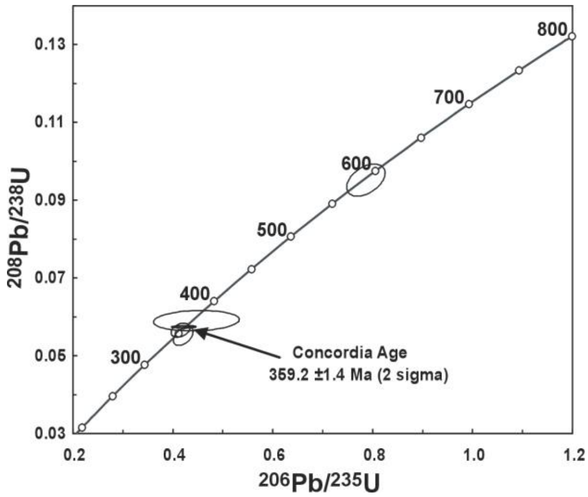

Fig. 2. Concordia diagram of LA-MC-ICP-MS U-Pb zircon analytical results for leucogranite from the Western Tatra Mts.

CONCLUSIONS

According to geochronological data, leucogranite bodies and migmatite leucosome (Burda 2007) present in the metamorphic basement, represent the same stage of partial melting occurred during thrusting and metamorphic inversion related to the Upper Devonian/Lower Carboniferous continent-continent collision around

360 Ma. It resulted in the intrusion of the Western Tatra granite (the Younger Granite *sensu* Poller et al. 2000), which emplacement was dated at 350-360 Ma. The local presence of inherited, neo-Proterozoic magmatic zircon cores (590 Ma) may indicate the presence of a magmatic component (orthogneiss?) in the melted source.

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MINERALOGIA POLONICA – SPECIAL PAPERS
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Jolanta BURDA[1], *Urs KLÖTZLI*[2]

LA-MC-ICP-MS U-Pb ZIRCON GEOCHRONOLOGY OF THE GORYCZKOWA TYPE GRANITE - TATRA MTS., POLAND

Abstract: New U-Pb isotopic data obtained by LA-MC-ICP-MS analysis of single-phase zircon crystals from the Goryczkowa type granite of the Western Tatra Mts. (Tatric Superunit - Central Western Carpathians) yield a concordia age of 356.0±8.4 Ma (2 sigma), which is interpreted as the age of magma emplacement. This is consistent with the main magmatic event in the Western Tatra Mts. that led to the formation of the Younger Granites (*sensu* Poller et al. 2000). Recycling from a Precambrian continental crust with an age from Neoproterozoic (ca. 580 Ma) to Paleoproterozoic (ca.1800 Ma) is indicated by the detection of an inherited zircon component in the Goryczkowa type granite.
Keywords: LA-MC-ICP-MS U-Pb dating, zircon, granite, Western Tatra Mts.

INTRODUCTION

The Tatra Mts. are the northernmost part of the Tatric Unit which belongs to the Central Western Carpathians. The crystalline basement of the Tatra Mts. is dominated by polygenic granitoid intrusions consisting of a few petrographical varieties, which reflect the following magmatic events (Kohut, Janak 1994; Poller et al. 2000): intrusion of the Older Tatra Granite (now present as orthogneisses- dated at ca.405 Ma); formation of the Younger Tatra Granite - subduction-related granodiorites-tonalites, which intruded the Western Tatra metamorphic complex around 350-360 Ma; formation of leucogranites of the same age (360 Ma), resulting from partial melting of the metamorphic complex during thrusting and metamorphic inversion (Burda 2006, 2007); intrusions of quartz diorites (ca.341 Ma) found as small dykes and sills cutting the metamorphic rocks (Poller et al. 2000; Gawęda et al. 2005); porphyritic granodiorite and equigranular biotite monzo- to syenogranites (ca.314 Ma) and untill recently undated Goryczkowa type granite, restricted to northern margins of the crystalline core. Our study provides the first zircon U-Pb geochronological results for the Goryczkowa type granite.

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ANALYTICAL TECHNIQUES

Whole- rock analyses of major and trace elements were carried out by XRF and ICP-MS methods in the ACME Analytical Laboratories, Vancouver, Canada.

The sample was processed using standard mineral separation techniques. Forty grains, 50-250 μm in diameter, were mounted with standards in epoxy and polished. Cathodoluminescence images (CL) have been used to identify internal structures of individual zircon grains using a FET Philips XL 30 electron microscope (15 kV and 1 nA) at the University of Silesia, Sosnowiec.

Zircon $^{206}Pb/^{238}U$ and $^{207}Pb/^{206}Pb$ ages were determined using a 193nm solid state Nd-YAG laser (NewWave UP193-SS) coupled to a multi-collector ICP-MS (Nu Instruments HR) at the University of Vienna.

Ablation in a He atmosphere was either spot- or raster-wise according to the CL zonation pattern of the zircons (Fig. 1). Spot analyses were 15 - 25 μm in diameter whereas line widths for rastering were 10 - 15 μm with a rastering speed of 5 μm/sec.

SAMPLE DESCRIPTION

A representative sample of Goryczkowa type granite was collected from Beskid near Kasprowy Wierch. This granite has a porphyritic fabric with pinkish K-feldspar up to 2 cm in length. The mineral assemblage mainly consists of perthitic K-feldspar, plagioclase (25-28% An), quartz, muscovite and biotite. Accessory phases comprise apatite, zircon and monazite.

Porphyritic granites are peraluminous (A/CNK = 1.6) with silica content around 73 wt.%, characterized by $K_2O > Na_2O$ and high Rb/Sr ratio = 2.5. The chondrite-normalized REE diagram show LREE enrichment expressed as $(Ce/Yb)_N > 5$ and negative Eu anomaly (Eu/Eu* = 0.71). Normative corundum is about 3.8%. Porphyritic granites show low Zr and Y content (31 ppm and 6.3 ppm respectively). Pearce et al. (1984) diagrams suggest VAG geotectonic regime of analysed granites.

LA-MC-ICP-MS U-Pb RESULTS

Zircon crystals from the analysed samples (JBB2) are generally euhedral, clear, colourless grains with aspect ratios < 4:1. Grain size varies in length from ca. 50 to 250 μm. In most zircons the [110] prism is better developed than [100], with the [101] bipyramid dominating over the [211]. The most characteristic subtypes are S4, S3 and S8 (Pupin 1980). CL investigations show that the short- and normal prismatic crystals usually exhibit two different domains: an internal part (core) with well-developed oscillatory zoning indicating an igneous source, surrounded by a younger rim with oscillatory zoning also. The long prismatic crystals (single-phase crystals) show only the oscillatory zoning (Fig. 1).

Twelve measurements on nine crystals were made (Fig. 1). All data points are concordant within the assigned error (Fig. 2). Nine single-phase zircons with oscillatory zoning give a concordia age of 356.0±8.4 Ma (2 sigma). Two from inherited cores give an age of ca. 560 Ma and one ca.1800 Ma.

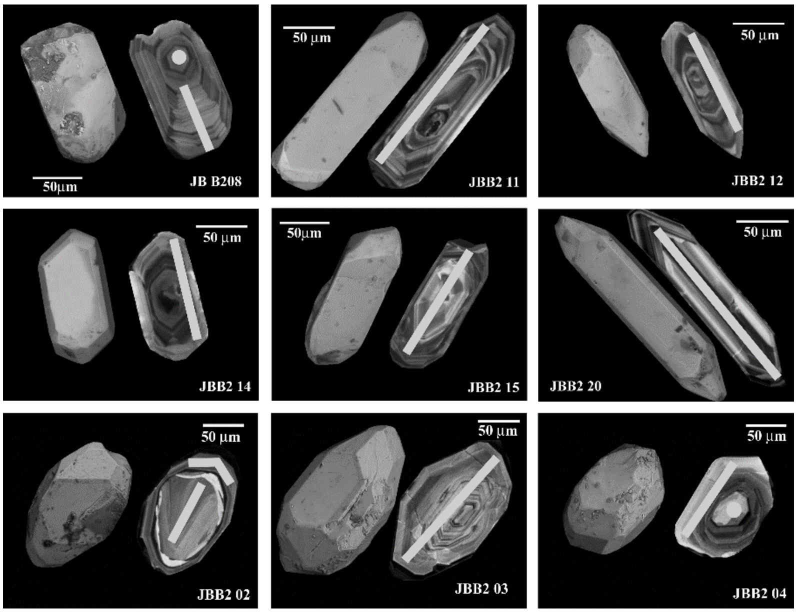

Fig. 1. Secondary electron and cathodoluminescence images of representative zircon crystals from Goryczkowa type granite. The grey lines and points show the approximate locations of laser ablation trenches and spots.

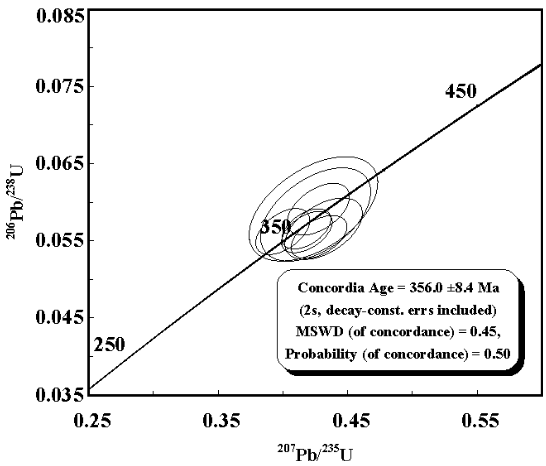

Fig. 2. Concordia plots of U-Pb zircon data from Goryczkowa type granite from the Western Tatra Mts.

CONCLUSIONS

The analysed rock with high a A/CNK value and normative corundum shows typical features of S-type granites (Chappell, White 1974). Based on the presence of growth oscillatory zoning from centre to rim in the analysed crystals the concordia age of 356.0±8.4 Ma is considered to represent the crystallization age of this granite. The presented U-Pb LA-MC-ICP-MS zircon data indicate an Upper Devonian/Lower Carboniferous age of the Goryczkowa type granite. It is contemporary with the main magmatic event in the Western Tatra Mts.

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MINERALOGIA POLONICA – SPECIAL PAPERS
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Justyna CIESIELCZUK[1]*, Magdalena SIKORSKA*[2]

SUITABILITY OF THE CATODOLUMINESCENCE METHOD IN THE INVESTIGATION OF HYDROTHERMAL ALTERATION IN GRANITOIDS

Abstract: The inexpensive cathodoluminescence method is applied to the investigation of hydrothermally altered granites. Tiny mineral grains, commonly formed in the initial stages of alteration, are often overlooked in microscopic examinations. However, many of these grains display luminescence and, thus, may be easily identified using CL. With their real volume in the rock now known, the mass balance calculated for the whole rock can be properly determined. In addition, the degree of granite alteration, and especially the alterations to the feldspars, is well seen in CL images.
Keywords: granitoids, cathodoluminescence method, hydrothermal alteration, Sudetes Mts.

INTRODUCTION

Granites are affected by hydrothermal alterations towards the end of their cooling histories. The degree of alteration mainly depends on the mineralogy, chemical composition, the shape and size of the granitic body and its internal structure. Hydrothermal fluids, penetrating granite along fractures, microfractures, cavities, mineral interstices and cleavage planes, are responsible for the crystallization of primary hydrothermal minerals directly from the fluids or for secondary, metasomatic, replacements of primary magmatic minerals. The parameters (pH, redox potential, ion concentration, temperature, pressure) of the hydrothermal fluids are very likely to change in time due to interaction with the penetrated rocks.

More rigorous microscopic observations indicate that granite alteration can be more advanced than it might appear to be at first sight on the basis of standard macroscopicy. Ciesielczuk & Janeczek (2004) calculated that at least 20% of the Strzelin massif had been influenced by hydrothermal fluids. Thus, the accurate recognition of altered zones, and of the initial stages of alteration as indicated by extremely small hydrothermal mineral phases, is important.

On the basis of the occurrence, size and quantity of hydrothermal minerals within granite adjacent to a vein, Ciesielczuk & Janeczek (2004) characterised the intensity of alteration as weak, moderate and strong. The methods used included petrological microscopy, scanning electron microscopy SEM, microprobe analysis and XRD. Slightly altered granite differs from unaltered granite in containing plagioclase of lower An content, post-biotite chlorite prevailing over biotite, increased Fe/(Fe+Mg) in black mica (up from 0.70 to 0.79) and small quantities of minute crystals of new hydrothermal minerals. In moderately altered granite, almost no biotite remains,

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spherulitic chlorite prevails over post-biotite chlorite, the plagioclase is oligoclase/albite and Fe/(Fe+Mg) in black mica, at 0.81, is the highest encountered. In addition, new hydrothermal minerals are more common and larger in size. Strongly altered granite contains no biotite, the plagioclase is albite and hydrothermal minerals are abundant.

The use of catodoluminescence can facilitate the identification of hydrothermal minerals as many of them are characteristised by distinctive luminescence colours, e.g., calcite (orange), prehnite (yellow), fluorite (bluish). The CL method has been used in investigations of granite genesis and metamorphism (Breiter et al. 2002, Zachovalova et al. 2002, Reichmann et al. 2003, Słaby, Gotze 2004). The CL effects of rock alteration have been described by Sikorska (2005).

The aim of the present contribution is to demonstrate how the CL method is useful in (1) establishing degrees of granite alteration, (2) estimating volume percentages of altered- as against unaltered rock and (3) identifying hydrothermal minerals occurring as grains of minute size. Granites from three localities were chosen for investigation, namely biotite granite exposed in the Main Quarry of the Strzelin granite, altered hornblende-biotite granite present in an 80 m thick shear zone in the Borów 17 quarry (Strzegom-Sobótka Massif) and porphyritic granite from the Szklarska Poręba Huta quarry in the Karkonosze granite.

METHODS

Forty-three thin sections (21 from Strzelin, 15 from Borów and 7 from Karkonosze) were examined using a polarising microscope and CL. Cathodoluminescence studies were made at the Polish Geological Institute on a CCL 8200 mk3 Cambridge Image Technology apparatus linked to an Optiphot 2 NIKON polarising microscope. Chemical analyses were made using a scanning microscope Philips XL 30 ESEM/TMP with EDS analyses (EDAX type Sapphire) operated by Ewa Teper in the Faculty of Earth Sciences, University of Silesia and an electron microprobe (Cameca SX-100) operated by Piotr Dzierżanowski and Lidia Jeżak in the Faculty of Geology, Warsaw University.

RESULTS AND DISCUSSION

Prehnite

Prehnite is easily visible in CL because of the characteristic yellow colour. It occurs within altered plagioclase grains and forms veins of varying thickness. CL tints indicate at least two episodes of prehnite vein formation but no difference in mineral composition was detected. Fluid penetrated active tectonic zones in the granite and a later generation of thinner fractures formed during the same episode of hydrothermal activity.

Titanite

Titanite shows differing CL responses; some grains have an olive CL colour of varying intensity and some are non-luminescent. The microprobe analyses indicate that the CL colour correlates with relatively high and diversified Al contents and not with Fe, Mn, V, Mg contents as was expected. The intensity of the titanite CL colour is probably related to defects within the crystal structure caused by Al^{3+} substitution of Ti^{4+} and subordinate Si^{4+}.

Clinozoisite

Minerals of the clinozoisite-epidote group are non-luminescent. However, clinozoisite crystals coexisting with prehnite in hydrothermal veins show a dark bluish-grey luminescence mainly in the central parts of grains. These zones contain more Fe_2O_3 (8.16%) than do the non-luminescent parts (4.66% Fe_2O_3).

Calcite

Calcite, as the last hydrothermal mineral, forms tiny, needle-like crystals scattered within altered feldspars, monomineralic veins in the cleavage planes of biotite and feldspars and polymineralic veins within altered granite. The Cl study revealed two generations of calcite - non-luminescent and red-luminescent. Both are chemically and microscopically identical.

Fluorite

Fluorite occurs on a macro- and microscopic scale in narrow veins within the Borów granite. CL images supported by chemical analyses reveal the presence of minute crystals within the granite also. These add to the Ca content of the bulk rock and influence mass balance calculations for the altered rocks.

Feldspar alteration

Plagioclase alteration is much better seen in CL- than in standard microscope images. The dark altered parts of feldspars contrast with the blue luminescence of unaltered K-feldspar and the green luminescence of plagioclase. The intensity of feldspar alteration is easy to estimate on CL images. In images from ordinary polarizing microscopes images, small relics of fresh feldspar in grains apparently completely altered may be easily overlooked.

CONCLUSIONS

Cathodoluminescence is very useful in the investigation of hydrothermal activity in granites. Minute crystals of common hydrothermal minerals, e.g., calcite, fluorite and prehnite, easily overlooked among other secondary alteration products under a polarizing microscope, are revealed by their characteristic luminescence colours.

Degrees of feldspar alteration can be established using CL. Variously altered granite samples collected from three localities verify this. Samples from Strzelin reveal variable degrees of hydrothermal alteration. Samples of the Borów granite are characterized by uniformly strong alteration. The Karkonosze granite samples display only weak alteration.

The CL investigation outlined here confirms the degrees of alteration established by other methods. Thus, in the estimation of levels of alteration and the volumes of altered material in granite bodies, and in the more complete identification of hydrothermal minerals present and their quantities, the cheap CL method is a valuable tool. In conjunction with standard petrological microscopy, and before involving the use of more expensive methods, the use of CL is recommended.

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MINERALOGIA POLONICA – SPECIAL PAPERS
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BIOMARKERS ASSEMBLAGE IN LITHOTYPES OF MIOCENE TURÓW BROWN COAL (SW POLAND)

Abstract: The molecular composition of biomarkers in Miocene brown coal lithotypes, deriving from lower, middle and upper seams, indicate low maturity of coaly material and diversity of gymnosperms-angiosperms into their formation. Vertical succession in paleo-peat development of the middle and upper seams is testified by increased abundance of gymnosperm-derived terpenoids. Angiosperm fossil wood is characteristic for lower seam, while gymnosperm for middle and upper seams. Fusitic and gelified xylitic coals are the products of decay-resistant conifers reworked by bacteria under oxidative conditions, while more anaerobic conditions for detritic coal and pyropissite formation are assumed.
Keywords: Brown coal lithotypes, gymnosperms, angiosperms, biomarkers, GC-MS

INTRODUCTION

Apart from the coal petrological, palynological and paleobotanical data on coal-forming environment, more recently biomarker analyses of the coal soluble organic matter increasingly contributed to the understanding of the paleoenvironment in the mires and provided clues to the botanical input involved in their formation. In addition, from organic geochemical studies information about the effects of humification, microbial activity and paleoenvironmental changes during coal formation have been revealed (Bechtel et al. 2003, 2005, 2007).

In this paper we present the organic geochemical characterization of the Tertiary brown coal lithotypes from the Turów deposit, SW Poland.

GEOLOGICAL SETTING

The Miocene Turów brown coal deposit fills a tectonic depression in NE part of the Żytawa trough and includes three brown coal seams: 1 - lower, 2 - middle and 3 - upper (Bieniewski 1966). Their basement is build of crystalline rocks: granites, gneisses and granite-gneisses, which were cut by basaltic intrusion in the central part of the deposit during Oligocene-Miocene period. The upper seam cover is composed of Quaternary sediments (Raniecka-Bobrowska 1970).

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MATERIALS AND METHODS

The brown coal lithotypes: **fusitic coal** (stain luster, friable, like charcoal, forms a thin layers and lenses), **xylitic coal** (bright to dark brown well preserved fossil wood), **detritic (earthy) coal** (homogenous dark brown, more abundant in lower and middle seams) and **pyropissite** (yellow, waxy like layers. More abundant in lower seam) were handpicked in the Turów open pit from different localities of each seam. **Bituminous material** of the middle seam**,** formed at bottom boundary, as well as **gelified xylitic coal** were also collected. Powdered samples were solvent extracted (dichloromethane/methanol – 93/7, v/v), using a Soxhlet system. The *n*-hexane–soluble fractions of the extracts were separated into resinous, aromatic and saturated fractions using TLC. The molecular composition of biomarkers contained in the aliphatic and aromatic fractions were analysed on biomarker composition by GC-MS.

RESULTS

The amount of extractable bitumen is brown coal lithotype dependent and on everage it constitutes following percent of the coal lithotype mass: 2.8% of xylitic coal, 3.1% of fusitic coal, 8.5% of detritic coal and 10.2% of pyropissite. The aliphatic fractions comprise 1.5 – 4%, while aromatic fractions 1 – 3% of the bitumen mass.

***n*-Alkanes and isoprenoids**. In the *n*-alkane chromatographic profiles of all brown coal lithotypes the long-chain homoloques (n-$C_{25–33}$) with a marked predominance of odd-over-even carbon numbered homologues (maximum intensities exhibit the n-C_{29}), dominate. They are the main components of higher terrestrial plant waxes. The detritic coals exhibit the highest values of the carbon preference index (CPI = 4 to 8) as compared to other lithotypes (CPI = 3 to 5). Additionally, in the fusitic, gelified xylitic and xylitic coals the bimodal pattern of low- (n-$C_{15–20}$) and mid-chain (n-$C_{21–25}$) *n*-alkanes (indicators of algae and/or microorganisms presence) are recognized in relative proportion 5 – 15% to the total *n*-alkane concentrations, while their content in detritic coals and pyropissites is minor. The long-chained *n*-alkanes are the diagenetic products of even carbon numbered carboxylic acids and alcohols present in leaf and cuticular waxes (Tissot, Welte 1984). Considerable concentrations of the carboxylic acids (as methyl esters) were found in the gelified xylitic and detritic coals, where long-chain *n*-alkanes are also abundant. However, the pyropissites, in spite of highest concentration of long-chain *n*-alkanes, contain rather small amount of carboxylic acids. Moreover, only in the detritic coals presence of the methylketones was found, which are absent in other lithotypes.

The pristane over phytane (Pr/Ph) ratio for the investigated brown coal lithotypes (except for drtritic coals) is typical of humic coals; its value scatters in the 0.9 – 1.5 range. Also for the detritic coals Pr/Ph values are higher and average 3.7, however overall concentrations of the Pr and Ph in the detritic materials are very low.

Terpenoids. All brown coal lithotypes from the Turów deposit contain several unidentified C_{15} mono-unsaturated sesquiterpenoids of the drimane and cadinene types in considerable quantities (Fig. 1). The C_{20} diterpenoids are represented by 16β(H)-

kaurane, 16α(H)-phyllocladane, abietane, pimarane, isopimarane, fichtelite, *ent*-beyrane, norabietane and norisopimarane, where in lithotypes from middle and upper seams, particularly in xylitic coals, 16α(H)-phyllocladane predominates by far (Fig. 1, traces B and C). In all lithotypes from lower seam additional unidentified C_{18} and C_{19} diterpenoids are present, while relative concentration of 16α(H)-phyllocladane is comparable with concentration of other terpenoids (Fig. 1, trace A). The biological precursors sesquiterpenoids and diterpenoids are the resins of the coniferales families (gymnosperms). Drimane and cadalene type sesquiterpenoids as well as phyllocladane type diterpenoids are widespread in species of Podocarpaceae, Araucariaceae and Cupressaceae conifers (Noble et al., 1985), while pimarane and isopimarane type diterpenoids have been detected in recent species of Pinaceae, Taxodiaceae, Araucariaceae and Cupressaceae (Sukh 1989). Non-hopanoid tetra- and pentacyclic triterpenoids are represented by the oleanane, olean-13(18)-ene, olean-12-ene, olean-18-ene, urs-12-ene and des-A-oleanenes and des-A-ursene. The non-hopanoid triterpenoids are significant constituents of leaf waxes, wood, roots and bark of angiosperm species (Sukh 1989). Particularly high abundances of non-hopanoid triterpenoids were found in brown coal lithotypes from lower seam: in xylitic-like coal (fossil wood) (Fig. 1, trace A), as well as in detritic coal and pyropissite from this seam. The angiosperm wood has rather low preservation potential, therefore occurrence of fossil wood, containing biomarkers indicating angiosperm origin, gives new light on stability of some angiosperm species. In succession from the bottom seam to the top seam composition of the terpenoid biomarkers indicate the increasing proportion of gymnosperm-derived biomarkers (sesquiterpenoids and diterpenoids) relative to the sum of gymnosperm- plus angiosperm-derived terpenoids (oleanane-type triterpenoids).

The microbial oxidative reworking and low maturity of the brown coal lithotypes is reflected by the hopanoids pattern, which are characterized by the predominance of the 17α,21β(H)-homohopane-(22R) and 17β,21β(H)-homohopane as well as in lower concentration of their C_{30} counterparts. Other constituents are the C_{27} and C_{29} neohop-13(18)-enes and hop-17(21)-enes, deriving from eukaryotic phyta (e.g., ferns, mosses, lichens, fungi) and hopanoid-producing bacteria. Elevated contents of C_{31}-homohopanes, reflecting microbial activity under dysoxic conditions during peatification (Rohmer and Bisseret 1994), are observed in fusitic coals, advanced gelified xylitic coals and most investigated xylitic coals. Much lower concentration of C_{31}-homohopanes occur in detritic coals and pyropissites, particularly in these lithotypes deriving from the lower brown coal seam, where in some samples the discussed triterpenoid compounds are in traces. This implies on more anaerobic conditions in the mire during detritic coal and pyropissite formation.

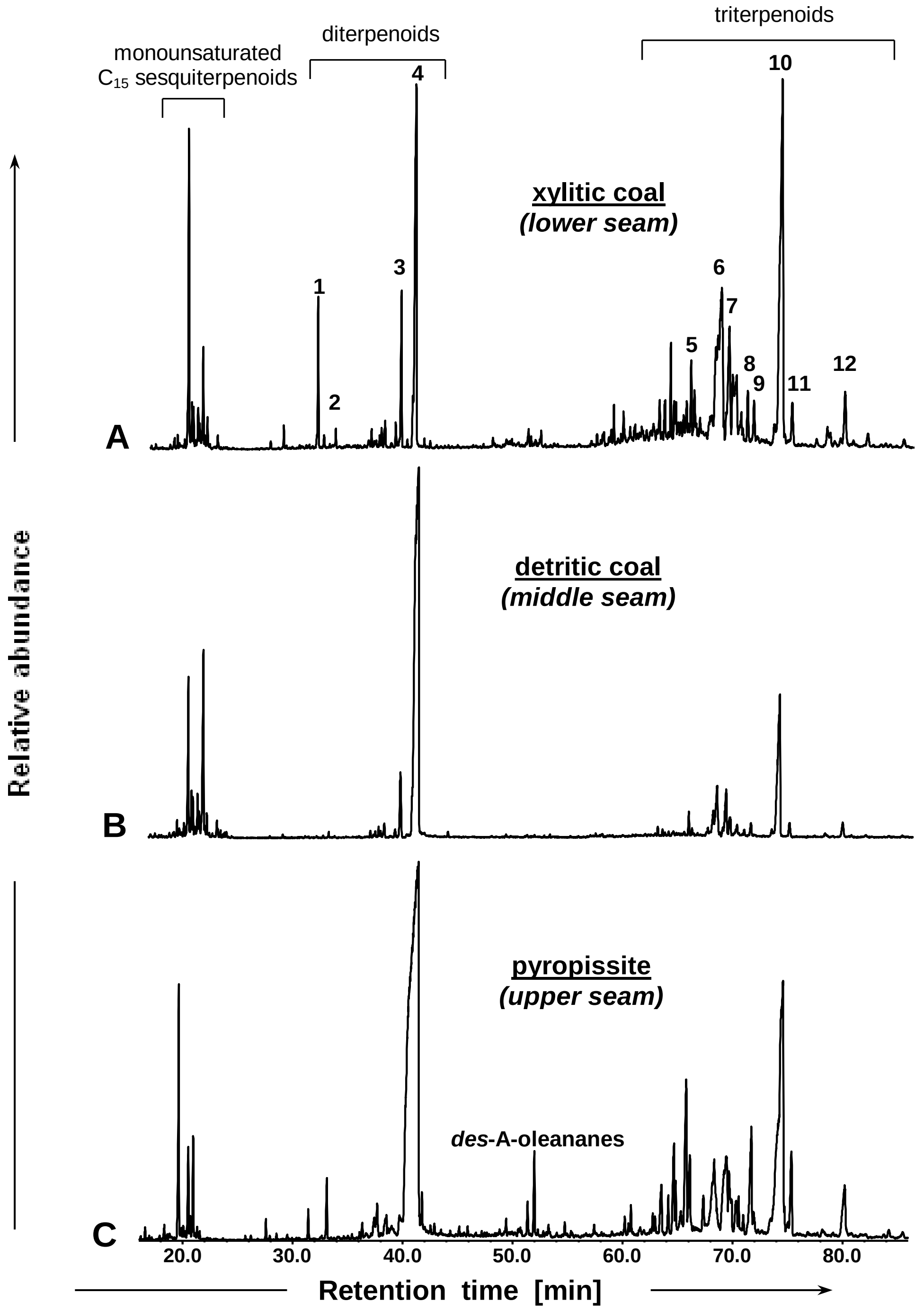

Fig. 1. Mass fragmentograms of terpenoid compounds (*m/z* 123 + 191) in selected brown coal lithotypes from theTurów open pit.

Aromatic hydrocarbons. The aromatic sesquiterpenoids are dominated by cadalene, with minor amounts of cuparene, 5,6,7,8-tetrahydrocadalene and calamenene. The aromatic diterpenoids consist of compounds of the abietane type e.g., dehydroabietane, abieta-6,8,11,13-tetraene, simonellite and retene. Partly or completely aromatised tetra- and pentacyclic triterpenoids occur as tetramethyloctahydrochrysenes, trimethyltetrahydrochrysenes, 24,25-dinoroleana-1,3,5(10),12-tetraene, 24,25-dinorursa-1,3,5(10),12-tetraene, tetramethyloctahydro-picenes, trimethyltetrahydropicenes and dimethylpicenes. There is no consistency in constitution of the aromatic compounds in relation to coal lithotype, even for given lithotype samples deriving from the same seam. For instance, in the fusitic coal from northern part of the middle seam aromatic hydrocarbons are characterized by the retene domination and absence of simonellite, while in this lithotype from southern part of the same seam it reverses, simonellite is abundant while retene was not detected. Both these compounds are absent only in some samples of xylitic and detritic coals as well as pyropissite, and are present in various proportions in the other samples. Perylene predominates in most investigated xylitic coal samples deriving from all three seams, and surprisingly, also in the detritic coal from the lower seam, where simonellite and retene is lacking. High abundance of the perylene in the samples, which also occurs in pyropisite from the lower seam, is accompanied by the presence of short chain triaromatic steranes: pregnane, homopregnane, bishomopregnane and trishomopregnane in these samples, which are presumed products of increased water salinity episodes. Phenenthrene and methylphenantrenes fingerprints are similar in all coal lithotypes and reflect low maturity of their organic materials. This supports bacterial involvement in the fusitic coal formation.

CONCLUSIONS

Geochemical data on variation in molecular composition of the aliphatic and terpenoid biomarkers (chained hydrocarbons, sesqui- and diterpenoids, oleanane and ursane type triterpenoids) imply on the vegetation type changes in the mire due to increased contributions of conifers vs. angiosperms to peat-formation in successive brown coal seams, allow to asses redox conditions during depositional and postdepositional periods as well as low maturity of the brown coal lithotypes.

The Turów brown coal lithotypes from lower seam were formed mainly of the angiosperm rich-herbaceous type flora. Most interesting for the lower seam is identification angiosperm-related biomarkers in the preserved fossil wood fragments.

Legend to Fig. 1: **1** – C_{18} diterpenoid, **2** – C_{19} diterpenoid, **3** – pimarane, **4** - 16α(H)-phyllocladane, **5** – 22,29,30-trisnorhopane (Tm), **6** – olean-13(18)-ene + olean-12-ene + olean-18-ene, **7** – hop-17(21)-ene, **8** – 18α(H)-oleanane, **9** – 17α(H),21β(H)-hopane, **10** – 17α(H),21β(H)-homohopane-(22R), **11** – 17β(H),21β(H)-hopane, **12** – 17β(H),21β(H)-homohopane-(22R).

In contrary, the xylitic coals from the middle and upper seams are the fragments of decay resistant gymnosperm wood, as is evidenced by the high relative proportion of diterpenoids in their lipids. In the upper seam conifer families become a predominant vegetation species in the peat-forming vegetation. Biomarkers in fusitic and gelified xylitic coals indicate bacteria were involvemed in the gelification of plant tissues and contributed to aromatisation of the terpenoid hydrocarbons.

Macroscopically distinct thin coaly layers of pyropissite and fusitic, xylitic and detritic coals reflect changes in paleoenvironmental conditions during deposition, mainly caused by changes in freshwater inflow and level of water table, which influenced vegetation type, Eh and pH values, microbial activity controlling the extend of sedimentary organic material reworking.

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MINERALOGIA POLONICA – SPECIAL PAPERS
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PETROLOGY AND GEOCHEMISTRY OF DYKE SWARMS AT WADI ERIER CENTRAL EASTERN DESERT, EGYPT: IMPLICATIONS FOR LATE NEOPROTEROZOIC CRUSTAL EVOLUTION

Abstract: The basement rocks at Wadi Erier Central Eastern Desert, Egypt intensely invaded by post-orogenic calc-alkaline dyke swarms. They composed of a mafic (basalt, basaltic-andesite and andesite) and a felsic (dacite and rhyodacite) groups. Although the geochemical characteristics for the dykes indicate subduction-related setting, field observations clearly support within-plate setting. Major and trace elements geochemistry indicate that the investigated mafic and felsic magma types are not related via fractional crystallization. The incompatible trace element patterns favor the derivation of the mafic and felsic magmas separately from garnet-bearing and garnet-free sources. The mafic and felsic dykes then modified by fractional crystallization processes. This implies variable source characteristics at the end of the Pan-African in the Central Eastern Desert, Egypt.
Keywords: Neoproterozoic, Erier dyke swarms, geochemistry, petrogenesis, Egypt

INTRODUCTION

The basement complex of Egypt – including the Eastern Desert and Sinai- is part of the Arabo-Nubian Shield (ANS) formed during the Neoproterozoic Pan-African orogenic event (850-614Ma).The final Pan-African phase of igneous activity is characterized by the emplacement of bimodal Dokhan volcanics, high level younger granitoids, and numerous mafic to felsic dyke swarms (Stern et al. 1988). Chronologically, three episodes of dyke emplacement have been distinguished in the Eastern Desert and Sinai: 1) deformed and metamorphosed syn-tectonic dykes (800-650 Ma), 2) unmetamorphosed post-orogenic dykes (591-459 Ma) and 3) Neogene dykes (30-12 Ma) related to the updoming and opening of the Red Sea Rift system. The Wadi Erier dyke swarms belong to the second episode i.e. late- to post-orogenic. The present study is focused on the petrology and geochemistry of Wadi Erier post-orogenic dyke swarms. Their geological setting and magma source(s) could place new constraints on magmatic-tectonic processes acting during the Late Neoproterozoic crustal evolution in Egypt.

GEOLOGICAL SETTING

The basement rocks at Wadi Erier (24° 39̀ N and 35° 02̀ E) Central Eastern Desert, Egypt are composed of 1) island-arc metagabbro-diorite complex, syn- to Post orogenic granitoids cited in the geological map of Egypt (1987). Neogene and Quaternary sediments occupy the eastern flank of the basement rocks. Based on field

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observations the mafic and felsic dykes are contemporaneous, unmetamorphosed and occur in closely parallel sets forming swarms. They crosscut all Precambrian rock units in the study area, but they are more abundant in the syn- and post-orogenic granites. In the study area the mafic dykes are the most abundant and widespread than felsic ones. The dykes have prevailing strikes of ENE, NNW and due N.

PETROGRAPHY

Microscopically, the mafic dykes are composed of basalts and basaltic-andesites and andesites. Basalt and basaltic-andesite dykes composed of twinned, occasionally zoned plagioclase feldspar (labradorite: $An_{55\text{-}60}$), pyroxene (augite) and hornblende illustrating porphyritic and ophitic textures. Minor amounts of chlorite, epidote, opaques and apatite are observed. The andesite dykes are texturally similar to basaltic dykes, they only differ in the proportion of hornblende and augite and the composition of plagioclase. Andesite dykes have more hornblende and relatively more sodic ($An_{30\text{-}35}$) plagioclase.

Felsic dykes are composed mainly of dacite and rhyodacite with pronounced porphyritic texture. Microscopically, they are composed of plagioclase feldspar, quartz, potassium feldspar with minor hornblende. Biotite, opaques, zircon and apatite are encountered in the groundmass matrix.

GEOCHEMISTRY

Methods

Major and trace elements were determined by X-ray fluorescence spectrometer technique using a Philips PW 2400 instrument at Bergen University, Norway. Rare-earth elements were determined using Jobin-Y von 70 ICP spectrometer at the Polish Institute of Geology, Warsaw. Analytical precision based on duplicate analyses are expressed in terms of relative percentages and are found to vary from 1-3% for major elements and from 10-15% for trace elements.

Chemical Characteristics

On the Zr/TiO_2 vs SiO_2 diagram (Fig. 1a) after Winshester and Floyd (1977), the Erier dykes can be divided into mafic group (basalt, basaltic-andesite and andesite), and felsic group (dacite and rhyodacite), matching with petrographic classification. The calc-alkaline affinity of mafic and felsic dykes can be detected on Fig. 1a. On Fig. 1b the mafic and felsic dyke samples illustrate two different trends; i.e. not related to each other and produced from different magmas.

The MORB-normalized diagram for the mafic dykes (Fig. 1c) show a marked enrichment in LILEs: Sr, K, Rb, and Ba relative to HFSEs: Zr, Nb, Y,and Ti with a negative anomaly for Nb. The felsic dykes illustrate similar pattern to mafic dyke but with lower HFSE contents and pronounced depletion of Nb, P and Ti.

The chondrite-normalized REE-patterns (Sun, 1982) are shown in Fig. 1d. All dyke varieties are light-rare earth elements (LREE) enriched over heavy rare-earth elements (HREE). The mafic dykes are characterized by parallel moderately fractionated patterns $(La/Yb)_n$ = 9-10 with slightly negative Eu-anomalies (Eu/Eu* = 0.97-0.85).This pattern suggest the presence of residual garnet in the source. The

REE pattern for the felsic dykes is characterized by lower contents of HREE, a pronounced Eu anomaly (Eu/Eu* = 0.6) and a highly fractionated pattern $(La/Yb)_n$= 30; suggest their derivation from a garnet-free source.

DISCUSSION

Tectonic Setting

The investigated mafic dykes have the geochemical characteristics of calc-alkaline basalts emplaced in within-plate setting by using Zr vs. Zr/Y (Fig. 1e). On the other hand, the felsic dyke samples plot in the fields of volcanic-arc granite and within-plate granite on the Rb vs (Y+Nb) diagram after Pearce (1996, Fig 1f); but all samples lie in the field of extensional-related A-type granite. The investigated felsic dykes belong to the A_2-type according to the classification of Eby (1992).

Magma sources for Erier dyke swarms

The variation diagram (Fig.1b), MORB (Fig.1c), and REE-patterns (Fig.1d) suggest that there are significant geochemical differences between the mafic and felsic dykes. This means that two different magma types being produced and emplaced at the same time and not related to each other.

There is no field evidences for the effect of magma mixing in the evolution of the investigated mafic dykes. The parallel nature of the normalized REE-patterns with increasing abundance of REE with increasing SiO_2; suggest that the Erier dyke swarms were produced by fractional crystallization. The mafic dykes could be generated after melting of an enriched garnet-bearing mantle source, small degrees of olivine and clinopyroxene fractionation generated a magma composition similar to the calc-alkaline basalt. Different degrees of further fractionation of olivine, clinopyroxene, amphibole and zircon led to basaltic-andesite, and andesitic magmas. Normalized incompatible trace element abundance diagrams for the felsic dykes display patterns strongly modified by fractional crystallization (Fig. 1c). Low content of Sr and presence of significant negative P and Ti anomalies; suggest crystallization of plagioclase, apatite and Ti-magnetite before emplacement is likely. Also, the negative Eu-anomaly indicates plagioclase fractionation.

The enrichment of the investigated extensional-related dyke swarms in LILEs indicate enriched lithospheric mantle source for these rocks and they were produced during the collision of the crust during the Pan-African orogeny in the Arabo-Nubian Shield. The investigated mafic and felsic dykes can be related to an intra-continental setting and this was accompanied by chemical evolution of the sub-continental lithosphere.

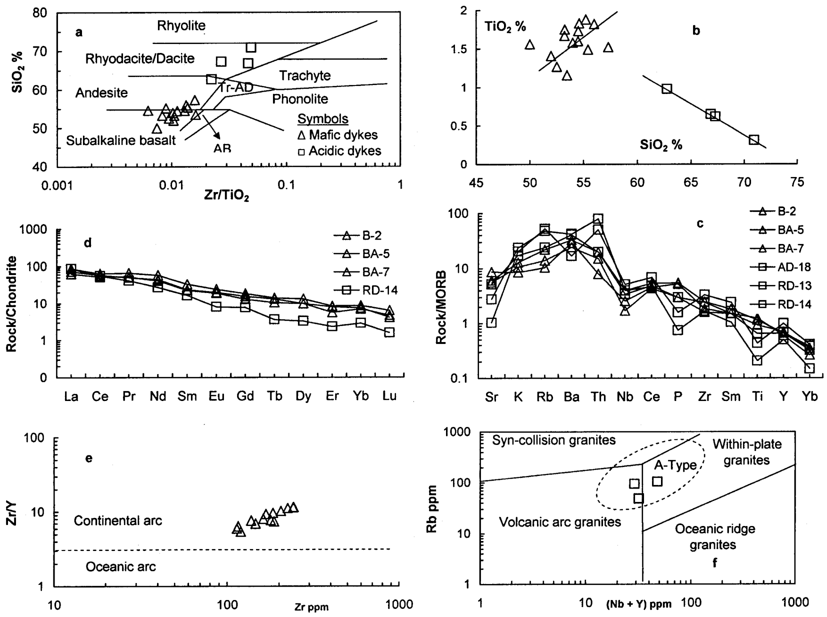

Fig. 1. The investigated Erier dyke swarms, mafic: Δ , and felsic: □

a) SiO_2 vs. Zr/TiO_2 (Winchester and Floyed,1977), b) SiO_2 vs. TiO_2, c)N-MORB normalized trace element patterns (Pearce, 1983), d) Chondrite normalized patterns values after Sun (1982), e) Zr vs. Zr/Y, f) Plot of Rb vs. Y+Nb (Pearce, 1996).

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GEOCHEMISTRY OF „MAFIC MICROGRANULAR ENCLAVE – HOST ROCK“ PAIRS FROM GRANITOIDS OF EAST PART OF THE BRNO MASSIF

Abstract: Thirteen mafic microgranular enclave-host rock (ME-HR) pairs were examined microscopically and geochemically. Mutual relation between modal composition of both members is apparent, particularly in mafic minerals contents. All ME display SiO_2 depletion and are enriched by MgO, Fe_2O_3t, CaO, Cr_2O_3, NiO and Co, indicating basic and more primitive source of ME melt compared to their respective HR. Also, the REE contents are elevated in all ME. It seems that the presence of plagioclase xenocrysts in ME, apparently cognate spidergram patterns and obvious elements correlations indicate mutual mechanical and chemical magma interactions.
Keywords: the Brno Massif, mafic microgranular enclave, granitoids, geochemistry, chemical correlation, magma interaction

INTRODUCTION

The Brno massif is exposed by the east margin of the Czech Massif as a uncovered part of Brunovistulian unit of Cadomian age consolidated during Variscian orogenesis. Dark, rounded to lens shape enclaves occur in some varieties of granitoid host rocks of the east part of the Brno massif. Based on their macroscopic (shapes, dimensions, colors, fine grained and igneous textures, dark „chilled“ margins) and microscopic features (plagioclase xenocrysts, acicular apatites) they appear to be mafic microgranular enclaves. Their origin end evolution is related to felsic-mafic magma interaction recently.

METHODS

Optical microscopy was applied to identify and quantify mineral phases besides of minerals relationship and rock fabrics analysis. To reveal feldspars and hornblends microchemistry and for determination some accessory, opaque and secondary phases the SEM was use. ACME Analytical Lab. Ltd., Vancouver, Canada, performed the whole-rock chemical analysis of the major and trace elements as well as REE using ICP-ES and ICP/MS methods.

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RESULTS

The most of ME (mostly bt-hb bearing diorites) occur in more mafic varieties of the HR (hb-bt bearing granodiorite to bt-hb bearing tonalite). The HR without hornblende lack any ME or sporadically contain very slight and only bt bearing ME. Also, these ME usually contain less of the mafic minerals, generally only biotite and are free of plagioclase phenocrysts. On the other hand ME in hornblende-rich HR show obviously higher content of mafic mineral, hornblende especially. The abundance and sizes of ME rise up herewith.

All ME are basic, based on SiO_2 content (48 - 53 wt %) which is less variable then in the HR of intermediate to acid composition (53 - 69 wt %). The ME display calk-alkaline meta-aluminous character, whereas HR are mostly peraluminous. Slightly increased content of Al_2O_3 in ME is the consequence of higher volume of plagioclases in comparison with HR. Markedly enhanced CaO is the effect of large plagioclase and hornblende contents. Due to considerable bulk of hornblende in ME they display increased MgO and $Fe_2O_3^t$ too. In addition, the $Fe_2O_3^t$ content is elevated by enhanced opaque phases (magnetite, ilmenite) proportion in ME (see Fig. 1).

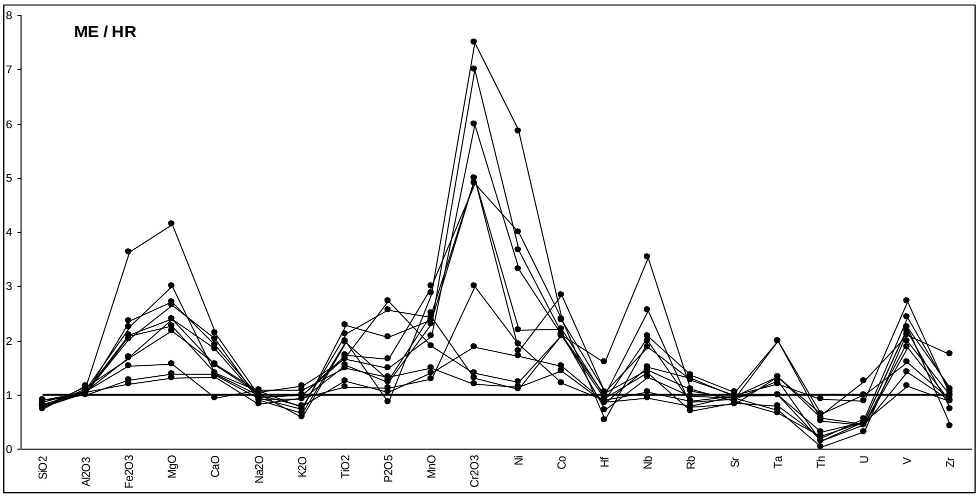

Fig. 1. Respective HR normalised contents of major abd trace elements in ME.

K_2O and Na_2O contents show obvious scatter in both members of ME-HR pairs relative to SiO_2 nevertheless comparable respectively. Enhanced P_2O_5 and REE in ME is caused by markedly higher apatite volume. Increased TiO_2 content in ME is probably connected with their higher hornblende proportions. Notable is the HFSE (Cr, Ni, Mg, HREE) enrichment in ME as well as broadly parallel primitive mantle normalized spidergram both for ME and MG (see Fig. 2). The rocks are LILE (Cs, Rb, Ba, U) strongly enriched and exhibit obvious REE enrichment in comparison to primitive mantle of Sun and McDonough (1989). Fractionation of HREE is somewhat lower for both members of ME-HR pairs. No Eu anomaly was indicated in HR in contrast to ME. Both ME and HR resemble with VAG by virtue of Rb relative to Y, Yb and Nb in plots (not shown) of Pearce et al. (1984), though the WPG affinity of the ME is apparent.

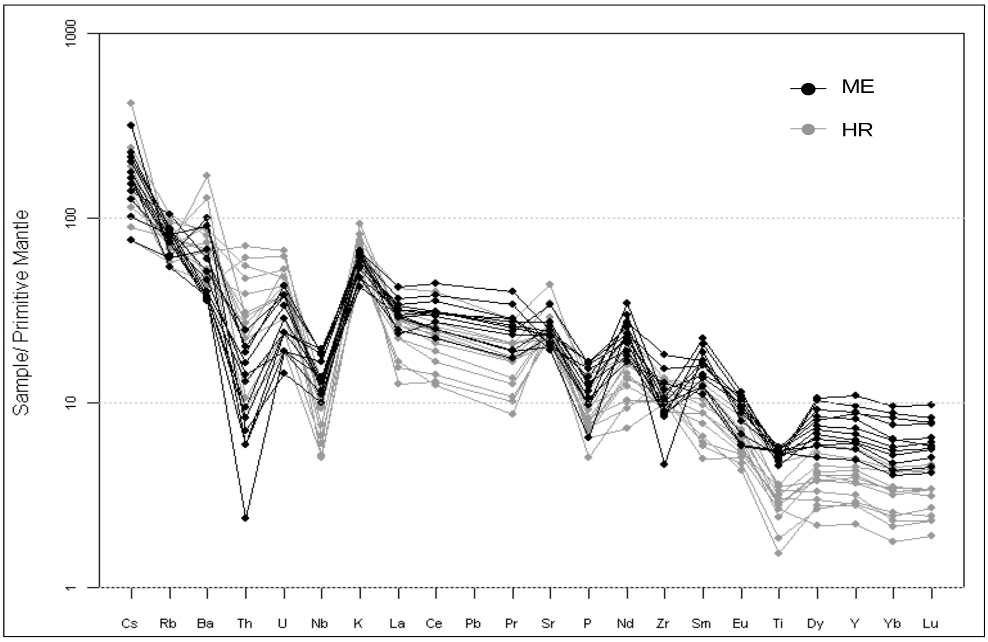

Fig. 2. Primitive mantle normalised some major, trace and REE elements in ME and HR, primitive mantle according Sun and McDonough (1989).

The plots on the Fig. 3 shows chemical correlations between some major elements. The most visible mutual relation indicate Mg/Fe+Mg ratio (corr.coef. = 0,84). Similar trends hold for most of major elements as well as contents of normative quartz, feldspars and total mafic minerals. Negative correlation Al_2O_3, MgO, CaO, TiO_2, P_2O_5 and $Fe_2O_3^t$ relative to SiO_2 is more evident for HR than for ME. Near-linear, positively correlated trends for $Fe_2O_3^t$, TiO_2, CaO and P_2O_5 against MgO can be observed for HR contrary to ME.

CONCLUSIONS

Igneous origin of studied ME seems to be unquestioned, considering their purely igneous fabrics and complete absence of metamorphic signs. During the coexistence of two contrasting melts intensive thermal, mechanical and chemical interactions took place resulting into dark „chilled“ margins, presence of plagioclase xenocrysts and chemical equilibration. Such explanation of origin and evolution was broadly accepted recently. The fact of increase of ME volume and their sizes in conjunction with decreasing color index of HR suggest supposition of uncompleted mixing and mingling.

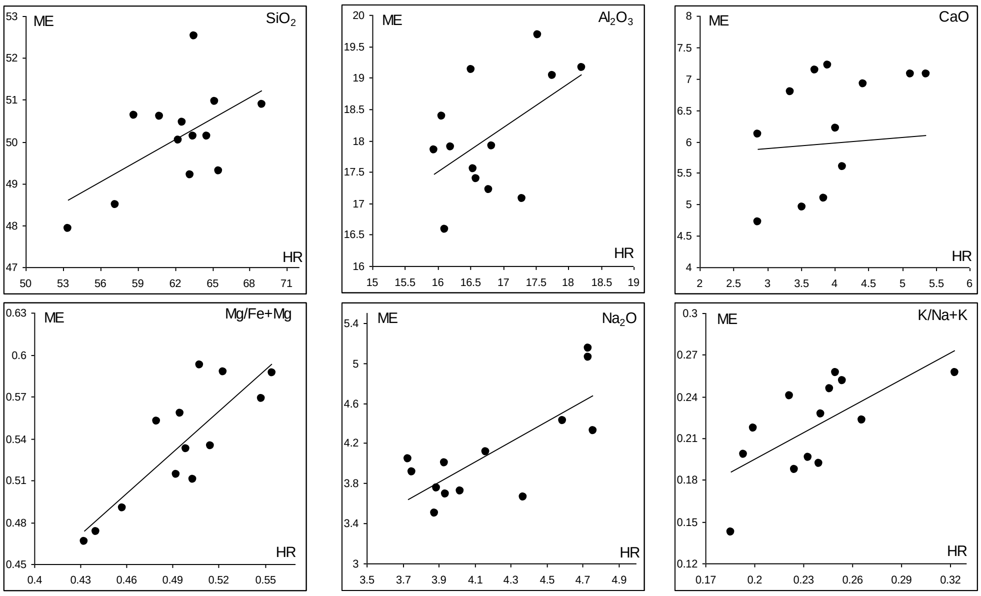

Fig. 3. Compared bulk chemical compositions of ME-HR pairs and their straight-line regressions. Oxide contents in wt.%; Mg, Fe, K and Na as millications/100g of rock.

Positively correlated components of ME-HR pairs, cognate spidergrams and similar composition of selected phases are consistent with interdiffusion theory of Debon (1991). Rather primitive original composition of ME melt was probable substantially changed by absorption of Si, LILE and possibly even H_2O from HR magma and depleted (in smaller extent) of some small mobile elements (Mg, Fe, Cr, Ni). The whole system underwent alkaline metasomathosis, which probably intensely equilibrated concentrations of highly mobile K, Na, Rb and Ba.

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Aleksandra GAWĘDA[1]

MAFIC MICROGRANULAR ENCLAVES IN THE HIGH TATRA GRANITE – PRELIMINARY REPORT

Abstract: The mafic microgranular enclaves in the porphyritic variety of High Tatra Granite were investigated. Their textures, mineral assemblages and geochemistry could be explained in terms of felsic and mafic magmas mixing-mingling processes. The restricted area of MME presence is interpreted here as a zone of hybridisation.
Keywords: mafic microgranular enclaves, mixing-mingling, High Tatra Mts.

INTRODUCTION

The presence of mafic microgranular enclaves (MME) are thought to be a key feature for interpretations the history of granitoid intrusions as they provide the information of a role of mafic magma input and hybridization processes in the evolution of calc-alkaline granitoid magmatism. The petrographic, geochemical and isotopic features of MME are a subject of the debate (i.e. Didier, Barbarin 1991, Vernon 2004, Barbarin 2005). As they are usually the products of mixing-mingling processes, the specific microstructures are diagnostic (i.e. Hibbard 1991, Vernon 2004).

SAMPLING & ANALYTICAL TECHNIQUES

MME in the High Tatra Granite were found and sampled in several localities: in the Morskie Oko vicinity, in the Gerlach Ridge and in Kozie Wierchy Ridge (Fig. 1).

Microprobe analyses of minerals and selected BSE mineral images were conducted on a CAMECA SX-100 electron microprobe in the Inter-Institution Laboratory of Microanalysis of Minerals and Synthetic Substances, Warsaw, using sets of natural and synthetic standards. Whole-rock analysis of major and trace elements was done by XRF and ICP-MS methods in the ACME Analytical Laboratories, Vancouver, Canada. For the comparison I used the analyses of granitoids and related rocks from the High Tatra Mts. from my own database.

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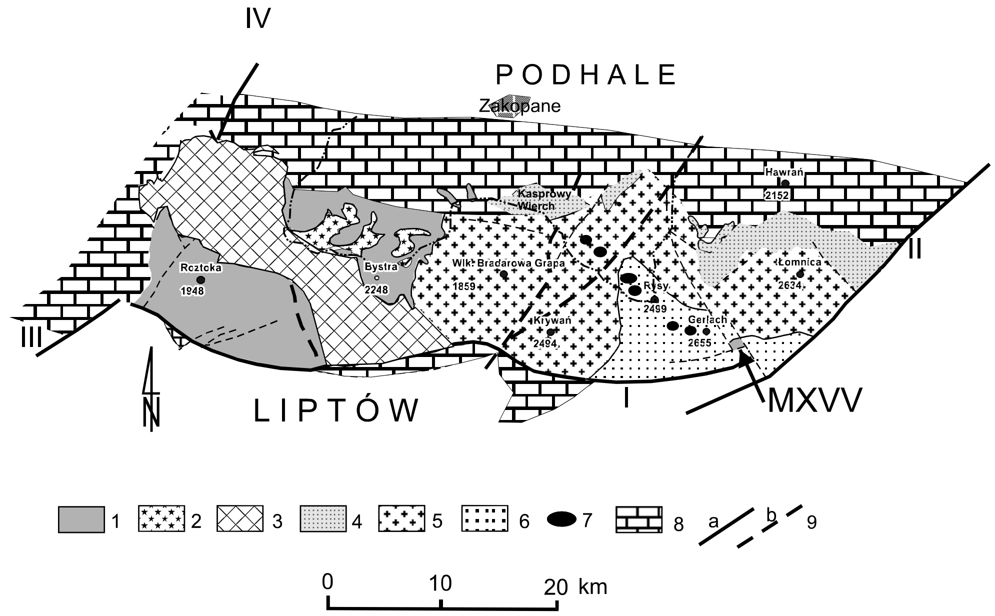

Fig. 1. Simplified geological map of the Tatra Mountains (compilation after Kohut, Janak 1994, Bac-Moszaszwili 1996, Gawęda et al. 2005). 1 – metamorphic cover, 2 – alaskites, 3 – Rohače Granite, 4 – Goryczkowa Granite, 5 – porphyritic granite, 6 – biotite monzogranite, 7 – MME samplig points, 8 – sedimentary cover, 9 – main faults: a – identified, b – assumpted.

PETROGRAPHY & GEOCHEMISTRY OF MME

MME are of different size and morphology: from small (3 x 8 cm), flattened black lenses with sharp contact to the granite to irregular portions up to several tens of cm in lenght and diffuse contacts to the granite (Fig. 2). MME show the fine-grained texture (Fig. 3) and are composed of plagioclase showing oscillatory zoning (An_{38}-An_{20}), blade-shaped biotite, magnetite-ulvöspinel (locally decomposed to ilmenite-hematite integrowths and overgrown by secondary titanite), K-feldspar porphyrocrysts showing irregular zonation in respect to Ba (0.02-0.05 Ba a.p.f.u.] and rich in Bt inclusions and muscovite. As accessory components the weakly zoned apatite (in respect of Y & Fe) and zircon are present. In enclaves with sharp contact to the granite the micaceous (biotite-muscovite) rim was developed, conserving the fine-grained interior of the enclave, showing almost no secondary alterations.

The chemical composition of MME is dioritic and strongly peraluminous (ASI = 1.335), possibly because of high plagioclase content. However, the presence of negative Eu anomaly (Eu/Eu* = 0.721) suggests the plagioclase component fractionation, while Ce/Yb = 16.12 points out the moderate REE fractionation, similar to that in granitoids (0.547-0.73 – compare: Gawęda, 2007). High Zr content (340 ppm) generates the high Zr-in-the rock temperature (845^{o}C, Watson, Harrison 1983). The temperature of ulvöspinel exsolutions, calculated according to Spencer & Lidsley (1981) procedure are in the similar range (883-900^{o}C).

Fig. 2. The irregular MME from Morskie Oko vicinity, showing diffuse margins to the host granite. Geological hammer as a scale. Phot. A.Gawęda.

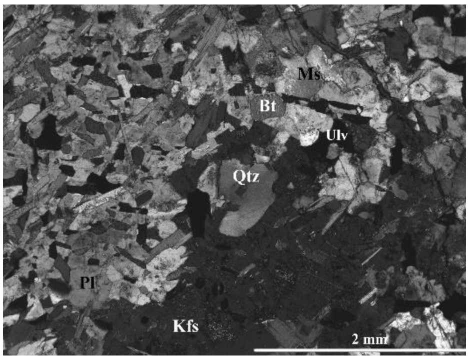

Fig. 3. Microphotograph of the fine-grained structure of the MME from Mały Kozi Wierch. Notice the presence of Kfs with numerous biotite inclusions and one quartz xenocrysts.

Granitoids at the contact show the presence of plagioclases with calcic spikes, zoned muscovites, locally zoned K-feldspar phenocrysts with numerous mineral inclusions (Gawęda 2007). Locally in the host granite near the contact the titanite-plagioclase-quartz ocella are present. As the presence of Mt-Ilm-Hem-Ulv exsolutions are popular in the host granite the temperature calculated according to Spencer & Lidsley (1981) procedure was in the range of 679-720°C, while in the contact zone with MME the temperature was 808-874°C. Zr and Y contents are relatively high (112-206 ppm and 13-23 ppm, respectively) what implies high Zr-in-the-rock temperature range (775-822°C).

DISCUSSION & CONCLUSIONS

The following textural features, found in MME and in the surrounding granites are thought to be attributable for magma mingling/mixing at both of the outcrop scale and at thin-section scale: fine-grained character of MME, blade-shaped biotite, presence of zoned K-feldspar phenocrysts with resorbed margins and inclusions of biotite, calcic spikes in plagioclases, zoned apatite, titanite-plagioclase-quartz ocella in host granites, as well as not decomposed ulvöspinel (Hibbard 1991, Tepper, Kuehner 1999, Baxter, Feely 2002). The character of the contacts between MME and host granite and the calculated temperatures suggest the hotter, mafic magma involvement during the formation of felsic component - porphyritic granite.

The presence of MME with hybrid features is restricted to the quite narrow, NW-SE trending belt (Fig. 1). It looks quite possible that this belt marks the hybridisation zone in the High Tatra Granite magma.

Acknowledgements: Mr Edward Lichota, the Tatra guide, is deeply acknowledged for the help during climbing and sampling in Gerlach area. The Ministry of Sciences and Informatics grant No. 2 PO4D 05629 founded this research.

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Aleksandra GAWĘDA[1]

MEGA-XENOLITH FROM THE VELICKA VALLEY (HIGH TATRA MTS., WESTERN CARPATHIANS): AN EXAMPLE OF "EXPLODING ELEPHANT"

Abstract: The petrographic investigation of mega-xenolith from the Velicka Valley revealed several features, suggesting the explosion of the originally heterogeneous xenolith during its sinking in the magma. Vapour-producing reactions and accumulation of vapour phase inside the xenolith are supposed to be the reason for "schrapnel" explosion and granite contamination around the xenolith.
Keywords: mega-xenolith, High Tatra Mts, granite, stoping

INTRODUCTION

The process of xenolith`s stoping in the magma chamber is still a matter of debate, since Daly (1903: in Clarke et al. 1998) recognized the blocks of country rocks sinking in the magma. Magmatic stoping could be an important mechanism of mass-transfer inside the magma chamber (Žak et al. 2006). At present stoped blocks are thought not to reflect the original stratigraphy of the granite envelope (ghost stratigraphy *sensu* Pitcher 1997) but provide information about emplace-ment mechanisms and indicate the position of the magmatic fabric (Paterson, Miller 1998). Stoping should produce a zone of xenoliths accumulation at the bottom of the magma chamber, traditionally called "elephant`s graveyard" (Clarke et al., 1998), in fact not observed till now in nature. They are supposed to be disin-tegrated both physically and chemically, depending on the temperature difference between the host magma and xenoliths. Moreover, the large xenolith blocks should significantly affect the thermal balance of the magma (Maury, Didier 1991).

The crystalline basement of the Tatra Mts. comprises a polygenetic granitoid intrusion and a metamorphic envelope that is preserved in the western part of the massif (Gawęda 2007a). In the eastern part metamorphic rocks occur only as xenoliths of different size, mainly in the so called High Tatra syeno- and monzogranites. The object of this study is the mega-xenolith of the Velicka Valley (MXVV) cropping out as the almost continuous profile along the touristic path in the upper part of the Velicka Valley (Fig. 1, Fig. 1 in Gawęda 2007 b, this volume), hosted in porphyritic granite, rich in micro-xenoliths and schlieren. As the variety of metamorphic xenoliths in that area is large I stress only to the so called "lower xenolith", accessible for the observations in the vicinity of "eternal rain" profile. This paper presents the hypothetical fate of the MXVV and its influence on the host granite fabric and mineralogy.

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PETROGRAPHY OF THE XENOLITH

The total thickness of the MXVV is up to 13 m, while the length is about 180 m. It is composed by many petrographical rock-types, including garnet-staurolite gneisses, migmatites, schists, calc-silicate rocks and amphibolites, showing the common clockwise P-T patterns and ductile deformation in amphibolite facies conditions (Janak et al. 1999, Gawęda 2005). U-Pb zircon dating point out the 355-357 Ma for migmatization event (Poller et al. 1999). The metamorphic foliation inside the MXVV is NW to N declined (312/35 – 350/35 do 20/15), in general parallel to the granite flow foliation, underlined by schlieren orientation.

Xenolith is cut by several sets of dens, concordant and discordant fractures, filled by schlieren granite (20 cm to 4 m thick), aplite and micro-pegmatite veins (0.5 cm to 20 cm) locally carrying the rock-clasts differing in petrography from the rock hosting the vein (Fig. 2). Locally the millimetre-scale subsolidus K-feldspar (adular?) - quartz - chlorite veins filled both diagonal and concordant fissures. The external contact with the granite at the top of the profile is discordant and sharp with leucocratic envelopes, often with micropegmatitic fabric. Approaching the terminations the younger, diffuse contacts of xenoliths with granite are observed (Fig. 3), while the portions of leucocratic envelopes show still brittle disaggregation.

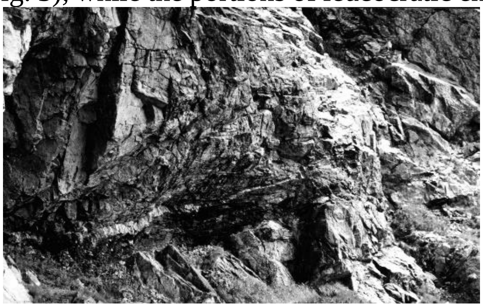

Fig. 1. Photograph of the main part of the outcrop of MXVV. Concordant fractures are filled by leucogranite melt (white veins), while he discordant ones are mostly perpendicular to the foliation planes.

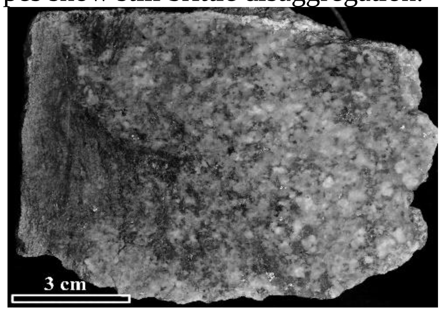

Fig. 3. A fragment of the satellite xenolith with decomposition of the metamorphic rock by the granite magma. Notice the contamination of the granite.

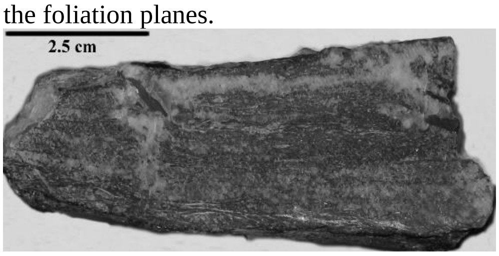

Fig. 2. A fragment of the internal gneiss from the MXVV, intruded by leucocratic micro-veins, carrying the clasts of biotite schists.

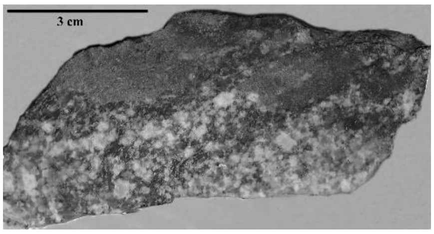

Fig. 4. Contaminated granite at the border with crushed portions of fine-grained gneiss from the upper part of MXVV.

Granite veins as well as the foliated porphyritic granite enveloping the MXVV are rich in biotite schlieren, centimetre-scale xenoliths and xenocrysts. Mafic varieties of host granites are in fact contaminated by xenocrystic biotite and opaque minerals (Fig. 4). Veins intruding the MXVV show the features of rapid cooling, with aplitic and micro-pegmatitic fabric. Schlieren in host granite are oriented parallel to the foliation in the MXVV, and – what is worth to mention – the biotite composition is identical to that in nearby metapelitic part of MXVV (Gawęda in preparation). The presence of K-feldspar phenocrysts ranging from 1 to 6 cm in length is a typical feature of the granites hosting the MXVV.

DISCUSSION & CONCLUSIONS

MXVV shows features suggesting both the rapid quenching of the granite magma against the xenolith body and the physical decomposition by the flowing magma. Such features are usually interpreted as contradictory in terms of thermal regime: rapid quenching occurs when the large temperature difference exists, while the physical disintegration is typically observed in "hot" xenoliths, with no important temperature difference to the host magma. The other important MXVV feature is the fracturing, both concordant and discordant, which are usually attributed to thermal stress. The concept of sinking assumes the physical integrity of xenoliths while it underwent both the thermal shock and chemical interaction with granite. As the host magma may intrude the xenolith only along fractures and cracks the fracturing should predate the injections. As the former petrological studies suggest the dehydration-melting reactions acting in the metapelitic xenolith after dropping to the granite magma (Janak et al. 1999), one can ask about the way of fluid loss from the large portion of the metamorphic rocks.

To understand the history of the MXVV we can assume that fluid released could lower the surface energy, mainly along the foliation planes, and promote the crushing by fracture propagation and volumetric expansion. That could result in explosion and fragmentation of xenolith during sinking (Daly 1933, Clarke et al. 1998). Explosion during magma flow could enable the further fragmentation and dispersion of small fragments in the host magma. The proposed sequence of events is as follows:

1. granite magma quench against the colder sinking xenolith, producing the almost hermetical envelope,
2. vapour-producing reactions (dehydration) and accumulation of vapour phase inside the "schrapnel"
3. explosion and disintegration (exfoliation) and further physical decomposition and contamination of the host granite.

Such a hypothetical row of events could enable to understand the high degree of fracturing of the MXVV, contamination of the granite growing when approaching MXVV in some hundred of meters distance and the presence of large amount of small xenoliths and schlieren. The last can be the result of exfoliation and partial melting of the external parts of MXVV.

Clarke et al (1998) proposed that the xenolith`s explosion "may explain the absence of "elephant's graveyard" on the floor of the granitic batholits". The internal vapour pressure should be high enough to explode the MXVV as the calculated degree of metapelitic xenoliths melting ranges from 66 to 80% (Maury, Didier 1991). As the MXVV is the biggest and one of the very lowest xenolithic portions in the

Tatra Granit, its position, size and structure can be best explained assuming the sinking and following explosion on the way down. Additionally, the presence of large, K-feldspar phenocrysts (and their zonation patterns) in the host granite can be better understand when assuming the fluctuation of water released from "exploded elephant", which couldn't manage to reach the floor of the magma chamber.

In conclusion it should be stated that the large xenoliths influence not only the thermal regime and cooling patterns of the granite magma but also the chemical composition and fabric of the host granite.

Acknowledgements: The Ministry of Sciences and Informatics grant No. 2 PO4D 05629 founded this research.

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MINERALOGIA POLONICA – SPECIAL PAPERS
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CALC-SILICATE ROCKS FROM THE MALÉ KARPATY MTS. & THE POVAŽSKÝ INOVEC MTS., WESTERN CARPATHIANS, SLOVAKIA: A COMPARATIVE STUDY

Abstract: A comparative study of two calc-silicate rocks from the Western Carpathians Core Mountains, formed during intrusions of Variscan granitoid magma, revealed the presence of contrasting mineral compositions and textures. These features are the result of different formation conditions. The main factors were: the fluid pressure, fluid composition (activity of alkalies, water and carbon dioxide) and protoliths composition.
Keywords: calc-silicate rocks, fluid pressure, Western Carpathians

INTRODUCTION

Mineral assemblages of calc-silicate rocks are good indicators of CO_2 regime and metamorphic conditions (P-T) of its origin. Contact metamorphism occurs as a result of a high geothermal gradient produced locally around intruding granitoid magma and significant chemical exchange (metasomatism), which takes place between the magma and the carbonate envelope, rocks. Such metasomatic rocks are referred to as skarns. On the other hand, some rock showing no metasomatic alterations and no trace zonation, typical of skarns, but influenced by temperature from the intrusion are referred as Ca-silicate hornfelses. The study of calc-silicate hornfels (erlans) and Ca-skarns has long tradition in the Western Carpathians since the work of Pawlica (1918), to more recent paper of Janák (1993). The aim of this contribution is to compare the formation conditions of calc-silicate rocks from the classical locality – Dolinkovský Hill (Malé Karpaty Mts.) with a newly discovered locality in Hlavinka Creek (Považský Inovec Mts.).

GEOLOGICAL SETTING

The Inner Western Carpathians consist of three main crustal-scale superunits which are, from north to south: the Tatric, Veporic and Gemeric and several cover-nappe systems: the Fatric, Hronic and Silica. The basement units together with the Mesozoic cover and nappe complexes were tectonically juxtaposed through north-directed thrusting during the Upper Cretaceous. The crystalline basement rocks together with the Mesozoic sediments are formed so called Core Mountains in the Tatric Unit. The Malé Karpaty Mts. and the Považský Inovec Mts. are classic representatives of the Core Mountains in the western part of Slovakia.

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SAMPLING & ANALYTICAL TECHNIQUES

For this study we sampled the following localities: 1) - the classical Harmonia quarry under the Dolinkovský Hill, with a contact skarn consisting of garnet, clinopyroxene, quartz and calcite, with accessory titanite and zircon. 2) - Fine-grained skarn from Hlavinka Creek forming small layers (up to 15 cm in diameter) within metapelitic rocks of the Hlavinka Group, showing visible foliation and lamination underlined by differences in mineral composition.

Microscopic observations using the Olympus BX-60 microscope and BSE images with FET Philips XL 30 at 15 kV and 1 nA were carried out at the Faculty of Earth Sciences, University of Silesia. Microprobe analyses of minerals and selected BSE mineral images were conducted on a CAMECA SX-100 electron microprobe in the Inter-Institution Laboratory of Microanalysis of Minerals and Synthetic Substances, Warsaw, using sets of natural and synthetic standards.

RESULTS

Dolinkovsky Hill.

The Harmónia Group forms the Devonian metamorphic series that were intruded by Hercynian granites 324 – 320 Ma (Bagdasaryan et al. 1982; Shcherbak et al. 1988). The metamorphic sequence is composed of interleaving metapelites and metapsammites, with intercalations of lenticular limestones and ophiolitic metavolcanites (Fig. 1).

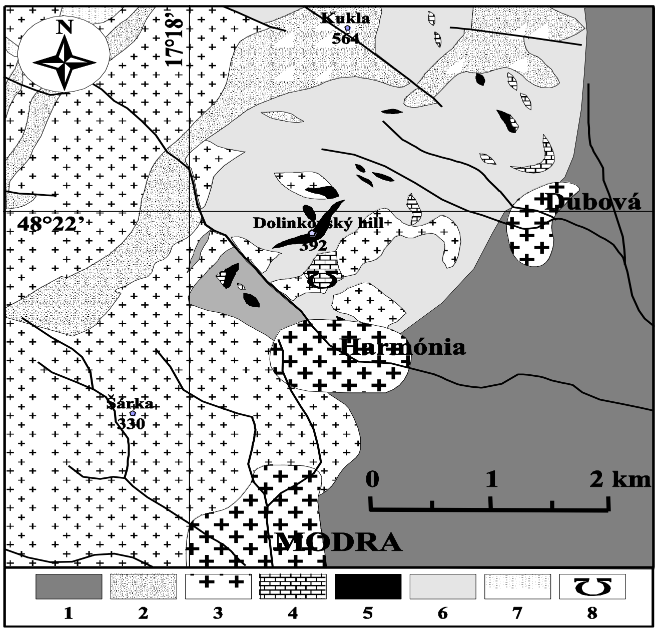

Fig. 1. A section from geological map of the Dolinkovsky Hill area (Maheľ & Cambel 1972). Explanations: 1) Neogene en block, 2) Lower Triassic quartzites, 3) Carboniferous granitoids, 4) Devonian metacarbonates, 5) basic metavolcanics, 6) phyllites 7) biotite paragneisses, 8) abandoned quarry – sample locality.

Contact metamorphism in this area is related to the granite intrusion. P-T conditions of contact metamorphism in the Modra massif are identical in metapelites and in calc-silicate rocks and point out the temperature range of 590 – 600 °C and pressure 150 – 200 MPa (Korikovsky et al., 1985; Cambel et al., 1989) while fluids show X_{CO2} = 0.05 – 0. 08. The internal zonation of the calc-silicate rock in question was described by Korikovsky et al. (1985) and Cambel et al. (1989).

The poikiloblastic or skeletal garnet porphyroblasts (up to 1 cm in size) show the grossular-rich composition ($Gross_{81}And_{15}Al_3$ – $Gross_{63}And_{37}$). Inclusions in garnet are: homogeneous diopside ($Wo_{51}En_{29}Fs_{20}$), calcite, quartz and titanite. Diopside crystals composing matrix outside the garnet porphyroblasts are zoned, with the outer part enriched in Fe ($Wo_{51}En_{28}Fs_{21}$ – $Wo_{53}En_{24}Fs_{23}$). In the garnet embayment the remnants of the quartz-calcite intergrowths as well as wollastonite needles could be observed. The skeletal quartz-grossular-diopside intergrowths, surrounded by calcite form the matrix. Calcite grains contain subordinate admixtures of Fe and Mg. Elongated titanite inclusions, up to 50 μm in length, are present only in garnet. They differ in Al substitution (2.78 - 0.87 wt.%) while Fe content is low and quite constant (0.33 - 0.5 wt.%).

Hlavinka Creek

The calc-silicate rocks have been discovered recently in the frame of a new mapping project of the Považský Inovec Mts. in its central part as a component of an unusual volcano-sedimentary complex (Kohút et al., 2005). The new field and petrological study proved that the dominant part of this complex consists of dark grey and fine-grained banded metapelites-metapsammites, with local sills of amphibolites and the purple-red iron-bearing metaquartzites – a typical analogue of the Lahn-Dill volcano-sedimentary iron ores (Kohut et al., 2006). The presence of graphitic metaquartzites and lydites, as well as calc-silicate hornfels (erlans) was also stated. The whole complex was named Hlavinka volcano-sedimentary metamorphic complex (Kohút et al., 2005). The Hercynian metamorphic overprint of this Devonian sequence reach to upper part of greenschist facies, respectively lower part of amphibolite facies with T = 500 – 550 °C and P = 300 – 350 MPa.

Metapelitic sequence was intruded by the Bojna granitoid, dated at 335±5 Ma. Lack of modern stratigraphic data from Hlavinka Group is partly supplied by EPM dating of uraninite (394 ± 2 Ma) and monazite (336 ± 18 Ma; Kohút et al., 2006). The calc-silicate rocks are present as thin intercalations among the metapelites, showing no internal zonation, but fine, microscopis-scale lamination (Fig. 2).

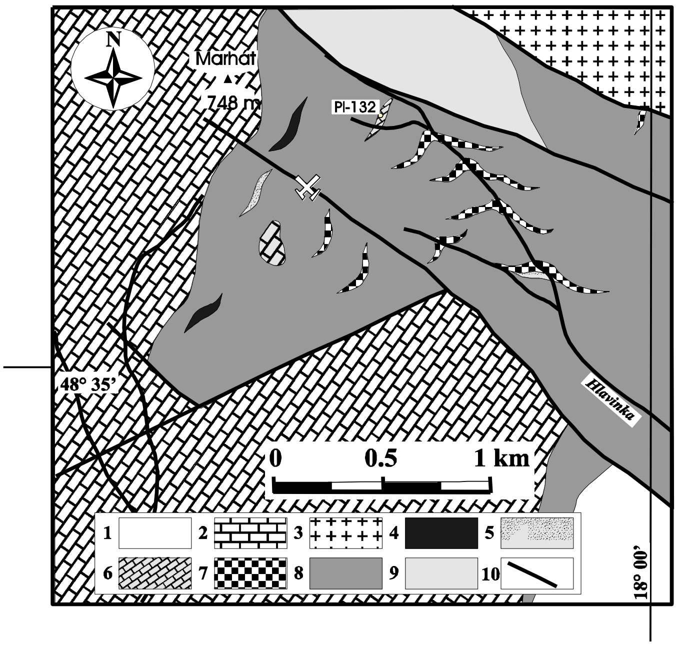

Fig. 2. A section from geological map (Ivanička et al., 2007). Explanations: 1) Neogene en block, 2) Mesozoic en block, 3) Carboniferous granitoids, 4) black schists, 5) hematite metaquartzites, 6) Devonian metacarbonates, 7) basic metavolcanics, 8) phyllites 9) biotite paragneisses, 10) faults.

The dark laminas are composed of garnet-pyroxene-epidote-K-feldspar-plagioclase with accessory barite, titanite and rutile. Light laminas are quartz-rich, with subordinate plagioclase and dispersed epidote, forming polygonal aggregates.

Pyroxenes are zoned in respect to Fe/Mg ratio ($Fs_{25\text{-}31}En_{25\text{-}19}Wo_{50}$). The cores are usually enriched in ferrosilicate component. Grossular-rich garnet ($Gros_{69\text{-}74}Alm_{14\text{-}20}Spes_{5\text{-}7}And_{4\text{-}8}$) forms the aggregates of hypidiomorphic blasts 20-100 μm in size, chemically homogeneous. Rare epidote (fe^{+3} ratio = 5.3 - 19.2) is overgrowing pyroxene-garnet aggregates. Locally the LREE-rich epidote (Ce>La) is overgrown by normal epidote (fe^{+3} = 18). There are two populations of plagioclase: andezine-labradorite ($An_{56\text{-}46}$) is characterised by normal zonation, while the oligoclase-andezine ($An_{28\text{-}38}$) - by inverted zonation. Iron-poor titanite is growing at the cost of rutile. The differences in Al substitution were observed in separate grains (1.5 – 8 % wt. Al_2O_3), but no zonation of the grains was observed. Polygonal grains of K-feldspars show Ba enrichment in the margins (up to 6 Cs at %). The small grains of K-feldspars, included in pyroxene aggregates are – in contrast – almost lacking Cs substitution (Cs < 0.1 at.%,). Barite grains are dispersed both inside pyroxene and garnet aggregates.

DISCUSSION

In case of the Dolinkovsky Hill the mineral components are typical of pyroxene-garnet facies conditions with stable calcite, what impose the temperature limits of

450 – 600 °C (Zharikov et al. 1998). The rock-structure with characteristic garnet porphyroblasts suggests the high fluid pressure, enabling the components migration and re-crystallization. The presence of disequilibrium structures represented by quartz-calcite and quartz-grossularite-diopside skeletal intergrowths can be interpreted as formed during superheating: 2 Cc + An + Qtz = Gros + 2 CO_2. The zonation of both garnet and diopside can be a result of a Fe-Mg exchange reaction: $2CaFeSi_2O_6 + Ca_3Al_2[SiO_4]_3 + 2\ Mg(OH)_2 + H_2O = 2\ CaMg\ Si_2O_6 + Ca_3Fe_2[SiO_4]_3 + 2\ Al(OH)_3 + H^+ + e^-$ (Zharikov et al. 1998). Titanite presence marks the high oxygen fugacity.

Fine-grained, compact structure and polygonal intergrowths of minerals in the Hlavinka Creek rock suggest the large temperature difference between the original rock and the granite magma and low pressure of the metamorphic reaction. There are no relics of carbonate minerals. Mineral association suggests pyroxene-garnet facies conditions. As there are no traces of intense deformation, the lamination could be the original feature of the rock, underlined by later metamorphic re-crystallization. The characteristic reaction is: Cpx + Pl + (K^+) = Kfs + Grt + (Na^+). That reaction can be also responsible for the presence of second generation of plagioclases as Ca was consumed by formation of grossularite component. The presence of K-feldspar together with grossularite-rich garnet implies the high alkalinity of the environment (Zharikov et al. 1998). Barium is rather immobile element so it was probably present originally in the rock. The presence of barite inclusions is an indicator of high oxygen fugacity. Ba liberated from primary host mineral was incorporated quite late to the second generation of K-feldspar. The replacement of primary rutile by titanite took place also in high oxygen fugacity conditions. Secondary epidote group minerals, replacing the primary mineral components are rare, what suggest the low water content.

CONCLUSIONS

In general – both calc-silicate rocks represent the same thermal regime, but contrasting fluid pressure and composition and protolith composition. In case of the Dolinkovský Hill fluid pressure was high enough to develop the grossular-andradite garnet porphyroblasts. The presence of calcite implies that main fluid component was CO_2. The remnants of quartz and calcite in the garnet embayments In case of the Hlavinka Creek the fluid pressure was extremely low, both water and CO_2 were insufficient for the development of coarse-grained structure and secondary reactions. The fine-grained structure of the rock blocked also the diffusion processes, so the original protolith composition could influenced the mineral reactions and present mineralogy.

We suggest that in case of Dolinkvsky Hill the rock can be interpreted as skarn, influenced by metasomatic processes, while the Hlavinka Creek exposure represents the Ca-rich hornfels, formed mostly by the temperature shock from the granite intrusion.

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MINERALOGIA POLONICA – SPECIAL PAPERS
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Bożena GOŁĘBIOWSKA[1], Adam PIECZKA[1]

CHEMICAL VARIATIONS OF THE TETRAHEDRITE-TENNANTITE GROUP MINERALS FROM RĘDZINY (SUDETES, POLAND)

Abstract: Various members of the tetrahedrite-tennantite group were identified within disseminated hydrothermal ore mineralization at the deposit of dolomitic marbles in the Rędziny (Western Sudetes, Poland). Microprobe analyses indicate high content of Bi in tetrahedrite (up to 15.86 wt.%) and tennantite (up to 18.41 wt.%) Tennantite is commonly poor in Ag, in contrast to tetrahedrite, in which Ag reaches a maximum of 12.47 wt.%. Freibergite contains up to 32.3 wt.% Ag, considerable amount of Fe (7.91 wt.%) and low of Zn (0.63 wt.%). The fahlores from Redziny are poor in Pb, Cd, Mn and Sn. Our data show strong correlations of As/Sb vs Bi, Cu vs Ag, and Fe vs Zn.
Keywords: tetrahedrite-tennantite series, Bi and Ag substitution, Rędziny, the Sudetes

INTRODUCTION

Tetrahedrite-tennantite solid-solutions belonging to the fahlore-group are the most common sulphosalts and are present in many sulphide deposits. Their general formula is $(Cu,Ag)_{10}(Fe,Zn,Hg,Cd,...)_2(Sb,As,Bi,Te)_4(S,Se)_{13}$, (Makovicky, Karup-Møller 1994) where: tennantite $M_{12}(As{\geq}3...)_4S_{13}$, tetrahedrite $M_{12}(Sb{\geq}3...)_4S_{13}$, freibergite $M_2(Ag{\geq}4...)_{10}Sb_4S_{13}$, goldfieldite $M_{12}(Te{\geq}3...)_4S_{13}$ and others. Mercury-bearing fahlore are widely known as *'schwazite'*. In the nature are also known Zn, Fe, Pb and Bi varieties of the fahlore-group. In the tetrahedrite and tennantite structure there is a complete solid solution between antimony and arsenic. Bi replaces partly only for Sb and As. Breskova and Tarkian (1994) found a limit of solubility of bismuth at 1.69 atoms p.f.u from 214 analyses of natural fahlore group minerals. Solubility of bismuth in the tetrahedrite and tennantite containing Fe and Zn was studied by Klunder et al. (2003).

This paper presents characteristic chemical variations within the fahlore-group from Rędziny.

GEOLOGICAL SETTING

The deposit of dolomitic marbles in the Rędziny, localized within the schist series of the Kowary-Czarnów unit (Kozdrój 2003) as a result of Hercynian movements has been fragmented into several parts, separated by schist zones of the NNW-SSE trend. These zones favoured migration of hydrothermal solutions derived form the nearby Varsican intrusion of the Karkonosze granite. Primary mineralization is represented mainly by sulphides and sulphoarsenides: arsenopyrite, chalcopyrite,

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pyrite, pyrrhotite, galena, sphalerite, and others. Sulphide mineralization has been affected by hipergenic alterations, resulting in a wealth of secondary minerals, described in earlier papers.

In Rędziny, minerals belonging to the fahlore-group are associated with sphalerite, chalcopyrite, Ag-bearing galena, Cu(Ag)-Pb-Bi(Sb) sulphosalts and tin sulphides of the stannite group.

METHODS OF INVESTIGATION

Optical observations in the reflected light were carried out using an OLYMPUS BX-51 microscope. Chemical compositions of the minerals were established at the Inter-Institute Analytical Complex for Minerals and Synthetic Substances of the Warsaw University. A Cameca SX-100 electron microprobe operated in the WDS mode under the following conditions: excitation voltage 15 kV, beam current 20 nA, peak count-time 20 s, background time 10 s; standards and spectral lines: Zn – sphalerite (K_{α}, LIF), Cu – chalcopyrite (K_{α}, LIF), Fe – chalcopyrite (K_{α}, LIF), Mn – rhodonite (K_{α}, LIF), As – GaAs (L_{α}, TAP), Se – ZnSe (L_{α}, TAP), S – chalcopyrite (K_{α}, PET), Ag – metallic Ag (L_{α}, PET), Cd – greenockite (L_{α}, PET), In – InSb (L_{α}, PET), Sn – cassiterite (L_{α}, PET), Sb – InSb (L_{α}, PET), Te – PbTe (L_{α}, LIF), Pb – galena (M_{α}, PET) and Bi – Bi_2Te_3 (M_{α}, PET).

RESULTS

The members of the fahlore-group found in Rędziny in various ore assemblages show chemical diversity. The composition of the fahlores was calculated using ΣMe = 16 apfu. The total number of atoms in the minerals analysed ranges between 28.41 and 29.51 (ideally it is 29 atoms pfu). Similar contents were observed in many fahlores from various deposits. The Sb-As-Bi diagram (Fig. 1) shows compositional range of the tetrahedrite-tennantite members from Rędziny. The total concentration of these elements vary from 3.86 to 4.24 apfu. The maximum value of the Bi/(Sb+As) ratio in tetrahedrite is 36/64, and of the Bi/(As + Sb) in tennantite – 38/62, which correspond to 15.86 and 18.41 wt.% Bi, respectively. However, some fahlores are poor in Bi with its contents close to 0.00 wt.%. Our data of the Bi-rich fahlores display negative correlation between Bi and Sb+As. The Bi-rich fahlores usually are associated with (Ag,Bi)-bearing galena, Bi-sulphosalts and also occur in assemblage composed of Sn-bearing sulphides, chalcopyrite and bornite.

Cooper content varies from 26.47 to 36.42 wt.% (7.76-9.84 apfu) in tetrahedrite and 36.33 to 44.37 wt.% (9.52-10.26 apfu) in tennantite. The Cu replacement by Ag is present mainly in tetrahedrite containing 0.29 to 12.47 wt.% Ag (0.05-2.07 apfu). Tennantite is commonly more poor in Ag; its maximum content is 0.16 wt.% (0.03 apfu). In pyrrothite there have been found tiny inclusions of the freibergite (Ag-rich fahlore) containing 32.3 wt.% Ag. In the Fig. 2 is shown a negative correlation between Cu and Ag in Sb- and As-bearing fahlore.

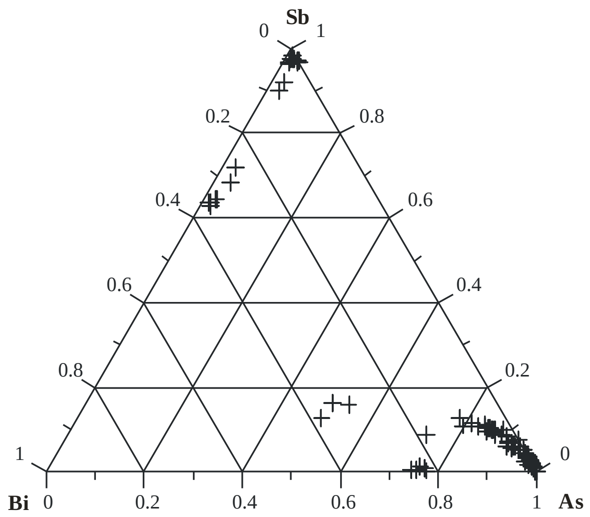

Fig. 1. The fahlore members from Rędziny in the Sb-As-Bi compositional system.

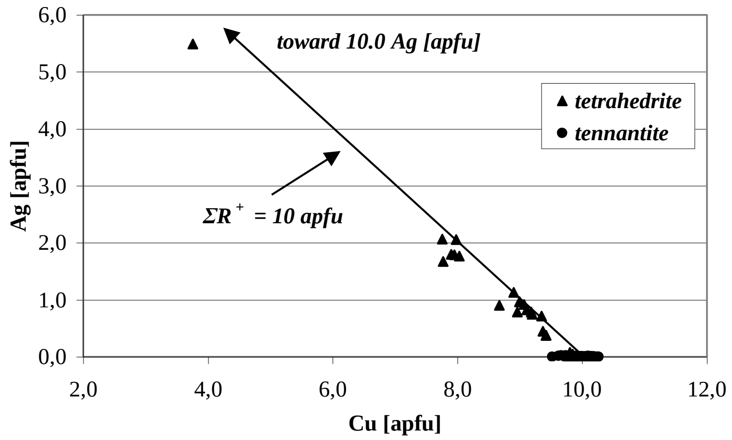

Fig. 2. The Cu↔Ag substitution trend in the fahlores from Rędziny.

Iron and zinc are principal bivalent metals, but their concentrations are highly variable. Fe ranges from 0.31 to 6.22 wt.% (0.09-1.99 apfu) and correlates negatively with a Zn content of 1.06 – 9.04 wt.% (0.26-2.02) (Fig. 3). In freibergite Fe reaches up to 7.9 wt.% (2.59 apfu). The highest Zn (9.04 wt.% - 2.02 apfu) has been encountered in tennantite associated by pale sphalerite, the lowest in freibergite (0.63 wt.%, 017 apfu). Low contents of cadmium were found both in tetrahedrite (max. 3.11 wt.% - 0.52 apfu) as well as in tennantite (max. 0.4 wt.%, 0.05 apfu).

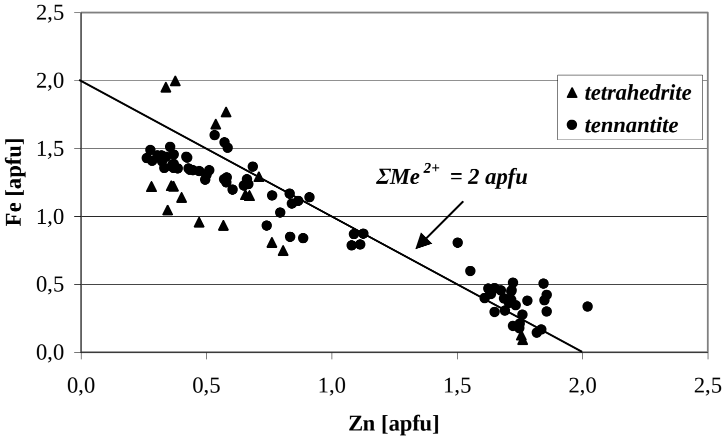

Fig. 3. The Zn↔Fe substitution trend in the fahlores from Rędziny.

The fahlores from Rędziny generally are poor in other elements. Pb, Mn, and Sn only in low concentrations were recorded. No correlations between Fe and Zn vs Cd, Pb and other elements were found in the present study.

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MINERALOGIA POLONICA – SPECIAL PAPERS
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Piotr GUNIA[1]

PETROLOGY OF VAG-RELATED PLAGIOGRANITES WITHIN SZKLARY SERPENTINITES (FORE-SUDETIC BLOCK, SW POLAND) NEW GEOCHEMICAL DATA

Abstract: New geochemical data about felsic plagiogranites within of Szklary serpentinites (Foresudetic Block, SW Poland) indicate that they can be clasiffied as: 1) plagiogranites, probably formed by fractional crystallisation of mid-ocean ridge-like basaltic magmas in a back-arc basin, 2) anorthosites, which may have reflect partial melting or fractional crystallisation of mafic island arc tholeiitic magmas and 3) allochtonic dykes cutting the serpentinites have originated by partial melting of mafic rocks at the base of a thick pile of ocean floor- and island arc-derived rocks stacked onto the outermost part of a continental or microcontinental margin. The obtained results demonstrate petrogenetic evolution of Szklary aplites from the formation of oceanic crust, through island arc development, to post-obduction magmatism The conclusions reached here thus support of idea, that the Early Palaeozoic ophiolite suite in the Sudetes has been formed as part of extensive island arc/back-arc system.
Keywords: VAG, plagiogranites, ophiolites, Foresudetic Block, SW Poland

INTRODUCTION

Petrological data for the creation of oceanic lithosphere obtained from MAR and SWIR crest zones shows suggest, that three different types of acidic plutonic rocks are present at mid-cceanic ridges. It includes: 1) a diorite-monzonite-granite suite derived from the most evolved and fractionated portion of MORB parental melts in the fast spreading ridges, 2) plagiogranites, unrelated to gabbroic host and originated from other anomalous geochemically magmatic sources (hybrid or anatectic) typical for slow spreading cold litosphere, and 3) granitic rocks being relics of continental litosphere preserved in oceanic basins (allochtonous sensu: Silantyev et al. 2004).

The geodynamic evolution of plagiogranites from normal MORB to more subduction influenced granitoids is consistent with evolution of mafic cumulate members of an ophiolite suite. This magmatic evolution of the Sudetic ophiolite appears to be compatible with formation and evolution of an oceanic back-arc basin (Narębski et al. 1982).

The aim of this study is to attempt to classify of Szklary plagiogranites on the basis of new geochemical data, focusing on their pristine geotectonic settings.

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GEOLOGY

The Szklary serpentinite Massif is situated at the southern edge of the Niemcza dislocation zone (Foresudetic Block) near the eastern margin of Sowie Mts. gneissic block. This massif forms small, N-S elongated and tectonically separated, serpentinized ultrabasic body about 10 km long and 3 km wide. The ulttrabasic rocks are covered by rusty weathering cover, which is locally transecting by na-rrow opal and chalcedony (chrysoprase) veins (Gunia 2000).

The presence of felsite acidic rocks has been reported firstly from north-eastern part of the Szklary Massif, where these, leucocratic rocks form a bigger vein up to 250 m in thickness. It generally strikes N-S with N shortening, and is bordered by steeply dipped fault on south. According to Niśkiewicz (1967) they can be classified as medium-grained to fine-grained diorites, with unoriented or oriented texture and had regarded as a continuation of younger Koźmin granitodiorites exposed on north of Szklary massif.

Other occurrences of plagiogranites are known within of Szklary serpentinites or in weathering zone. It forms narrow veins consist of fine-grained aplites, coarse-crystalline pegmatites and sporadically lamprophyres (spessartite, kersantite). These veins range from 0,2 to 3 m in thickness and strike of N-S, NW-SE or E-W with high angles of dipping (Niśkiewicz 1967). Some of leucocratic veins are surrounded by reaction rims composed of sheared talc-anthophyllite, tremolite-chlorite or chlorite-bearing schists (Dubińska 1993). On the basis of typomorphic sets of minerals occurring in some pegmatite veins from Szklana Góra hill, their allochtonic position from source primarily localized in the Moldanubian Sowie Mts. gneisses is postulated (Pieczka 2000).

SAMPLING AND PETROGRAPHY

Samples for petrologic studies were taken from several small outcrops localized in the central part of massif as well as from the boreholes localized on: N and NW slopes of Koźmickie hill (10 specimens from three boreholes), S slopes of Tomickie hill (3 specimens from one borehole) and N, S slopes of Siodłowe Hill (7 specimens from three boreholes).

On basis of petrographic features two groups of fine-grained felsic rocks have been distinguished. One, represents “white-coloured” variety, occasionally with gray veins and patches and the second group described by Niśkiewicz (1967) as a “grey-coloured” variety, which shows of stripped appareance.

The plagioclase-bearing (white) aplites are fine-grained monomineral rocks composed of panxenomorphic laths or xenomorphic grains of plagioclases (An_{30-34}.) commonly up to 1 mm in size with showing often traces of multiple albite rarely pericline twins. Most of them underwent intensive shearing and recrystalization and the poikilitic (sieve-like) structures are found in the background.

The quartz-bearing (grey) felsites consists of plagioclases with minor amounts of quartz, microcline, biotite, green common hornblende and accesoric: sphene, garnet, and Fe-Ti oxides. In the background the small xenomorphic individuals of plagioclases (An_{28-35}) prevail, which occupy about 70 vol% of rock. They also surround single tables of potasium feldspars (up to 5 mm in size) and are accompanied by mosaics composed of small xenomorphic quartz grains or occasionally by single sets of bent and chloritized biotite platelets. Occasionally, the plagioclase-amphibole-bearing assemblages form banded intergrowths with the larger sets of paralelly oriented panidiomorphic prisms of green hornblende.

Modal composition of Szklary aplites plotted on IUGS Q-A-P triangle shows the granodiorite/tonalite and quartz diorite/quartz gabbro affinity of studied granitoids.

GEOCHEMISTRY

Whole-rock chemistry of 10 representative samples was performed in the ACME Laboratory (Vancouver, Canada) using combined XRF, ICP-MS and INAA analytic methods. The Szklary plagiogranites are generally peraluminous A/CNK >1, enriched in CaO, poor in K_2O, with high Na_2O/K_2O ratio characteristic for I-type granites. Their normative mineralogy plotted on Al-An-Or diagram shows their trondhjemite composition (except one sample of granite). Majority of studied aplites exhibits alkali-lime values of Peacock's index.

On R1-R2 plot (Batchelor, Bowden 1985) they can be classified as syn-collisional varieties, except one sample in the field of late-orogenic granitoids.

On ORG-normalized diagram three shapes of pattern can be recognised. One, is characterised of flattened profile line along the standard level with small Zr (negative) and Sm (positive) anomalies. It probably reflects fractionation of MORB to acid composition . The second profile line is exemplified by slight enrichment of LILE with strong Zr depletion and Sm enrichment. It can be indicative of derivation of acidic melt from incompatible element enriched mantle (Pearce et al. 1984). It should also noted, that third group of Szklary plagiogranites exhibits patterns, where Rb, Th and Ce, Sm are enriched relative to lower Nb, Ta abundances. Such selective enrichment can be attributed to crustal involvement (Pearce et al. 1984), however in case of ophiolitic plagiogranites also might be caused by variable mobilisations of LIL elements under lower greenschist conditions of metamorphism (Floyd et al. 1998). These patterns of the Szklary plagiogranites are similar to those of the "supra-subduction zone" granites or the granites originated in ensimatic island arcs.

Chondrite- normalized REE patterns of three samples show slightly sloped profile with absence of negative Eu anomaly. It pointing out, the cumulative plagioclase acumulation during slow fractional crystallization at the magma chamber. The other Szklary geochemical group is characterized the presence of varying negative Eu anomaly. indicative of feldspar involment during fractiona-tion or melting (Floyd et al. 1998). It might to indicate of dynamic evolution of magma chamber, when partial melting of hydrated gabbro and extreme fractionation of basic liquid produced the acidic melt.

CONCLUDING REMARKS

The obtained geochemistry results allow to recognise of three geochemical groups among the fine-grained felsic rocks within Szklary serpentinites. One group can be assumed to be a product of slow fractional crystallisation of hydrous gabbros at the mid-ocean ridge-ennviroment. The second (anorthositic) may have formed by partial melting or fractional crystallisation of mafic island-arc tholeiitic magmas influenced of crustal contamination. The last generation of acidic melt is represented probably by allochtonic? felsic dykes formed by partial melting of mafic rocks at the base of a thick pile of ocean floor and island arc-derived rocks stacked onto the outermost part of a continental margin.

The detailed recognition of role of oceanic or continental protoliths of studied plagiogranites in connection with development of rifting processes require further geochemical studies of plagogranite dykes occurring in the various parts of Sudetic ophiolite suite. Such studies are actually in progress.

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STONE RAW MATERIALS USED IN CENTRAL EUROPE DURING PRAEHISTORY

Abstract: In the following under consideration are territories of nowadays eastern Austria, Czech Republic, southern Poland, Slovak Republic, Hungary and the northernmost part of the Balcan penninsula. From the geological point of view mentioned territory is a part of the Easten Alps, Bohemian Massif, Western Carpathians and Pannonian Basin, as well.

Archaeological field surveys realised during few last decades and following laboratory studies by the use of geocsientific methods and laboratory devices, brought facts not only on raw materials used, but also on ready-made implements distribution as well as information on original geological bodies, which have been sources of used raw materials.

Central Europe already in the Palaeolithic was densily populated areas of the Old Continent. After the continental ice cap retreat to the north (some 13-11 thousands years BP) central European human tribes settled. This change of living (change from the hunters´ – gatherers´style of living to agriculture and domestification of some animals as the main man´s activities supplied the majority of daily food needed). In such way man used gradually more-and-more stone implements for elaboration of various tools and arms.

Based on the technology of inorganic raw material elaboration the praehistory is divided into the Palaeolithic period (chipped industry) and the Neolithic one (polished industry). Both mentioned technologies needed raw materials of different physical properties. The main types of them and probable primary sources are characterized.

Keywords: Stone Age, central Europe, main raw materials types

PALAEOLITHIC

For this time period the submicroscopically grained silicic rocks, namely cherts, radiolarites and acid volcanic glass were the leading raw material types.

Flint in the area under consideration has its occurences in the forms: i) irregular bodies within the Jurassic, and in less amount also in Cretaceous limestones namely in southern Poland, and i) in the form of blocks and gravels occurring in the Quaternary morainic unsorted sediments in southern Poland and northeastern part of the Czech Republic.

Based on this local raw material type occurrences, mentioned territories are characterized by the prevalence of just this silicic raw material type used during the Palaeolithic. It ought to be mentioned that just southern Poland subsurface beds and lenses of flint in Jurassic limestones were mined already in the last millenia of the Palaeolithic. Vertical pits reached to 8, rarely even 10 meters of depth. From the various vertical levels praehistoric „miners“ made also horizontal galleries.

Quantitative evaluation of the flint made implements in comparision to the other raw material categories in the discussed region was not published yet. Taking into

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account syntetic papers by Přichystal (2000), Hovorka & Illášová (2002),Bíró 1988, Bíró & Szakmány (2000), Foltyn et al. 2000, Prinke & Skoczylas 2000 and the others should be concluded that population from flint made implements, in accordance to distance of flint occurrences, diminishes.

Radiolarites/radiolarian shales represent accumulations of siliceous shells of radiolaria mostly in the deep water (but not only) environments. Sedimentation of radiolarites is characteristic namely for Jurassic period. The use of radiolarites in the central Europe was limited; by the fact, that the majority of geological terranes with Jurassic strata were during Alpine orogenic processes strongly tectonized. As the consequence radiolarite bodies were intensively crushed, so only a part of them should have been elaborated. From the available published informations it seems that the highest concentration of implements made from radiolarites are areas adjacent to the Pieniny Klippen belt in western Slovakia, the eastern territories of the Czech Republic and the western and northhwestern part of Hungary, as well.

Obsidian in spite of above raw material types occurring within sedimentary strata of several geological units, this type of acide volcanic glass has occurrences practically in the only area – Zemplin county both in the eastern Slovakia and northeastern Hungary territories. In mentioned areas obsidian was during the Palaeolithic the leading raw material type, but implements from mentioned territory were identified as far as in Germany. The quantity of obsidian made implements from the raw material occurrences to the west and southwest decreases.

Hydroquartzite/limnoquartzite. In the intramontagne basins within the Late Tertiary volcanics, namely in the cetral Slovakia, there occur several hydroquartzite deposits. They originted by precipitation from postvolcanic hydrotherms. Hydroquartzites are composed of various forms of SiO_2. They are compact or porous with pores of irregular shape. Characteristic for them is the presence of footprints and remnants of leaves and silicified plants. Hydroquartzite occurrences on the rim of the Žiarska kotlina basin (central Slovakia) supplied raw material implements namely in the direction to the west. During the Palaeolithic practically all utilized kinds of implements were made.

Except of mentioned leading raw material types during the Palaeolithic also various locally occurred types of raw materials were used. For example in the province of the middle Slovakia Late Tertiary volcanics or in its neighbourghood from various silicified sedimentary as well as igneous rocks made implements are known to occur. To this category belong implements made in the Bohemian basin from mountain crystal (Přichystal 2000).

NEOLITHIC/AENEOLITHIC

In comparisom to the Palaeolithic the number of raw materials used singificantly increased. The main factor was the change of elaborating technology from chipped to the smoothed/ polished techniques. For such elaboration some rock lithologies belonging to the all main categories (eruptive, sedimentary as well as metamorphic) of rocks were used. For the main raw material types used in the Neolithic/Aeneolithic common physical properties are characteristic. They are:

i) fine-grained character of the raw material, its compactness and homogeneity; i) aproppriate hardness but on the other side also needed elasticity; i) freshness, lack of veinlets filled up by secondary minerals; i) in some special determinations (symbols of power?) also color and lustre were important.

Igneous rocks of all main types were identified among the Neolithic/Aeneolithic implements. From the point of view of their stratigraphy they are Early and Late Palaeozoic, Mesozoic and Caenozoic in age. Characteristic is prevalence of effusive rock types over intrusive ones. On territory of the Slovakia Hovorka & Illášová (2002) described fresh and simultaneously intensively altered rock types. Though intrusive rocks of the granite clan are widely distributed on surface namely in the Czech and Slovak Republics, practically no implements (except of crushers) were made from these lithologies. From the point of view of areal distribution from igneous rocks made implements it is evident, that such implements were made in areas where Late Tertiary volcanic rocks represented the widely distributed and easily accessible raw material types. Example is territory of present Hungary (Szakmány et al. 2001), where higher quantity of the other appropriate raw material types are more-or-less lacking.

Among implements those, elaborated namely from the following rock lithologies, were till now identified: palaeobasalts, porfyrites, porphyries, spilites, melaphyres, teschenite rocks-clan, gabbros, dolerites, andesites, trachytes and also the others. From the igneous raw material types namely axes, hammer-axes, hammers and chisels were made. Their size and morphology in such extend area is variable. Majority of implements made from igneous rocks are bored types.

Other main rock category is represented by **sedimentary rocks.** They are softer in comparison to igneous as well as metamorphic lithologies. So siltstones, limestones, laminated volcaniclastic rocks, sandstones, limy claystones, quartzites, shales with high amount of limy matter, and several others are present in lesser amount. There do not exists data dealing with the quantitative proportions among individual sedimentary raw material types on the one side, and proportion of sedimentary rock made implements to the others, on the other one. It ought to be mentioned that main rock lithologies used in the Palaeolithic were continuously used in the Neolithic/Aeneolithic, too. Given sedimentary rock types were used in various proportions mostly as local raw materials types in the whole territory of the central Europe. It should be generally stated, that sedimentary raw material types were preferently used for ornamental, symbolic or power documented implements.

Metamorphic rocks represent the most variable raw material types. Among them slightly metamorphosed types as well as products of high pT conditions recrystallization are documented from the discussed territory. Practically in the whole area following rock lithologies for implements elaboration were used: the greenschists, antigorite serpentinites, glaucophane schists (blueschists), marbles, metaquartzites, amphibolites, leptynites, eclogites, jadeitites, various hornfelses, metaconglomerates, metagraywackes, in seldom cases also talkschists ao.

As dealts with implements made from metamorphic rocks it should be mentioned:

i**)** the greenschists, amphibolites, metagraywackes and marbles represent raw material occurring in several geological units in the whole discussed territory,

i) antigorite serpentinites do occur in the several units of the Bohemian massif, the Western Carparthians and the Eastern Alps, but the majority of serpentinite made implements were produced in the southwestern Poland (Hovorka, in print),
i) known eclogite implements have sources in the Bohemian Massif,
i) glaucophane schists (blueschists) have their source bodies mainly in the Mesozoic Meliata unit in the inner Western Carpathians,
i) from Moravia (Schmidt, Štelcl 1971) and western Slovakia (Spišiak, Hovorka 2005) described jadeitite axes have their sources in bodies just on the joint areas of the frontiers of Italy, Switzerland and France (the Western Alps).

CONCLUSIONS

i) Among raw material types used in the central Europe in Preahistory there are leading types, (silicites in the Palaeolithic, the greenschists and amphibolites in the Neolithic/Aeneolithic) and simultaneously types represented by individual implements (eclogites, jadeitites).
i) From the point of the distances between raw material occurrences and the places of implements discovery, we distinguish: a) in situ occurring raw material types (Banská et al. 1989); b) short distance transport (= one day walking tour); c) long (more than one hundreds kms) distance transport (blueschists, leptynites); d) transcontinental transport (jadeitite made axes; Hovorka, in print).
i) During the Neolithic for elaboration of stone implements new techniques were introduced; it was namely boring (two types; Hovorka 2006) and sawing.
i) Except of stone raw material types in the middle of Neolithic various clay for ceramic production (pots, statues = ceramic Neolithic) were used
i) Among inorganic raw material type native gold and copper ought to be added, which start to be used to the end of Neolithic. We have not to forget inorganic colors (oxids and hydroxids of iron, copper ao.) used for ceramic decoration.




Fig. 1 Fig. 2 Fig. 3 Fig. 4

Fig. 1 Obsidian core (Palaeolithic): Zemplin county, Slovakia.
Fig. 2 Stone wedge (Palaeolithic): Prepost cave, Prievidza, Slovakia
Fig. 3 Serpentinite axe (Neolithic): Svodín, Slovakia
Fig. 4 Quartzitic hammer (Neolithic): Nitriansky Hradok, Slovakia

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FROM WITHIN PLATE ALKALINE BASALTS TO MORB-LIKE THOLEIITES – A TALE OF THE BYSTRZYCKIE MTS. METABASIC ROCKS

Abstract: The protolith for metabasites from the southern part of the Bystrzyckie Mts. was probably formed and emplaced in environment of progressively extending continental lithosphere. At earlier stage alkaline melts were generated at greater depths from low-degree melting of metasomatically modified subcontinental lithospheric mantle and emplaced at crustal levels forming dykes and veins that now crop out near Poniatów; it is not excluded that these magmas were formed in enriched (?plume-related) asthenosphere. Tholeiites from the Gniewoszów area originated during subsequent extension and were generated at shallower levels in response to different degrees of partial melting of heterogeneously depleted asthenospheric source. Since some crustal contamination effects are still detectable and despite their significant N-MORB signature, melts were presumably generated beneath strongly thinned and attenuated lithosphere.
Keywords: metabasites, alkaline, tholeiitic, magma generation, Bystrzyckie Mts., Orlica-Śnieżnik unit, Sudetes

INTRODUCTION

The volcano-sedimentary succession of the Stronie series of the Bystrzyckie Mts. is traditionally interpreted as Neoproterozoic up to Early Palaeozoic (Gunia, Wierzchołowski 1979). This fairly thick sequence (4000-5000 m) is composed of metapelites intercalated with marbles and intruded by bodies of mafic and felsic metavolcanics. According to Szczepański (2003), Ilnicki & Szczepański (2005) rocks of the southern part of the Bystrzyckie Mts. recorded a Barrowian type sequence of metamorphism resulting in the westward increase in temperature from biotite up to staurolite zone as recorded by metapelites and metabasites alike. Mafic metavolcanics in the Stronie series occur as (1) small, up to 2-4 m thick, lenses as well as (2) relatively large, up to 50-70 m thick, bodies. The first of the described types crop out near Poniatów and the second prevail in the vicinity of Gniewoszów. In both cases longer axes of the mentioned bodies are parallel to the main foliation preserved in the surrounding metasediments.

Geochemistry of metabasic rocks from the Bystrzyckie Mts. was not hitherto investigated, however, the whole metabasic suite in the Orlica-Śnieżnik Massif (OSM) was interpreted by Floyd et al. (1996) to be emplaced in the intraplate setting

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and correlated with onset of continental rifting at the turn of Cambrian and Ordovician. According to Nowak & Żelaźniewicz (2006) the mafic magmatism recorded in the Stronie group was developed in a probably rift-related back-arc setting. Therefore the main goal of this study was to determine the initial tectonic setting of the metabasites in the Bystrzyckie Mts. as well as to characterize the source and processes modifying chemical composition of their protholith.

RESULTS AND DISCUSSION

Twelve samples collected near Gniewoszów (GMB) and Poniatów (PMB) were crushed and powdered, next fused with lithium meta-borate prior to analysis by means of ICP-AES for major elements and ICP-MS for trace elements at Acme Analytical Laboratories Ltd., Canada.

According to TAS diagram (Le Bas et al. 1992) these rocks are classified as basalts (two samples fall in trachybasalt and basaltic andesite fields) and show mostly alkaline affinity, while some samples straddle the line separating tholeiite from alkaline series. However, due to position of these rocks on several discrimination diagrams of less mobile high-field strength elements (HFSE) and particularly on those with values of the Nb/Y ratio (in this case <0.5) their tholeiitic character is revealed, except for the sample from vicinity of Poniatów (Nb/Y = 1.8). Their Mg# values lie between 73 and 47 (for majority of samples from 69 to 56) and moderately well correlate with concentrations of major elements showing roughly positive trends for CaO and Al_2O_3, and negative ones for the remaining major oxides. Ni and Cr contents generally correlate positively with Mg# or Zr content, although these correlations are poorly defined and tight linear or exponential trends are not observed. On the contrary, most immobile trace elements display positive linear trends when plotted against Zr. Also tight positive trends on bivariate diagrams for pairs of incompatible elements indicate that primary, magmatic concentrations of HFSE and REE were not disturbed by metamorphic processes. Moreover, metabasites of the Poniatów area (PMB) are distinguished from the samples of metabasites from Gniewoszów (GMB) by their higher ΣREE, more varied HFSE concentrations and differences in ratios of incompatible elements (e.g. for the GMB low Ti/V: 40-50 and Zr/Y: 3.3-4.9; for the PMB high Ti/V: 65-100 and Zr/Y: 9.5-14.0).

The chondrite-normalized patterns for GMB display moderate enrichment in LREE [aver. $(La/Yb)_{CN}$ 1.9 ± 0.7; CN stands for chondrite normalised], although samples showing either more distinct enrichment or depletion are also present. No regular positive or negative Eu anomaly is apparent. The HREE patterns are fairly flat, however, their $(Tb/Yb)_{CN}$ are slightly elevated (aver. 1.3 ± 0.1). By contrast, the REE patterns for PMB reveal considerable LREE enrichment [$(La/Yb)_{CN}$: up to 17.0] and fractionation of HREE [$(Tb/Yb)_{CN}$: up to 2.2]; the most enriched sample has a REE signature even higher that typical of ocean island basalt (OIB). The MORB-normalized diagrams of trace element concentrations for GMB show variable enrichment in LILE or LREE contents up to 6 x MORB abundances and systematic decrease of concentration from La towards least incompatible elements. There is a minor negative Nb anomaly and also a distinct Nb-Ta trough for one sample appears.

The patterns for PMB display negative slope and significant enrichment in LILE and LREE (up to 90 x MORB) and similar to GMB abundances for least incompatible elements; a negative anomaly in Nb is also observed. On diagrams discriminating geotectonic affinity (e.g. Meschede 1986, Cabanis, Lecolle 1989) the PMB fall in within-plate alkali basalts, while the GMB samples plot consistently within N-MORB field, however, quite often they spread on diagrams towards either E-MORB or within-plate tholeiitic basalt fields.

Despite the pronounced N-MORB signature, the GMB most probably were not derived by simple melting of depleted asthenospheric mantle. More likely, their source was more enriched than that for N-MORBs as it is evidenced by their REE and multi-element profiles. Moreover, ranges and variations of their incompatible trace element ratios (e.g. Ta/Yb, Zr/Nb, La/Yb) ratios may account for a slightly enriched (fertile) asthenospheric source which was subjected to moderate yet different degrees of partial melting (approx. 10-15%). Alternatively, a heterogeneous source in which depleted and enriched (non-depleted) components were mixing and melting produced the observed compositional features. It is also plausible that both factors, i.e. variable degrees of partial melting and source heterogeneity could have concordantly contributed to the magma composition. Conceivably, some geochemical characteristic of GMB might have been attributable to fractional crystallisation process which, however, is rather unlikely to produce such variations of trace element ratios as those apparent for GMB. If fractional crystallisation would actually be effective, then one would also expect systematic changes of REE concentration with Mg# coupled with exponential negative trends for Cr and Ni brought about by fractionation of olivine + clinopyroxene ± spinel assemblage, a feature lacking in the studied samples. On the other hand, the observed negative Nb anomaly and variation of Nb/U ratio could be result of assimilation-contamination process often associated with fractional crystallisation (e.g. De Paolo 1981).

Geochemical characteristic of PMB points to magma generation from enriched mantle source. High REE ratios [$(La/Yb)_{CN}$ up to 17, $(La/Sm)_{CN}$ up to 3.8] indicate particularly strong LREE enrichment which may stem from: crustal contamination, small degrees (<5%) of partial melting and/or enriched source (plume-related or metasomatised subcontinental lithospheric mantle) or very high degrees of fractional crystallisation. Crustal contamination process which undoubtedly affected PMB was not equally intensive in every case, since it failed to produce systematic and pronounced Nb(-Ta) negative anomaly. Furthermore, it is tentatively postulated that due to prominent fractionation of LREE over HREE and low Ta/La ratio low-degree partial melting of metasomatised mantle occurred. Metasomatic modification of the source could be linked to either previous introduction of subduction-derived component to the lithospheric mantle or its veining by silicate alkaline (OIB-like) melts rather than carbonatitic metasomatism. Unfortunately, at present state of study it is difficult to unambiguously discern effects of crustal contamination process imposed on magma composition from those of subduction-related metasomatism of the source. Alternatively, the enriched nature of PMB could be explained by derivation of magma from garnet-bearing asthenospheric enriched mantle.

CONCLUDING REMARKS

In conclusion it is hypothesised that the protolith for metabasites from the southern part of the Bystrzyckie Mts. was probably formed and emplaced in environment of progressively extending continental lithosphere. At earlier stage alkaline melts were generated at greater depths (ca. 60-70 km) from low-degree (<5%) melting of metasomatically modified subcontinental lithospheric mantle and emplaced at crustal levels forming dykes and veins what favoured various impact of contamination on the magma composition. It is not excluded altogether, that these magmas were originated in enriched (?plume-related) asthenosphere. During subsequent extension melts were generated at even shallower levels (< 55 km) in response to different degrees (up to 15%) of partial melting of heterogeneously depleted asthenospheric source. Although investigated rocks bear significant N-MORB signature, some crustal contamination effects are still detectable and therefore it is suggested that melts were generated beneath strongly thinned and attenuated lithosphere.

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MINERALOGIA POLONICA – SPECIAL PAPERS
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GEOCHEMICAL TYPES OF THE METAMORPHOSED IGNEOUS ROCKS IN THE LEPTYNITE-AMPHIBOLITE COMPLEX OF THE VEPORIC UNIT (WESTERN CARPATHIANS) AND THEIR GENETIC IMPLICATIONS.

Abstract: The leptynite-amphibolite complex (LAC) in the Veporic Unit of the Western Carpathians contains besides anatexites also multi-stage metamorphosed igneous rocks mostly basic in composition. Based on major and trace element distribution as well as mineral and petrographic characteristics following groups of metaigneous rocks have been identified: (1) retrogressed eclogites with OIB signature, (2) retrogressed eclogites and amphibolites close to IAT or N-MORB basalts, (3) gabbros/metagabbros with BABB signature, (4) leptynites close to tonalites/trondhjemites with VAG signature, (5) several types of nonconformable granitic mobilizates and (6) rocks of mixed origin formed probably by hydration crystallization mostly intermediate in composition. Entire complex of metaigneous rocks mentioned above was generated in suprasubduction setting as a part of the lower arc crust and was substantially modified by partial melting, rock/melt interactions and metamorphic alteration during its uplift.
Keywords: gabbros, basalts, tonalites/trondhjemites, metamorphism, melting, geochemistry, arc crust, Early Paleozoic, Western Carpathians

INTRODUCTION

The leptynite-amphibolite complex (LAC) is one of the main lithostratigraphic units of the Early Paleozoic of the Western Carpathians. LAC (sometimes also termed bimodal igneous complex) is supposed to be lower crustal in origin and was proposed as a probable candidate for the Western Carpathian Carboniferous granitoid rocks source. LAC is relatively common lithology in the western European Variscides as well as in the Alps (Hovorka et al. 1997).

GEOLOGY

LAC builds up mostly the northernmost part of the Veporic Unit in the contact with the Tatric Unit. Strong heterogeneity of the LAC is a result of its complex metamorphic evolution, partial melting and migmatitization. Various types of anatexites, massive amphibolites, banded amphibolites intercalated with leptynites as well as their retrogressed analogues as micaschists and phyllites are among the most widespread rock types. Retrogressed eclogites, metaultramafic rocks and gabbros/metagabbros occur as small enclaves up to several tens of meters in size. Aplite, leucogranite and pegmatite veins penetrate the entire rock complex.

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PETROGRAPHY

Only retrogressed eclogites, metaultramafic rocks, gabbros/metagabbros, massive and banded amphibolites as well as leptynites from the Veporic Unit LAC have been studied. Retrogressed eclogites are mainly composed of garnet and clinopyroxene-albite symplectite, variable content of amphibole and lesser amount of quartz, Fe-Ti oxides, clinozoisite and biotite are also present. Metaultramafic rocks contain olivine, orthopyroxene, apmhibole and lesser amounts of ilmenite, sulphides, chromspinelide, Al-spinel, chlorite and garnet. Two types of gabbros with preserved magmatic mineral assemblage have been found: (1) cumulative troctolite containing olivine, plagioclase, chromspinelide and in subordinate amount also pyroxene and ilmenite together with secondary amphiboles, orthopyroxene, Al-spinel, kyanite, clinozoisite, biotite and garnet typically with coronitic texture and (2) noritic gabbro composed of clinopyroxene, orthopyroxene and plagioclase, subordinary also of ilmenite in association with secondary amphiboles, biotite, magnetite and clinozoisite with characteristic gabbro-dolerite texture. Due to more intensive hydration both types of gabbro were transformed to various types of amphibolites. Mineral composition of massive and banded amphibolites is rather similar, amphiboles and plagioclases are predominant components, ilmenite, clinozoisite, biotite and sometime garnet are present in subordinate amounts. Some banded amphibolites are relatively felsic and continuous transitions seem to exist between banded amphibolites and leptynites by the rising of plagioclase content, even though such rocks occur rather rarely. Leptynites are fine-grained, mostly massive light colour rocks of quartz-plagioclase composition with low content of other minerals like amphibole, garnet, clinozoisite and ilmenite. Granulite-like texture with quartz ribbons is common. Migmatitization of these rocks results in K-feldspar and biotite formation and grain coarsening.

GEOCHEMISTRY

Major and trace element bulk analyses of 52 metamorphosed igneous rocks performed by ICP-OES and ICP-MS methods (ACME Analytical Laboratories Ltd., Canada) have been used to evaluate their original petrographic and geochemical types, fractionation and tectonic setting. We used mainly element ratios of elements relatively immobile during metamorphism (HFSE, REE, V, Cr, Ti) for interpretations, but the influence of potential mobility of these elements during migmatitization has been also taken into account. Retrogressed eclogites in the LAC of the Veporic Unit belong to two different geochemical types. First type is only related to the LAC segment northward of the village Heľpa and is represented by rocks of OIB (more precisely OIT) signature. Strong fractionation is typical – composition of rocks varies from basaltic to picritic. Metaultramafic rocks occurring in the same segment of the LAC were surprisingly identified as picritic marginal member. Composition of these rocks is matches the olivine-rich cumulates from OIT magmas. Enrichment in HFSE (Nb=11.7-27.6 ppm, Nb/Y=0.50-1.15) and selective LREE/HREE enrichment (sloped REE patterns- La_N=43.46-103.37, La_N/Yb_N=3.30-9.26; Fig. 1A) are typical for the retrogressed eclogites and metaultramafic rocks of OIB type. The second type of retrogressed eclogites (including products of their

further alteration – garnet amphibolites and some massive amphibolites) shows characteristics close to IAT (rarely also to
N-MORB). This type seems to be common in the entire Veporic LAC.

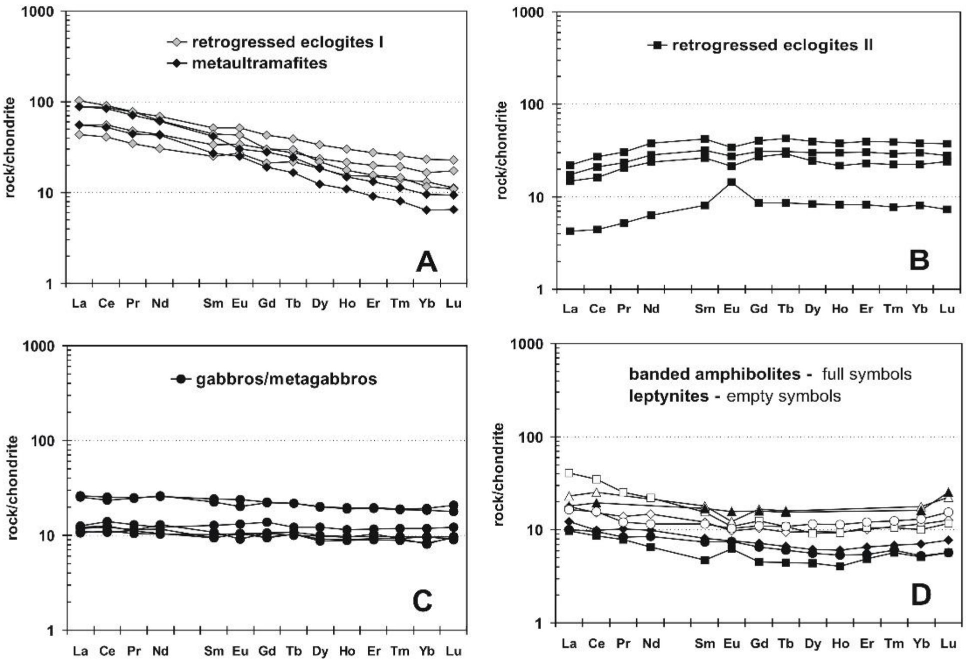

Fig. 1. Chondrite normalized REE patterns in the metaigneous rocks from the Veporic LAC

The protolith of the second type of retrogressed eclogites crystallized from the fractionated magmas characterized by deficiency of Nb and Ta (Nb=0.8-1.2 ppm, Nb/Y=0.03-0.12) and flat REE patterns with LREE depletion (La_N=4.21-23.63, La_N/Yb_N=0.52-0.94; Fig. 1B). Gabbros/metagabbros are geochemically similar to the BABB. They are also characterized by lack of Nb and Ta in comparison to N-MORB (Nb=1.5-2.0 ppm, Nb/Y=0.10-0.13) and their REE patters are flat without significant difference between troctolitic and noritic types (La_N=10.54-26.16, La_N/Yb_N=1.07-1.47; Fig. 1C). Leptynites can be characterized as trondhjemitic rocks with relatively low total REE content and flat patterns in some case with distinctive LREE enrichment (La_N=11.49-97.97, La_N/Yb_N=1.26-4.06, Tb_N/Yb_N= 0.82-1.09; Fig. 1D). Their REE patterns are very similar to the patterns of adjacent banded amphibolites. Some enrichment in total REE, locally in LREE and small deficit in Eu are the only differences. In the Ta-Nb or Rb-(Yb+Ta) discrimination diagrams by Pearce et al. (1984) leptynites are plotted the volcanic arc granite (VAG) field. Leptynites differ significantly from non-conform granitic mobilizates by absence of marked Eu-anomaly and strong LREE or selective LREE/HREE enrichments. At least three geochemical types of mobilizates have been discerned yet. Geochemical characteristics of some amphibolites and leptynites seem to be a mixture between original magmatic rock and mobilized acid melt compositions.

DISCUSSION AND CONCLUSIONS

Evolutionary history of the metamorphosed igneous rocks from the LAC of the Veporic Unit seems to be extremely complex. A part of these rocks have mostly preserved their original geochemical features and rarely also relics of magmatic minerals. Others were transformed during metamorphic evolution to the rocks of mixtured (migmatitic) origin. Enclaves of the basic magmatic rocks with OIB, N-MORB or primitive IAT signature which experienced eclogite facies peak metamorphism could be interpreted as relics of the formerly subducted oceanic crust. Gabbros/metagabbros, dolerites and related more evolved rocks geochemically close to BABB contain only relics of granulite-facies metamorphism and were probably generated as components of an arc-related lower crustal igneous complex. Several stages of fluid penetration, partial melting and metamorphism were related to the exhumation of this complex. Leptynites seem to be a product of one such stage, created by hydrous melting of basic igneous rocks. Some of mobilized partial melts interacted with additional magmatites transforming them by a process similar to that termed by Beard et al. (2004) as hydration crystallization. There are enough indications to assume that LAC of the Veporic Unit could be an analogue of arc-related lower crustal plutonic complexes as the Tanzawa plutonic complex in Japan (Kawate, Arima 1998).

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MINERALOGIA POLONICA – SPECIAL PAPERS
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GEOLOGY AND PETROLOGY OF THE TERTIARY BASALT FROM "RUTKI" NEAR NIEMODLIN (SW POLAND).

Abstract: Two types of volcanic rocks occur in the "Rutki" quarry: basalt and basanite. They form several separate lava flows. Both contain olivine which zonation suggests two stages of crystallization separated by resorption probably due to decompression during ascent and/or eruption.
Keywords: basalt, basanite, olivine and clinopyroxene composition

INTRODUCTION

Tertiary basaltoids outcropping in the active quarry „Rutki-Ligota" 6 km south-east from Niemodlin belong to Central European Volcanic Province (CEVP) trending from the Eifel in the west, through Germany, Czech Republic, Lower Silesia to Moravia in the east. The volcanic rocks overly Cretaceous marls and siltstones and are covered by younger Cenozoic sediments. Basaltoids from "Rutki-Ligota" were dated by K-Ar method on 27.5 Ma (late Oligocene, Birkenmajer, Pécskay 2002).

The "Rutki-Ligota" quarry is divided into two separate parts: "Rutki" in the north - east and "Ligota" in the south - west. In this abstract we describe field relationships, petrography and mineral composition of basaltoids from the "Rutki" quarry. Mineral compositions were measured by microprobe at the Institute of Mineralogy, University of Hannover (Germany) and Geological Institute in Copenhage.

FIELD RELATIONSHIPS, PETROLOGY AND MINERAL COMPOSITION

Mapping of the „Rutki" quarry was done on basis of seventy three samples (Fig. 1). Two types of volcanic rocks occur in the "Rutki" quarry: basalt and basanite. Basalt dominates, whereas basanite occurs only in central part of the quarry. Two types of basalt occur:

1) basalt with large (up to 200 μm) plagioclase laths in the groundmass and,
2) basalt with only subhedral plagioclase in the groundmass.

These two types form separate exposures in the „Rutki" quarry (Fig. 1). Otherwise basalts are similar to each other and characterized by porphyric and glomerophyric texture with olivine (200 μm – 4 mm) and clinopyroxene porphyrocrysts (200 μm – 1mm) and clinopyroxene glomerocrysts. Olivine porphyrocrysts are often characterized by embayed surfaces. The groundmass is composed of olivine, clinopyroxene, plagioclase, Fe-Ti oxides and apatite. It is characterized by occurrence of oval to strongly flattened, sometimes vesicular

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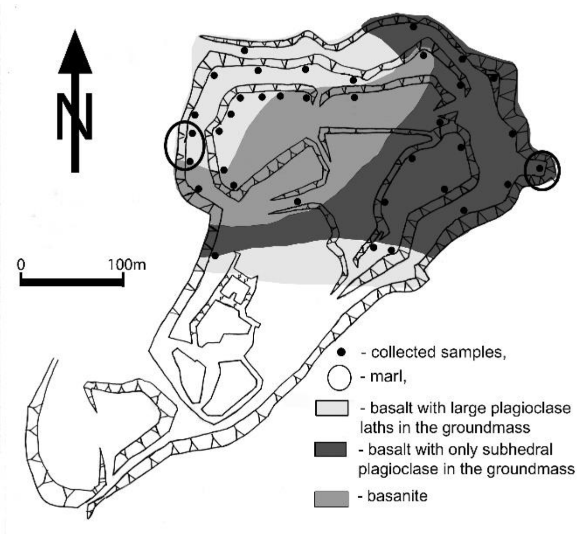

Fig. 1. Rock kinds in the „Rutki" quarry.

domains that are finer-grained than the surrounding groundmass. The size of porphyrocrysts inside the domains is similar to that outside.

Basanite is porphyritic and contains only olivine porphyrocrysts (300 μm – 2 mm). Olivine margins are strongly porous. The groundmass is composed of olivine, clinopyroxene, plagioclase, nepheline, analcite, Fe-Ti oxides and apatite.

Plagioclase, nepheline and analcite occur as large (up to a few mm), irregular poikilocrysts enclosing much smaller grains of olivine and clinopyroxene.

MINERAL COMPOSITION

Basalt: Cores of olivine phenocrysts have higher forsterite (Fo 86-87%), Ni (1900-2700 ppm) and lower Ca contents (800-1100 ppm) than rims (75-78 %, 600-1900 ppm and 1900-3000 ppm respectively). The rims composition partially overlaps with the composition of olivine from groundmass which has 63-80% of forsterite, 300-1600 ppm of Ni and 2700-5200 ppm of Ca (Fig. 2a,b).

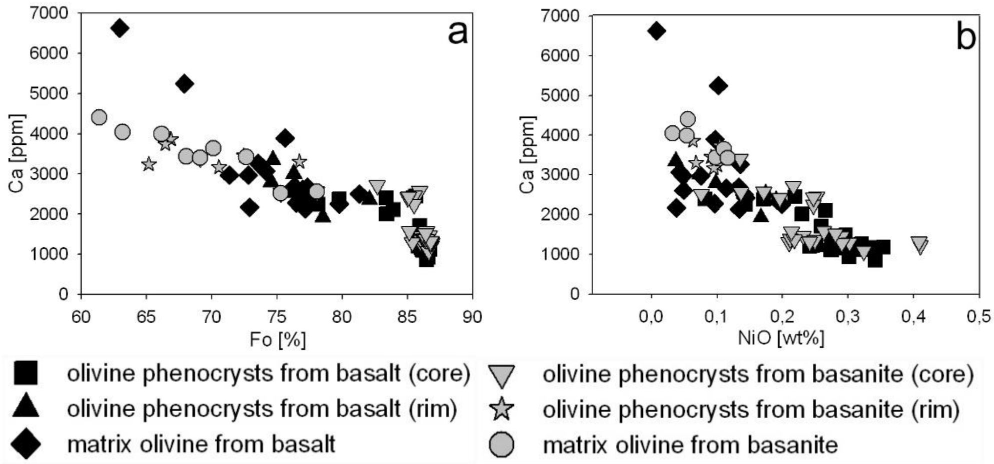

Fig. 2. Relationships between Fo (forsterite) to Ca in olivine (a) and NiO to Ca in olivine (b).

Pyroxene phenocrysts have the composition of Na – diopside (Fig. 3). Mg/(Mg+Fe) ratio varies from 0.79 to 0.84 between zones, T i concentrations from 0.04 to 0.05 a pfu and Al from 0.14 to 0.19 a pfu. Ca varies from 0.91 to 0.93 and Cr is always below 0.03 a pfu. The groundmass pyroxene is characterized by lower Mg/(Mg+Fe) ratios (0.68–083), lower Cr content (always below 0.02 a pfu) and higher Al (0.16-0.48 a pfu) and Ti content (0.04-0.13 apfu) relative to that forming phenocrysts. Anorthite content decreases from An_{50-64} in the cores to An_{29-48} in the rims of plagioclase grains.

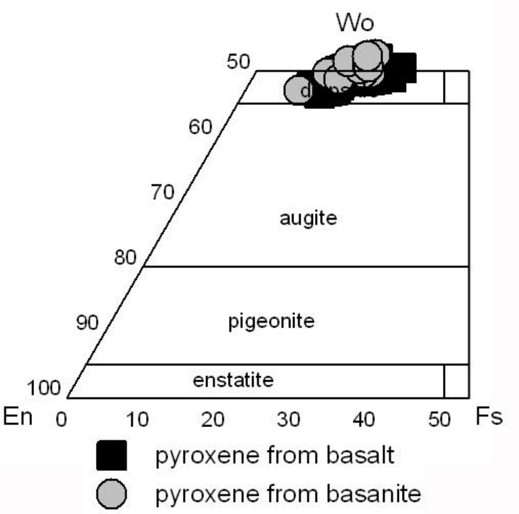

Fig. 3. Pyroxenes from basalt and basanite in the diagram of Morimoto (1989).

Basanite: Cores of olivine phenocrysts have higher forsterite (85-87%), Ni (1300-3200 ppm) and lower Ca contents (1200-2700 ppm) than rims (65-77%, 500-800 ppm and 3200-4300 ppm respectively). The rims composition partially overlaps with the composition of olivine from groundmass which has 61-73% of forsterite, 300-900 ppm of Ni and 3400-4400 ppm of Ca (Fig. 2a,b). Therefore, most of the olivine composition in basanite is similar to that in basaltic olivine. Only rims of phenocrysts in basanite have much lower Fo and Ni and higher Ca contents than those of olivine phenocrysts in basalt.

Mg/(Mg+Fe) ratios in pyroxene ranges from 0.69 to 0.81, Ti are 0.01-0.14 a pfu, Al – 0.03-0.46 a pfu, Ca – 0.92-0.93 a pfu and Cr below 0.02 a pfu. Therefore, Mg/(Mg+Fe), Ca and Cr values are similar in basaltic and basanitic pyroxene, whereas Ti and Al yield much lower minimum values in basanite.

Plagioclase occur in basanites as anhedral, amoeboidal grains containing 8 to 43% of anorthite.

CONCLUSIONS

1) Two types of volcanic rocks occur in the „Rutki" quarry: basalt and basanite with basalt dominating. This differs from the previous study of Birkenmajer & Siemiątkowski (1977) who distinguished only melabasanite and Wojno et al. (1957) who distinguished basanite and nephelinite.

2) Vesicular oval domains occurring in the basalt maybe remnants of outer crust of lava flow which cooled right after reaching Earth's surface. Fragments of the crust were cracked during flux of lava and reincorporated into the flow.

3) The different textures on basalt and basanite as where as differences in mineral composition suggest that both the rocks have had different pre and post eruption histories.

4) Low contents of Fo and Ni in olivine phenocrysts suggest that they are magmatic minerals not restites incorporated after mantle melting (Pearson et al. 2003; Cvetkovič et al. 2004).
5) Zonation and resorption in olivine phenocrysts suggest that they crystallized in two stages. The first stage probably took place at deep levels where homogenous olivine cores crystallized rich in Fo and NiO as well as pyroxene cores with high Mg/(Mg+Fe) ratios and low in Ti, Al and Na. The second stage is related to an abrupt magmas ascent when olivine phenocrysts were resorbed due to decompression (Nelson, Montana 1992) or spongy rims were developed on basanite olivines. Pyroxene records rapid cooling. Oscillatory and sector zoned mantles crystallized during magma ascent and final crystallization.

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MINERALOGIA POLONICA – SPECIAL PAPERS
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THE MĘCINKA BASALT (SW POLAND)

Abstract: The basalt occurring in Męcinka near Jawor (Lower Silesia, SW Poland, Tertiary Central European Volcanic Province) consists of olivine ± clinopyroxene phenocrysts embedded in plagioclase – clinopyroxene – Ti magnetite/ilmenite matrix. Five types of the rock can be distinguished in the basis of presence/absence of clinopyroxene phenocrysts and degree of red coloration of olivine phenocrysts. Variation in chemical composition of olivine indicates various conditions of crystallization in lava flow. The chemical composition of matrix minerals is very similar to that from Winna Góra basaltic plug located few kilometres from the Męcinka. Both basalts come probably from the same source.
Keywords: Basalt, mineral chemistry, Jawor, SW Poland

INTRODUCTION

Lower Silesian Formation of Cenozoic basalts is the easternmost part of the central European Volcanic Province (CEVP) extending from the Eifel Mts. in Germany through the Czech Republic to Lower Silesia and Opole Region in Poland. The Province consists of large separated fields and groupings of smaller intrusions (pipes, necks, flows, veins; Ladenberger et al. 2006). Volcanic activity in Lower Silesia begun at the turn of Eocene and Oligocene (33.4 Ma) and lasted up to early Miocene (18.5 Ma). Alkali basalts, basanites and nephelinites are most common and potassic lavas do not occur in Lower Silesia.

The remnants of one of the volcanic centres are located near Jawor in Lower Silesia. Two active quarries (Męcinka and Winna Gora) enable access to unaltered rocks here. The basalts occurring in Męcinka are described in this abstract and their relationship to the neighbouring basalts from the Winna Góra is discussed.

GEOLOGY, PETROGRAPHY AND MINERAL CHEMISTRY

Basalt occurrences in the vicinity of Jawor form volcanic plug, lava flows and dikes (Wierzchołowski 1993). The lava flow is exposed in the Męcinka quarry (6 km NW from Jawor) and volcanic plug in the Winna Góra (4 km to W from Jawor).The thickness of basaltic plate reaches 80 m in Męcinka. The plate is overlain and interbedded by tuffs (Jerzmański, 1956). Birkenmajer et al. (2002) classified those rocks as basanite and determined their age (K – Ar) to be 18.66 ± 0.82 Ma and 21.05 ± 0.85 Ma (Męcinka) and 21.62 ± 0.93 Ma and 21.96 ± 1.36 Ma (Winna Góra, the second phase of volcanic activity). Since the rock consists of plagioclase, pyroxene, olivine, Ti - magnetite and ilmenite, we use the term “basalt” in the following.

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The basalt occurring in Męcinka is light- to dark-gray, aphanitic with phenocrysts of olivine and pyroxene up to 4 mm across. The variation of the rock is due to presence/absence of pyroxene phenocrysts and degree of red coloration of olivine phenocrysts (Fig. 1) as well as due to textures and size of the phenocrysts.

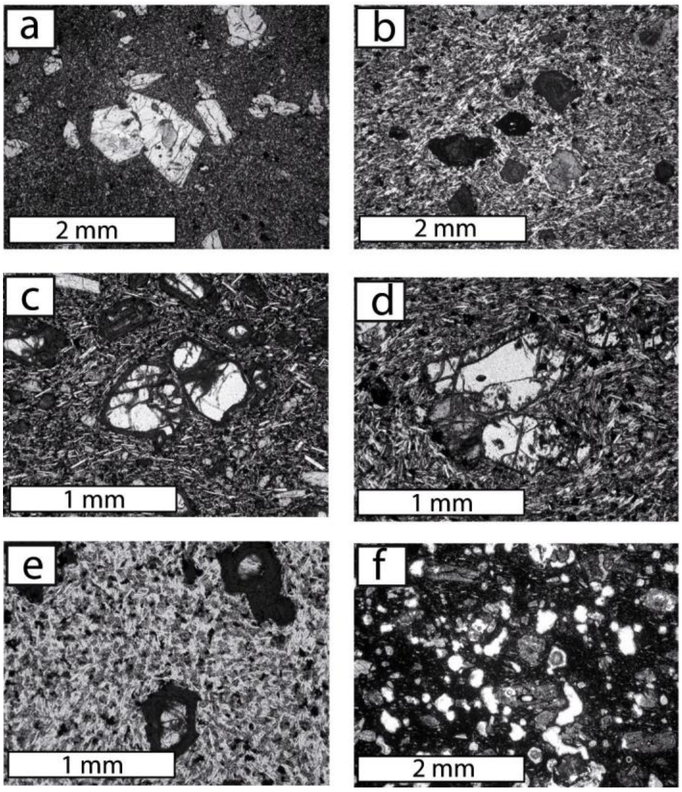

Fig. 1. Textural groups of the Męcinka basalt: a - group 1 (with fresh olivine phenocrysts, one polar), b - group 2 (with completely reddisch olivine phenocrysts, crossed polars), c - group 3 (with reddish rims on the olivine phenocrysts, one polar), d - group 4 (with reddisch cracks in olivine phenocrysts, crossed polars), e - group 5 (with reddisch olivine phenocrysts with fresh cores, one polar), f - tuff, one polar.

Mineral compositions have been studied in two varieties containing no (group 1) or little (group 4) decomposed and coloured olivine phenocrysts.

Plagioclase occurs in groundmass as elongated laths, fluidally arranged around olivine phenocrysts. It is zoned from 40 – 64 % of anorthite in cores to 17 – 38 % in margins (Fig. 2a). Pyroxene forms subhedral crystals of the composition of aluminian diopside, Mg/(Mg+Fe) varies from 0.70 to 0.79 (Fig. 2b).

Two opaque minerals occur in the Męcinka basalt: spinel and ilmenite. The former occurs in groundmass as well as in inclusions in olivine phenocrysts. Average matrix spinel composition is $Fe^{3+}_{0.87}Fe^{2+}_{1.24}Ti_{0.50}Mg_{0.23}Al_{0.11}Mn_{0.02}Cr_{0.01}O_4$ (Ti-magnetite) and that of spinel from olivine phenocrysts is $Fe^{+3}_{1.06}Fe^{+2}_{0.86}Ti_{0.08}Mg_{0.21}Al_{0.26}Mn_{0.02}Cr_{0.51}O_4$ (Cr-magnetite). Ilmenite (average composition $Fe^{3+}_{0.13}Fe^{2+}_{0.68}Ti_{0.93}Mg_{0.24}Mn_{0.01}O_3$) forms subhedral crystals embedded in groundmass.

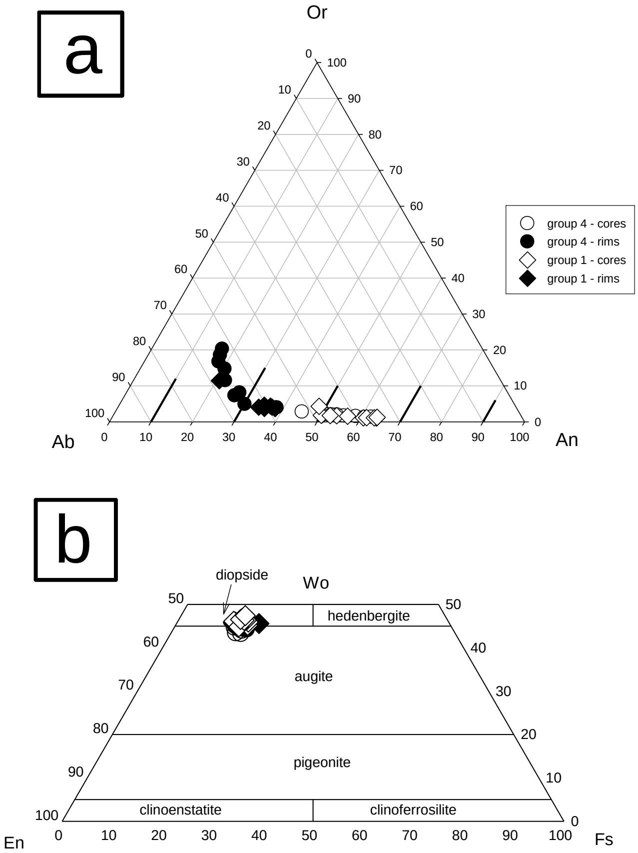

Fig. 2 Chemical composition of (a) plagioclase and pyroxene (b).

Two types of olivine phenocrysts occur: homogeneous and zoned. The homogeneous ones typically contain 77 – 78 % of Fo in group 1 and 69 - 70 % in group 4 of basalt. The zoned crystals typically contain 83 % of Fo in cores and 79 % in margins (group 1) and 73 % of Fo in cores to 71 % in margins (group 4).

CONCLUSIVE REMARKS

The Męcinka quarry exposes the lava flow consisting of a nepheline–free basalt. About 3 km to the S of Męcinka the Winna Góra basalt quarry is located. The age of rocks forming both the outcrops is slightly different (0.5 – 1.0 Ma). The chemical compositions of minerals forming groundmass of the Winna Góra (plagioclase 65 → 20 % anorthite, clinopyroxene of the Al-diopside composition, Ti-magnetite, ilmenite; Matusiak 2006) are similar to those forming the groundmass of the

Męcinka basalt. The basalt from Winna Góra hosts mafic and ultramafic enclaves and plagioclase megacrysts, which do not occur in Męcinka. No enclaves or megacrysts occur in Męcinka. Similar groundmass composition, small age difference and small distance between two basalts occurrences suggest, that they come from one magma chamber, but originated at different parts of it and/or erupted during different stages of activity of the volcano.

The chemical composition of olivine phenocrysts in the Męcinka basalt suggests that the cores of zoned crystals (73 and 83 % Fo in group 1 and 4, respectively) were formed first in Męcinka. In the second stage rims of zoned olivine and homogeneous grains crystallized (78 and 70 % Fo in group 1 and 4, respectively). Differences in chemical composition of olivine suggests various conditions of crystallization.

Acknowledgments. We are grateful to the "Męcinka" quarry head for the help during field works and providing information about the geology of the basalt deposit. The study was financed by the Institute of Geological Sciences, University of Wrocław project 2022/W/ING-31 to J. Puziewicz. The comments of prof. J. Puziewicz greatly improved the final version of the text.

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MINERALOGIA POLONICA – SPECIAL PAPERS
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HYDROTHERMAL AND WEATHERING PROCESSES IN THE KARKONOSZE GRANITE FROM STRACONKA HILL (JELENIA GÓRA BASIN, POLAND)

Abstract: The excavation in Straconka hill at Miłków village (about 10 km S from Jelenia Góra) is one of the biggest outcrops of grusified granite in Jelenia Góra basin. Three types of hydrothermally altered granites were distinguished. Granite subjected to grusification (arenitization) is poor in chemical weathering related minerals. Grus (arenite) is a product of alteration of rocks characterized by presence of epidote, titanite, ilmenite, scheelite, fluorite, Fe-chlorite and absence of Mg-chlorite. Other rocks contain rutile as a main Ti mineral, Fe- and Mg-chlorite and are devoid of epidote and other Ca minerals. Hydrothermal alterations are important in grusification.
Keywords: Karkonosze granite, mineralogy, hydrothermal alteration, weathering processes

INTRODUCTION

The outcrop at Miłków is situated on the N-W slope of the Straconka hill (Fig. 1). The excavation is about 100 m long and to 6 m high (Migoń, August 2000). The porphyritic Karkonosze granite at different stages of weathering is exposed (from unweathered hard rock to arenite with core-stones). The aim of the study was to determine minerals and chemical composition of rocks in relation to different stages of weathering.

METHODS

Nine samples from the outcrop were studied. Optical microscopy (transmitted light) and cold field emission scanning electron microscope (FESEM) Hitachi S-4700 coupled with energy dispersive spectrometer (EDS) NORAN Vantage at the Institute of Geological Sciences of the Jagiellonian University were used. Bulk rock chemical analysis were performed at the Acme Analytical Laboratories Ltd. Vancouver, Canada by use of ICP-AES (for major elements) and ICP-MS (for trace elements).

RESULTS

Three working groups of samples were distinguished. Granites which belong to group I macroscopically are characterized by presence of white feldspars (phenocrysts and groundmass crystals) and black biotite. In the group II the feldspars are apple-green (groundmass crystals) and pink (K-feldspar pheno-crysts) and biotite

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is black with greenish tint. In granites of the III group (which form enclaves in granites of group the II) primary feldspar pheno-crysts are altered to dark green phyllosilicate aggregates. Samples of group I and II represent different weathering stages.

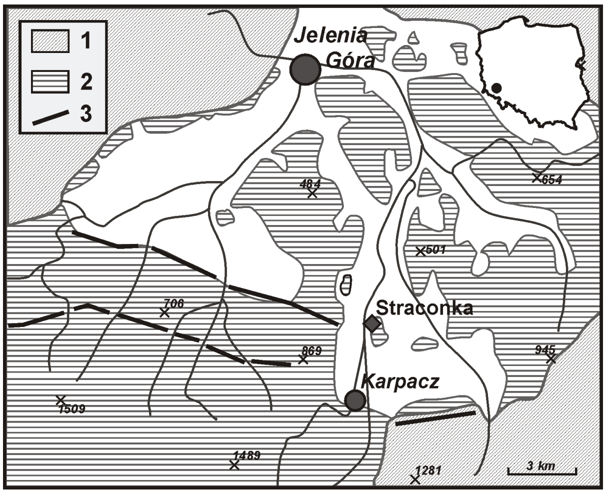

Fig. 1. Simplified geological sketch map of the Jelenia Góra Basin (after Migoń, August 2000, modified). 1. metamorphic rocks; 2. Karkonosze granite; 3. faults; diamond – Straconka hill.

Chemically granites of the group I are richer in CaO (Fig. 2) in comparison to the other groups. Higher content of calcium results in more An rich plagioclase (Fig. 3): the group I besides K-feldspar contains plagioclases from albite to andesine (0 mol% - 35 mol% An), plagioclases of the group II granite mainly albite to oligoclase (0 mol% - 11 mol% An). The group III granite contains only very pure albite (99%-100% Ab) and no K-feldspars.

Chemical analyses of phyllosilicates (Fig. 4) indicate, that biotite (beetwen annite and siderophyllite) was found only in granites of the group I. In the rocks of the groups II and III micas are present only as a white mica (connected with process of sericitization of feldspars). High values of A' in Fig. 4 can be interpreted as result of weathering process (initial kaolinite formation). Chlorite in the studied granites represents two main groups – more ferric (ripidolite – pycnochlorite – brunsvigite) and more magnesian (clinochlore – penninite). In the group I the Mg-chlorites do not occur.

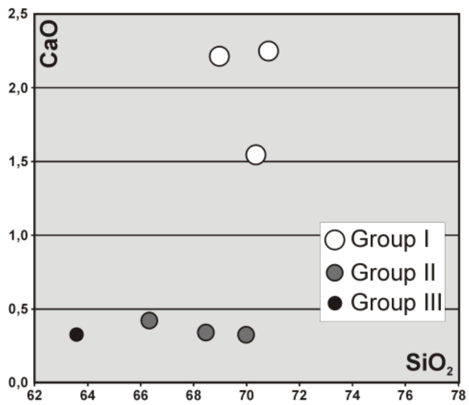

Fig. 2. Harker-type variation diagram CaO – SiO_2 for the granites from Straconka hill (Jelenia Góra Basin).

Titanite, as the main Ti-bearing mineral (Fig. 5), and minerals from the epidote group (and scarce scheelite and fluorite) are present in granites of I group what is connected with higher content of CaO.

Samples of both the group I and the group II differ macroscopically in stage of weathering from fresh rock, to slightly weathered and intensely weathered. In

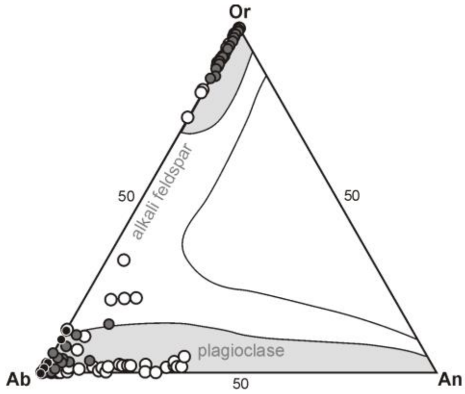

Fig. 3. Feldspars classification for Straconka hill granites; symbols as on Fig. 2.

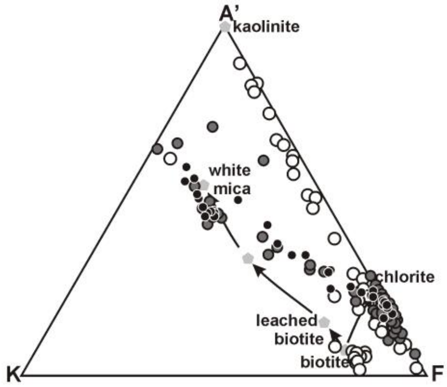

Fig. 4. A'KF diagram (molecular proportions) for phyllosilicates of Straconka hill; symbols as on Fig. 2 (after Almond et al. 1997, modified).

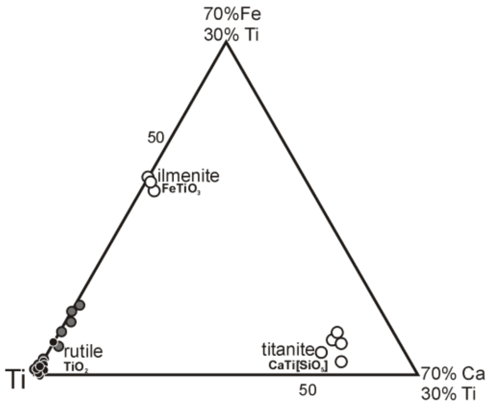

Fig. 5. Variety of Ti-bearing minerals in Straconka hill granites dependent of CaO content; symbols as on Fig. 2.

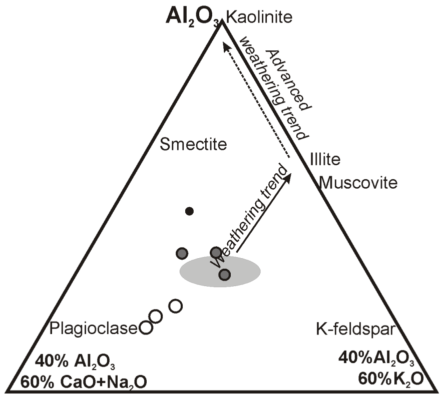

Fig. 6. A-CN-K ternary diagram for samples of the Straconka hill granite, symbols as on Fig. 2; gray field – average Karkonosze granite (after Rollinson 1993; modified).

both cases the more weathered rock the more rusty colour of sample and the lower hardness of the rock (sample Str-5, the most weathered of group I is in fact the grus) occur. Despite considerable difference in weathering stage of rocks, the mineralogical and chemical changes are rather low (Fig. 6).

CONCLUSIONS

Biotite chloritization, sericitization of feldspars, albitization, crystallization of secondary titanite and epidote, quartz veins formation point out importance of hydrothermal processes.

Granite subjected to grusification (arenitization) is poor in minerals considered to be a product of chemical weathering. Content of kaolinite in weathered granite is very low. Although all granite samples are hydrothermally altered, it is possible to notice differences in hydrothermal minerals assemblages in samples representing the groups I and II (the group III is similar to II in this respect). Grus (arenite) is a final product of alteration of the group I rocks characterized by presence of epidote, titanite, ilmenite, scheelite, fluorite, Fe-chlorite and absence of Mg-chlorite. Rocks of the groups II and III contain Fe- and Mg-chlorite, and rutile as a main Ti mineral, and are devoid of epidote and other Ca minerals. Hydrothermal alterations are important in grusification. This conclusion is in agreement with results of Evans and Bothner (1993).

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MINERALOGIA POLONICA – SPECIAL PAPERS
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MINERAL ASSOCIATION OF NODULES FROM IRON METEORITES SEELÄSGEN, MORASKO AND JANKOWO DOLNE

Abstract: Iron meteorites (IIICD or IAB type) are being found in areas of Morasko, Przełazy (Seeläsgen) and Jankowo Dolne. Comparison of mineral composition of nodule filler show exceptional resemblance within them. Phases of copper, sulphides, silicates, oxides and phosphates are identical practically under the account of chemistry. It allow to state with the big probability that meteorites are coming from one fall.
Keywords: iron meteorite, Morasko, Seeläsgen, Jankowo Dolne, nodules, mineral associations.

INTRODUCTION

Iron meteorites (IIICD or IAB type) of Morasko, Seeläsgen (Przełazy) and Jankowo Dolne are characterized by very big mineralogical resemblance. Their places of finds are found practically on one line over a distance area of about 170 km. There is a big probability that they are coming from the same fall. Mineral composition of main mass of these meteorites is similar. Principal minerals are diversified size crystals of kamacite, taenite with changeable contents of schreibersite and cohenite. Taenite is also accompanying by small amounts of tetrataenite (Dziel et al. 2007). Relatively rare in kamacite matrix accompanying by schreibersite occur sphalerite, troilite, altaite and small spherical graphite. Characteristic feature of iron meteorites of IAB and IIICD types are nodule of troilite-graphite containing silicates and phosphates. Silicates in them are being tied genetically with the unique group of meteorites – winionaites (Clayton, Mayeda 1996; Benedix et al. 1998, 2000; Karwowski, Muszyński 2006). In that paper authors focused their attention on mineral associations occurred in troilite-graphite nodules. The part concerning mainly results of pyroxenes study was presented earlier (Karwowski, Muszyński 2006).

SAMPLES AND ANALYLICAL METHODS

Samples were taken out from cut fragments of meteorites, which contain nodules, coming from the Morasko area, Przełazy and Jankowo Dolne (collection of Institute of Geology, Adam Mickiewicz University, collection of Faculty of Earth Sciences, University of Silesia and other collector specimens). Examinations were being made

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on polished slabs using an ore microscope. The main part of examinations was being led using a CAMECA SX 100 electron microscope in the Interinstitutional Laboratory of Microanalysis of Minerals and Synthetic Substances at the Faculty of Geology, Warsaw University.

RESULTS AND DISCUSION

Main mineral components of graphite-troilite nodule are graphite and troilite, which is acompany by considerable amounts of pyrrhotite (Dziel et al. 2007). Nodules rim are usually creating by a different thickness layer of cohenite-schreibersite. Schreibersite is poorer in Ni content with comparison to fine-grained variety – rhabdite, dispersed in kamacite. Quite frequent mineral is sphalerite, occurring in two forms. One forming big grains, containing from 19 to 20 at % of Fe and 0.3-4.0 at % of Mn, often containing small grains of secreting iron sulphide arranged along crystallographic directions and second poorer in Fe (~6 at %.) and Mn, creating small grains in rim parties of nodules.

Another common mineral in nodules is daubreelite, which form a microscopic, lengthened grains in iron sulphide or creating secretion grains in the association with troilite and graphite. Sometimes daubreelite is going together with sphalerite. During observation under BSE such sphalerite were a little bit brighter than daubreelites crystallizing in the distance from sphalerite. Under an ore microscopy differences in the colour and shades were not noticed in daubreelites. Systematic examinations permitted to find out also a Zn-bearing daubreelite (to 7.02 at % of Zn) which is a bridge to the isomorphic row of tiospinels daubreelite-kalininite ($FeCr_2S_4$ – $ZnCr_2S_4$).

There is relatively rare mineral in nodules which visual properties and chemical composition is close to djerfisherite ($K_6Na(Fe,Cu,Ni)_{25}S_6Cl$). It is diverging from the theoretical pattern a little bit with the K and S excess and with the additive of Co up to 1% at. and with deficiency of Na. It was indicated on the edge of nodules in the association of iron sulphide together with some bearing Ni unidentified sulphide phases, cohenite and schreibersite (Fig.1.).

Relatively often in the nodules there is copper which is creating small grains or inclusions in schreibersite or sphalerite. It usually contains distinct additive of Fe ~ 2 at. % and of Ni ~0.4 at %.

Practically, very common mineral in nodules is spinel represented by a typical chromite with little Mn additive and Zn, poor in Al. Ratio of Cr/(Cr+Al) is of range 98.23 – 100.00. Two kinds of chromite can be noticed which differs in Mg ratio (Fe+Mn)/Fe+Mn+Mg) contents - for poor ones Mg is 93-80, for richer Mg is 50-64. Chromite is co-occuring practically with the majority of minerals met in the whole nodules. It often forms automofphic grains, which sometime are strongly cracked.

A unique mineral in nodules is altaite (PbTe) occurring in the rim parties of nodules in the company of schreibersite and cohenite (Fig.2.) It was also recorded in iron matrix together with sphalerite and schreibersite. The uniqueness of this mineral relies on the fact that it was confirmed in meteorites for the first time. It contains distinct Zn additive (1-2 at %) and slight Sb admixture (~ 0.3 at %).

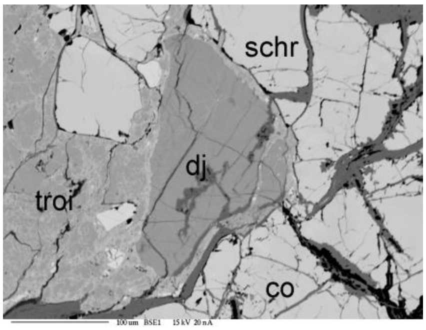

Fig. 1. BSE image of Djerfisherite (dj) surrounding by triolite (troi), schreibersite (schr) and cohenite (co). Morasko meteorite.

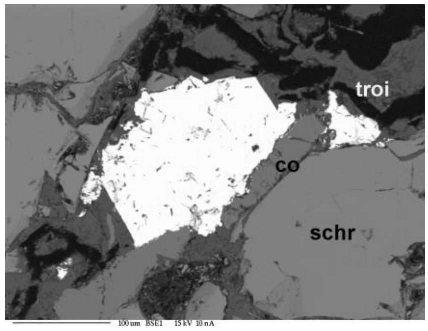

Fig. 2. BSE image of altaite (white) in the midst of cohenite (co), schreibersite (schr) and troilite (troi).

Titanium oxide – most probably rutile – is noticed only in graphite-troilite nodules, which are enriched in silicates and phosphates. It occurs as a xenomorphic grains intertgrowing with troilite and graphite and more rarely around silicates and phosphates. It contains distinct Cr additive (~0.24at %), Nb (0.27-0.29 at %.) and Fe (0.13-0.19 at %).

From all known silicate minerals in the nodules especially pyroxenes were presented by Karwowski & Muszyński (2006). Three main types were distinguished among them: I – Ca-Mg-Fe2+-pyroxenes (Quad); II – Ca-Na-pyroxenes and III – Na-pyroxenes (Karwowski & Muszyński 2006). The remained silicates are being represented by the unidentified silica (co-occurring with pyroxenes: enstatite as well as kosmochlor) and by feldspars: antiperthite and orthoclase. Albite is poor with the orthoclase molecule (3.75 – 4.31%) but perthitic orthoclase contains of 2.43 – 3.14 % albite molecule. Orthoclase occurs also as separate grains rich in the albite molecule (~9.5%). Both feldspars contain graphite and troilite inclusions. They rarely intergrown with pyroxenes or with phosphates.

Quite rare in nodules is olivine. It is not traced together which the association of other silicates. Some isolated grains are stuck in surrounding troilite. Olivine is typical forsterite which composition is: *mo*: 0.00; *fo*: 96,09-95.03; *fa*:4.86-3.80; *li*: 0.00-0.04; *te*: 0.12. His position among silicates is not yet clear.

Silicate phases (pyroxenes and feldspars) are often accompanied by phosphates. Till now only whitlockite has been identified (Dominik 1976). Author's research permitted to discover a few new phosphate phases. The most frequent is buchwaldite ($NaCaPO_4$), which is accompanying by brianite ($Na_2CaMg[PO_4]_2$). Together with the association of buchwaldite and brianite, some unidentified phosphate phases are noticed, which formulas are: Na_2MgPO_4 and $Na(Ca_{0.75}Mg_{0.25})PO_4$. Nodules built up in the majority by phosphides do not have the distinct schreibersite-cohenite rim.

Rarely fluoroapatite can be traced in form of very small inclusions most often in chromite. Some of phosphate phases are clearly secondarily hydrated; their mineralogical identification is difficult because of too small grain size.

CONCLUSIONS

Mineral compositions of nodule filler in Morasko, Seeläsgen and Jankowo Dolne meteorites show exceptional resemblance within them. In the examined meteorite nodules identical minerals were noticed which represent native elements, sulphides, tellurides, silicates and oxides. Only djerfisherite and rutile was found in Morasko meteorite nodules. The probability of founding such phases in Seeläsgen and Jankowo Dolne meteorites is very small from because of the scarce population of accessible material for examinations. Attention should be given to the presence of altaite in meteorites from explored areas which is a carrier of considerable Pb and Sb amounts. Tellurium and antimony are elements rather in trace amounts in meteoritic material.

Big resemblance of mineral composition of nodule filler in examined meteorites and their linear pattern in the field allow authors to state that examined meteorites most probably come from one fall.

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MINERALOGIA POLONICA – SPECIAL PAPERS
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THE INFLUENCE OF COOLING CONDITION ON MINERAL AND CHEMICAL COMPOSITION OF FRESH SLAG

Abstract: The composition of fresh slag is not different from stabilized one. Both varieties contain minerals of melilite group, larnite, wollastonite, merwinite, perovskite, anorthoclase, metallic Fe, Al-Mg alloys, Si, Ti, Zr, Fe and Al oxides. Usually they contain high amount of sulphur (MnS, CaS, but also various silicate and aluminosilicate contain ca. 4 wt % of this element). Geochemical data indicate that analyzed slag samples have almost similar chemical composition. Fresh slag samples contain similar amounts of harmful elements (Co, Cu, Zn, Pb, Ni, As, Cr). However diffusion of main elements did not occur, the amount of harmful elements is lower in outer glassy layer of the slag. Different cooling rate caused changes in crystallization conditions and appearance of different mineral assemblages in glassy layer and typical porous slag.
Keywords: fresh slag, cooling processes, mineral and chemical composition

INTRODUCTION

The mineral and chemical composition and weathering behavior of slag has been well recognized in many studies, but the composition and behavior of fresh, not stabilized slag has never been studied.

The aim of this study was to determine the influence of cooling conditions on chemical and mineral composition of fresh blast furnace slag taken from the slag-spout about 1.5 hour after heat of pig iron.

SAMPLES AND METHODS

Fresh slag samples were collected from the slag-spout about 1.5 hour after heat of pig iron. They did not subjected to stabilization and weathering processes on a heap that usually cause significant changes in composition and structure of slag but also can cause the release of harmful components into environment. For this study the most representative slag sample (with visible changes in structure) were used.

Slag was analyzed using various analytical methods: optical microscopy, X-ray diffraction (Philips X'Pert APD type diffractometer with a vertical PW 3020 goniometer; Cu Kα radiation monochromatised using curved graphite crystal monochromator) and field emission scanning electron microscopy with energy dispersive spectrometry (FE-SEM; Hitachi S-4700 and EDS; Noran Vantage).

Chemical analyses were made in ACME ANALYTICAL LABORATORIES (Vancouver) using ICP-ES (main elements) and ICP-MS (trace elements) methods.

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RESULTS

Macroscopically fresh slag is different than those on heaps. It is heterogeneous with dark yellow glassy upper outer layer (WP1-b) (ca 1 cm thick) with irregular cracks and grey lower (inner) layer with numerous small voids (WP1-a) (Fig. 1). Porous structure that is typical of blast furnace slag was observed near cracks in glassy layer. Analyzed slag is composed mostly of calcium silicates and calcium aluminosilicates (Fig. 5). Matrix of slag (both in outer layer and in internal part) is usually composed of melilite group minerals ($(Ca,Na)_2(Al,Mg,Fe)(Si,Al)_2O_7$) with variable amount of MgO and Al_2O_3. Melilite minerals are mostly rich in gehlenite end-member (Kasina, Michalik 2007).

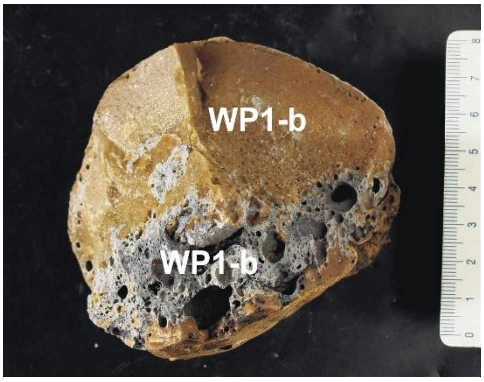

Fig. 1. Macroscopical view of fresh slag. WP1-a – inner layer, WP1-b – outer layer.

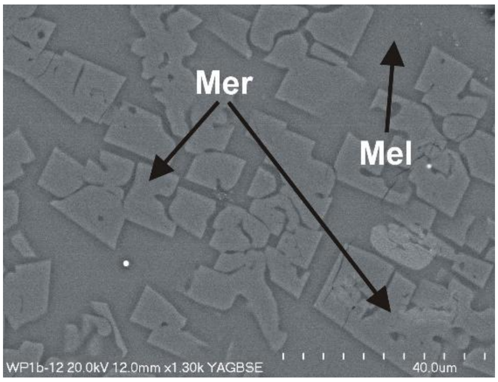

Fig. 2. Inner part of fresh slag sample. Mer - merwinite, Mel - melilite. SEM-BSE image.

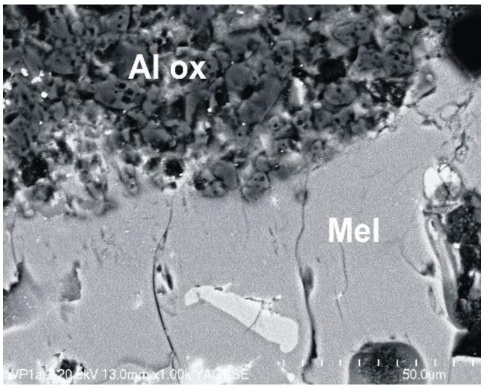

Fig. 3. Boundary between glassy layer and inner part of slag. Al ox – Al oxides, Mel – melilite. SEM-BSE image.

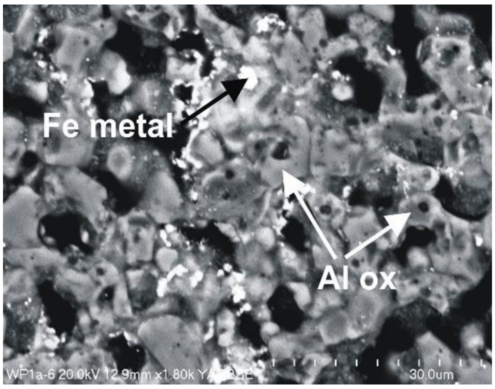

Fig. 4. Typical part of glassy layer. Fe metal – metallic iron, Al ox – Al oxides. SEM-BSE image.

Components present in melilite matrix of lower part of slag are: larnite which represents probably unstable alpha-phase (Ca_2SiO_4), wollastonite ($CaSiO_3$) and merwinite ($Ca_3Mg(SiO_4)_2$). Gradual decrease of MgO content and increase of CaO is observed in merwinite. Metallic Fe, Al-Mg alloys, Ti and Al oxides were determined as subordinate components (Fig. 2, 3).

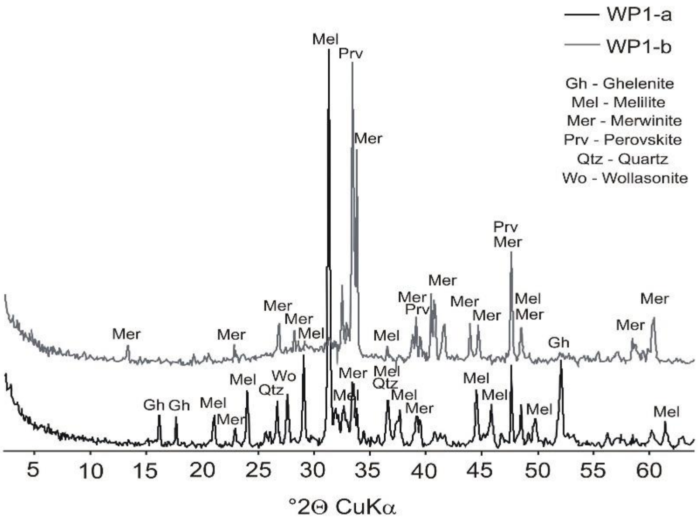

Fig. 5. X-ray patterns of fresh slag samples (WP1-a, WP1-b).

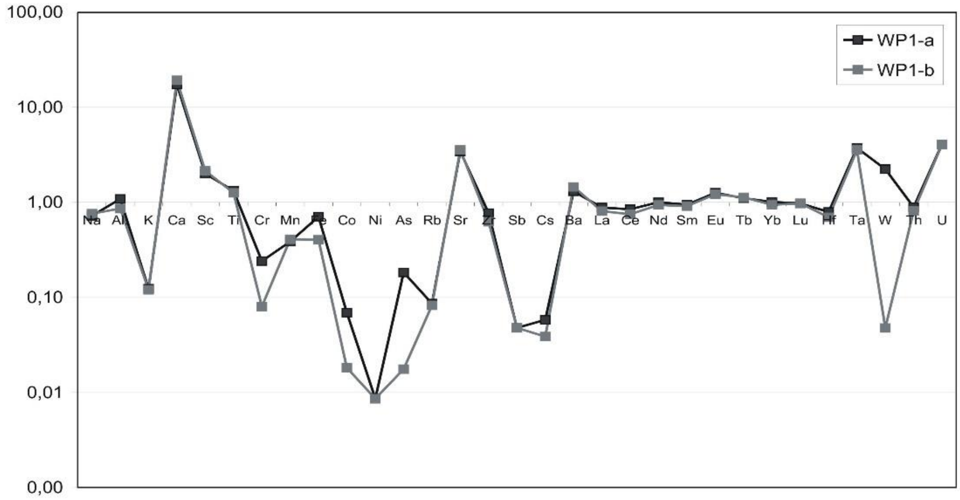

Fig. 6. Multi-element concentration normalized to the composition of NASC. High W content in sample WP!-a is a result of contamination from jaw crusher.

Perovskite ($CaTiO_3$), high temperature feldspar rich in K and Na (anorthoclase - $(K,Na)AlSi_3O_8$)) with small amount of BaO (~1 wt. %), and also and Si, Ti, Zr, Fe and Al oxides are more typical for glassy layer, but minerals such as larnite and merwinite and metallic iron were also noted (Fig. 3, 4).

Sulphides (CaS and MnS) were noted in melilite matrix in both part of slag but sulphur was also determined in EDS analyses of various silicate and aluminosilicate components and sulphur content ranges up to 4 wt %.

Samples WP1-a and WP1-b have almost similar chemical composition and similar basicity index values (Barna et al. 2000) (BI = $CaO+MgO/SiO_2$; 1.28 for sample WP1-a and 1.44 for sample WP1-b).

Concentrations of elements were normalized to North American shale composite (NASC) representing average crustal material (Gromet et al. 1984) (Fig. 6). Slight enrichment of inner part of slag in Cr, Co, As is visible (Fig. 6).

CONCLUSION

Outer glassy layer and inner part of slag exhibit differences in mineral composition related probably to different cooling rate and resulting different conditions of crystallization.

Similarity in chemical composition of outer glassy layer and inner porous part of slag indicates probably that cooling rate was too high for segregation (diffusion) of main elements.

Degassing process occurred within slag. In outer glassy layer rate of solidification was high enough to prevent separation of gaseous phase.

Harmful elements are contained mostly in the inner part of slag but differences in concentration are low what also suggest limited diffusion of elements.

Generally the content of harmful elements (Co, Cu, Zn, Pb, Ni, As, Cr) seems to be not dangerous, but it is necessary to keep in mind that slag is composed of unstable phases and can be reactive for many years. Under natural weathering conditions harmful elements can be released into environment and cause pollution of soils, surface waters and groundwater. Harmful metals are probably associated with silicate and oxide minerals that exhibit low solubility in water (Piatak et al. 2004).

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MINERALOGIA POLONICA – SPECIAL PAPERS
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Eva KLÖTZLI-CHOWANETZ[1], *Urs S. KLÖTZLI*[1]

SMALL MELT POCKETS IN BIG MIGMATITES: EVIDENCE OF IN-SITU PARTIAL MELTING

Abstract: The neosomes of migmatite areas have so far been addressed as melt fraction. These neosomes often exhibit fine grained patches of mainly plagioclase ± resorbed K-feldspar ± white mica ± kyanite ± garnet. We consider these textures to represent melt pockets within a recrystallised matrix, therefore reducing estimates of melt volumes considerably.
Keywords: melt pockets, migmatites

INTRODUCTION

In high-grade terranes the distinction between recrystallization processes in the solid state and partial melting is often not straight forward, but accurate recognition of the melt is needed to quantify its volume for further geodynamic interpretation.

So far, igneous looking parts of a migmatite were addressed as neosome/leucosome and believed to represent the melt fraction. Problems arise, when the inferred melt volumina definitely imply melt migration, field evidence however points against it.

In order to solve this contradiction, two schollen- and one stromatic migmatite area from the Austroalpine realm (Winnebach, Klopaier and Verpeil, Ötztal Crystalline Basement, Austria) were investigated. Since recrystallisation in the course of a post-anatectic deformational overprint would obliterate microstructures and grain size differences, only unfoliated migmatite domains were selected.

In this paper we show that particular textures within the neosomes are best interpreted in terms of representing former melt domains.

PETROGRAPHIC AND PETROLOGICAL EVIDENCE

The investigated migmatites are highgrade metapelites with a characteristic mineral assemblage of Bt + Qtz + Pl ± Grt ± Ms ± Ky in the schollen/paleosome. The neosome with Bt + Qtz + Pl + Ky ± Kfs ± Ms ± Grt exhibits an igneous-looking texture. Fine grained patches of mainly plagioclase ± resorbed K-feldspar ± white mica ± kyanite ± garnet embedded in coarse grained quartz and biotite are a common feature in the neosomes/leucosomes (Fig. 1). The difference in grain size between these aggregates and the surrounding matrix is about 1:10.

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Within these patches, plagioclase is commonly oligoclase (an_{15-20}). This is significantly lower than in the schollen-domains with $an_{25 \text{ to } 43}$ (Hoinkes et al. 1972). The K-feldspar crystals consist of 81 – 90 % orthoclase. The relative amounts of plagioclase versus K-feldspar are variable, ranging from c. 50% to 0% K-feldspar. Occasionally K-feldspar shows lobate resorption bays.

Abundant white mica can be correlated with an absence of K-feldspar. Subject to the migmatite area white mica is either coarse grained and intergrown with biotite, or fine grained within the feldspar patches. Relictic crystals show a distinct overgrowth. Coarse-grained white mica is nearly pure muscovite. The fine-grained white mica shows a slight increase in celadonite component.

Biotite shows progressive decay in contact with the fine grained patches. Fine grained kyanite occurs in variable amounts.

Almandine is mostly fine-grained (< 100 μm) and associated with biotite. Its growth is poikiloblastic at the contact to feldspar. The spessartine-component ranges between 3.6 and 18.7%. In garnet cores Fe/(Fe+Mg) ratios down to 0.67 were measured.

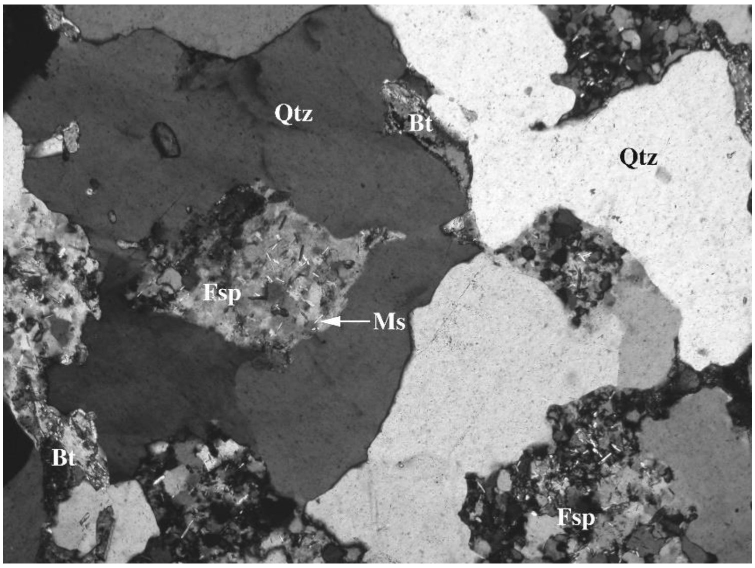

Fig. 1. Fine grained patches of feldspar with tiny white mica is surrounded by quartz islands, (crossed nicols, image width 1.2 mm).

DISCUSSION

The migmatite precursor rocks are Al-rich, Ca-poor metapelites, that probably formed already part of a dehydrated middle to lower crust at the onset of anatexis (Klötzli-Chowanetz 2001). These conditions permit the use of the petrogenetic grid for the NaKFMASH-system of Spear et al. (1999).

Assuming H_2O-undersaturation, production of a first melt fraction through the reaction ms + pl + qtz ➔ as + kfs + lq (1) is suggested. Reaction (1) accounts for the presence of K-feldspar in the neosome in contrast to its absence in the schollen. Due to H_2O-undersaturation the first K-feldspar to develop is solid (Bucher & Frey, 2002). However, as reaction (1) continues, additional water is generated and reaction (1) shifts to ms + pl + qtz ➔ as + lq with kfs-component. The continuous reaction bt + as + pl + qtz ➔ grt + kfs + lq (2) begins to operate on a small scale where biotite is in contact with fine grained plagioclase.

Lobate resorption of K-feldspar and beginning of biotite breakdown within the neosome infer incipient melting processes. Melting of the whole neosome however would have inevitably destroyed these textures. We therefore suggest that only parts of the neosome have reached the melt-stage, and that the fine grained feldspar ± kyanite ± white mica aggregates represent these former melt domains. The low amount of K-feldspar as well as the variable amount of kyanite combined with new growth of white mica suggest reactions (2) and (1) to have operated in reverse upon cooling. Feldspar aggregates similar in shape and identical in chemistry to those described in this paper have been observed in the Mönchalp orthogneiss by Poller (1994). The interpretation of this feldspar texture as anatectic melt implies the occurrence of a migmatic stage in the Mönchalp gneiss evolution already postulated by Streckeisen (1928) but again questioned by Maggetti & Flisch (1991).

Similar textures have been reported from the Southalpine Ceneri gneiss (Zurbriggen 1996) and have been produced experimentally during crystallization of partially molten granitic material (Attrill, Gibb 2003).

Clemens and Holness (2000) describe microgranitic areas composed mainly of quartz and feldspar in a quartzite of a contact aureole. They interpret these textures as melt pockets. The fine grain-size of the melt pockets is attributed by Clemens and Holness (2000) to rapid cooling to the subsolidus, in lower crustal levels equivalent to sudden melt crystallisation at crossing reaction (1).

The extremely low abundance of quartz within the feldspar-aggregates suggests that the quartz originally present in the melt has migrated out of the pl-kfs-qtz clusters to crystallize preferentially around non melted quartz grains, thus forming large quartz-islands in the neighbourhood of the melt pockets as described by Rosenberg and Riller (2000) and Clemens and Holness (2000). For melt volume estimates the quartz contained in the original melt can roughly be sized up at around 25% of the melt (considering a minimum melt composition, H_2O undersaturation and lower crustal pressures; Johannes & Holtz 1990).

Assuming the feldspar aggregates to represent around 30% of the neosome/leucosome, the entire melt volume increases to nearly 40% of the neosome. Even with a low amout of preserved schollen, the degree of melting should therefore lie below the threshold of 20 - 35 vol% given for melt migration by Clemens and Vielzeuf (1987).

CONCLUSION

The recognition of melt pockets in migmatites reveals that melt volume estimates considering the igneous textured parts are far too high.

The melt pockets can be regarded as “index mineral texture” documenting a partial melting event without melt migration in high-grade metapelitic, as well as in metamorphosed igneous rocks.

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MINERALOGIA POLONICA – SPECIAL PAPERS
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Joanna KOSTYLEW[1]

PROVENANCE OF THE MÉLANGES AND METAMUDSTONES OF THE RZESZÓWEK-JAKUSZOWA AND CHEŁMIEC UNITS (KACZAWA COMPLEX, SUDETES): GEOCHEMICAL EVIDENCE

Abstract: The provenance of mélanges and metamudstones from Stanisławów (Chełmiec Unit) and Rzeszówek (Rzeszówek-Jakuszowa Unit) in the northern part of the Kaczawa Complex (Sudetes, SW Poland) is assessed on the *Chemical Index of Alteration* (CIA) and discrimination function analysis using major element data and selected trace element data (Eu/Eu*, Zr/Sc, Th/Sc Th/U and Gd_N/Yb_N). The results of analysis suggest the acidic igneous rocks of the upper crust and recycled continental sediments as the likely main source for the sediments, with a minor component of the plagioclase-rich volcanic material.
Keywords: geochemistry, provenance analysis, mélange, metamudstone, turbidites, Kaczawa Complex, Sudetes

INTRODUCTION

Metasedimentry rocks from the northern part of the Kaczawa Complex (SW Sudetes, Poland) have been recorded in exposures along the Kamiennik stream between Rzeszówek and Jurczyce villages (Rzeszówek-Jakuszowa Unit, RJU), and in deep boreholes near Stanisławów (Chełmiec Unit, CU). These consist of various metamudstones and mélange-type rocks. Mélanges of the Kaczawa Complex are described as large bodies with a chaotic internal structure. They consist of a muddy matrix which contains clasts and larger blocks of various sandstones (mainly greywackes), as well as siliceous and volcanic rocks (Haydukiewicz 1987)[2].

Sandstones and slates of turbidite series can be seen in the most easterly part of the profile along the Kamiennik Stream (RJU), while the western part consist of mélange (Upper Devonian-Lower Carboniferous; Haydukiewicz 1987 and refs. therein). The lower part of the Stanisławów (CU) profile consists mainly of various fine grained metasediments (volcaniclastics and mudstones) with interleaved basic lavas and intrusions. This sequence is correlated with Ordovician volcanoclastics found elsewhere in the Kaczawa Mountains. The uppermost part of the Stanisławów profile is a thrust sheet over 200 m thick and is comprised of mélange (Baranowski et al. 1990, Collins et al. 2000).

The investigated mélanges were gravitationally redeposited within an oceanic trench and subsequently subjected to deformation and metamorphism during further evolution of the Variscan accretionary prism (Collins et al. 2000 and refs. therein).

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[2] *It is therefore recommended that the term "mélange" be used as a descriptive rather than genetic term for mélanges in this complex.*

This paper presents results of a preliminary provenance analysis of the metasedimentary rocks from the northern part of the Kaczawa Complex.

METHODS OF INVESTIGATIONS

32 samples (16 samples of each unit) were prepared as powder for bulk-sample analysis. Investigations were carried out in the Acme Analytical Laboratories Ltd. in Canada using ICP-MS technique. 58 elements (including major and trace elements) have been determined in each sample.

RESULTS & DISCUSSION

Increasing weathering generally leads to a shift towards an aluminum rich composition what can be noted by an increase in the *Chemical Index of Alteration* CIA (Nesbitt,Young 1984). The CIA is defined as: CIA = $Al_2O_3/(Al_2O_3 + K_2O + Na_2O + CaO^*)100$, in molecular proportions (Fig. 1A). For shales this value usually falls between 70-75 (McLennan et al. 1993).

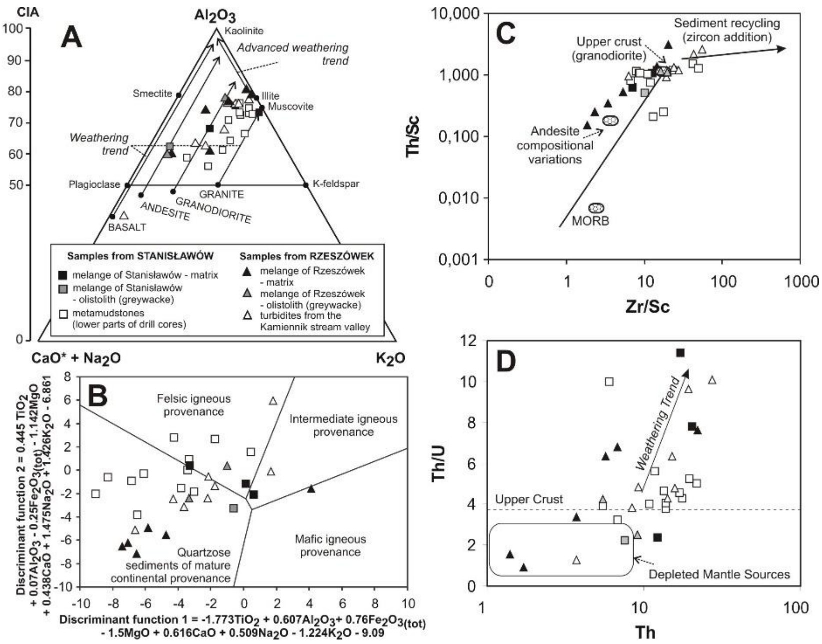

Fig. 1. A. Ternary plot for metasedimentary rocks from the Kaczawa Complex. Molecular proportions of Al_2O_3 - (CaO^* + Na_2O) - K_2O are displayed, with the CIA scale shown on the left (Nesbitt, Young 1984, modified by McLennan 1993, McLennan et al. 1993). Black dots indicate major minerals and rock types. CaO* is CaO in silicates only. B. Discriminant function plot of provenance signatures of metasediments from the Kaczawa Complex, based on major element data (after Roser, Korsch 1988). C, D. Provenance analysis based on various geochemical parameters (McLennan 1989, McLennan et al. 1993, McLennan et al. 2003, fide Veizer, Mackenzie 2003; Kostylew 2006).

The CIA values of investigated samples range from 40 to 84, with an average between 60 and 79, as should be expected for fine grained sedimentary rocks. These indicate the acidic igneous rocks of the upper crust as the main source for the most of the studied rocks (Fig. 1A).

Using the provenance models by Roser and Korsch (1988, Fig. 1B) the quartz-rich sediments of the mature continental provenance and the felsic igneous provenance can be proposed as the main sources for RJU turbidites and CU metamudstones. Material of the CU mélange matrix may be derived from the felsic or intermediate igneous provenance, while the the RJU mélange matrix – mostly from the quartzose sediments of the mature continental provenance. The only one sample of the RJU mélange matrix seems to originate from the mafic igneous provenance (Fig. 1B).

According to McLennan (1989), REE in sedimentary rocks display the following characteristic features: (1) LREE enrichment, (2) rather flat HREE patterns, where Gd_N/Yb_N[3] = 1.0 to 2.0, (3) negative Eu-anomalies with constant Eu/Eu*[4] values between 0.60 and 0.70 (McLennan 1989 and refs. therein). This pattern is generally interpreted as resulting from the mixing of various upper crustal components. The REE data obtained from the RJU and CU metasedimentary rocks only partly coincides with the pattern shown above: (1) LREE enrichment doesn't appear in all of the samples, (2) Gd_N/Yb_N values are always below 1.0, (3) there is a lack of negative Eu-anomalies in many samples, and a few have positive Eu-anomalies, (4) Eu/Eu* values in many samples are > 0.70 or < 0.60. The presence of positive Eu-anomalies (in four samples of CU metamudstones) may suggest a volcanogenic source with an increased plagioclase content (Nance, Taylor 1977, fide McLennan 1989). Geochemical features mentioned above suggest the recycled sediments of the upper crust as the main source of the material for investigated rocks (McLennan et al. 1993).

The Th/Sc ratio is stable during sedimentary processes, in shales this is constantly around 1.0 (McLennan 1989 and refs. therein). In the studied rocks, the average values of this ratio are as high as 1.08, which indicates the upper crust is the probable provenance for these rocks. Th/Sc and Zr/Sc ratios increase with increasing igneous differentiation of the source rocks. These strong trends break down in recycled sediments (e.g. turbidite sands from passive margins), consistent with Zr enrichment (McLennan et al. 1993; Fig. 1C). Comparison of the Th/Sc and Zr/Sc ratios in investigated samples indicates that the granodiorites of the upper crust may be the primary source of the provenance for the rocks, with a minor component of andesite-like (RJU mélange matrix) and recycled sedimentary rocks (RJU turbidites and CU metamudstones; Fig. 1C; McLennan et al. 1993). Similarly, when comparing Th abundances with the Th/U ratio, the upper crust appears to be the probable main source for the rocks, possibly with a subordinate component of depleted mantle sources in the RJU mélange (Fig. 1D).

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[3] *Subscript „N“ – C1-normalized values after Evensen et al. (1978; fide McLennan 1989)*
[4] *$Eu/Eu^* = Eu_N / (Sm_N * Gd_N)^{0,5}$ (McLennan 1989)*

CONCLUSION

The obtained data indicate acidic igneous rocks of the upper crust and recycled continental sediments as the likely main source for the most of investigated sediments. The metamudstone from the lower part of drill cores from Stanisławów may have had a separate (local?) source, with a large contribution of plagioclase-rich volcanic material (Kostylew 2006).

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MINERALOGIA POLONICA – SPECIAL PAPERS
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STATE OF PRESERVATION OF BIOAPATITES IN BONES FROM ANTHROPOLOGICAL EXCAVATIONS IN SOUTHERN POLAND – PRELIMINARY RESULTS

Abstract: Human skeletons represented by bones of skulls, ribs and long bones from cemeteries in Szarbia Zwierzyniecka and Samborzec were examined using mineralogical investigation methods. It was found that this material is contaminated by secondary calcite, quartz and, subordinately, clayey mineralization. These bones consist of carbonate hydroxyapatite, containing up to several percent carbonate ions. These apatites have recrystallized during burial what is evidenced by their higher crystallinity when compared with bioapatites from recent bones but much lower than in natural and synthetic hydroxyapatite. Apart from Ca, P and small amounts of Na, Cl and Mg - elements coming from bioapatite, increased amounts of K, Fe, Si and Al are related with contaminating admixtures.
Keywords: human remains, carbonate bioapatite, hydroxyapatite, bone, crystallinity.

INTRODUCTION

Human skeletal remains: fragments of skulls, ribs and long bones from Neolithic and Early Bronze Age cemeteries in Samborzec (Sandomierz prov., Bell Beaker Culture) and Szarbia (Kielce prov., Mierzanowicka Culture) have been investigated. Skeletons were excavated from graves a well as from settlements pits. Chronological frames confirmed by 14C dates locate Szarbia site between 2130 and 1664 BC (in calendar years) (Haduch 1997), Samborzec site is much more earlier, 2470-2270 BC (Budziszewski et al. 2003). Bones are not well preserved caused by ploughing and surface erosion, another agriculture activity and plant roots penetration. Both cemeteries were localised on hill slope, in fertile loess soil. Depth of grave pits varies from 20 to 120 cm. Fragmentation of bones may probably due to funeral rites, too.

METHODS OF INVESTIGATION

Microscopic examinations of thin sections were carried out in transmitted light using JENAPOL microscope. Morphology of the fragments of bones was observed using scanning electron microscopy SEM (JEOL 5410). The XRD powder patterns were obtained by means of a PHILIPS diffractometer using CuKα radiation (40kV, 30 mA); scan range: 4-80º [º2θ].

Chemical composition of mineral phases was defined by means of scanning electron microscopy SEM (JEOL 5410) equipped with an energy dispersive spectrometer EDS Voyager 3100 (NORAN) and of field-emission SEM (HITACHI

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S–4700) equipped with YAG (BSE) detector and EDS analyzer NORAN Vantage. According to the "standardless" procedure of calculation the data were normalised to atomic percentage.

The infrared (FTIR) spectra in the frequency range 400-4000cm^{-1} were scattered using BIO-RAD model FTS-165 spectrometer.

SEDIMENTARY ADMIXTURES IN BONES MATERIAL

The human remains studied were excavated from loess sediment. Though the period of burial of this material was not very long (about 4000 years), porous nature of bones was increasing its susceptibility to the influence of the deposit containing it.

Observation using optical and electron microscopy have evidenced the bioapatitic material of bones is contaminated by secondary calcite. This mineral is crystallizing as aggregates in vacuoles, pores and fissures, particularly in Haversian canals. In general, calcite crystals are rhombohedral in shape, up to several tenth um in size, sometimes arranged in catenary's forms. Apart from secondary calcite there appears also the quartz. The latter mineral occurs on the surface of bones as well as crystallized individuals or aggregates on pores. It is often accompanied by concentrations of clay minerals, evidenced by the presence of Si, Al, Fe and K estimated using EDS method. Among other admixtures worth mentioning are organic compounds occurring in soils. This is evidenced by very intense C and Cl peaks in some EDS patterns. The presence of calcite, quartz and clay minerals was confirmed by XRD analyses.

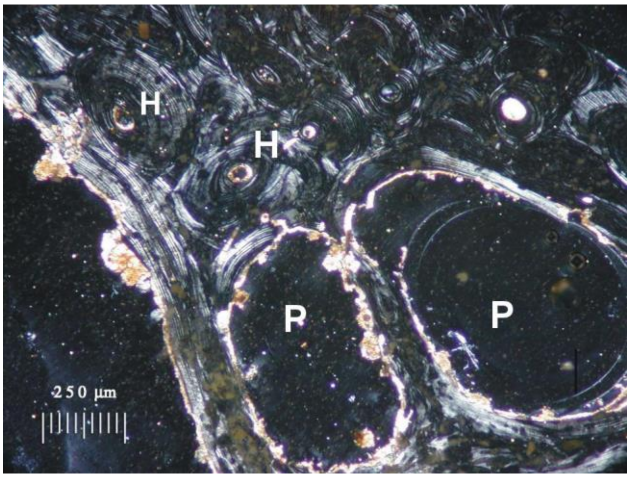

Fig.1. Calcite crystals (light) filling Haversian canals (H) in compact part of bone (*upper part of the photo*) and growing in pores (P) in spongy one *(lower part of the photo*).

BIOAPATITE FROM BURIAL HUMAN BONES

PXRD data of apatites studied are very close to those of hydroxy-apatite but indicate their lower crystallinity. The main differences in their powder X-ray diffraction patterns (B) when compared to bioapatite from bone of the individual of foetus age (A) and that of hydroxyapatite (C) (Maneghini et al., 2003) are presented in Fig.2. In general, in the patterns of bioapatites the backgrounds are much higher as in hydroxyapatites what can be due to the content of amorphous phase in them.

The lower crystallinity of bioapatites, in comparison to hydroxyapatites, is manifested by lower intensity of the diffraction maxima, which are broader and - in the case closely situated maxima - weakly separated.

On the diffraction pattern of the least crystalline bioapatite (Fig. 2A) the (211), (002), (310) and (213) maxima appear as the first. Besides, they are broad and show very low intensities. In the pattern of the apatites studied (Fig. 2B), showing higher crystallinity, on the right side of (211) maximum there appear additionally the (110), (300), (202) and (301) maxima. Moreover, other maxima show increased intensities.

In comparison to bioapatites from bones of an adult individual (Maneghini et al. 2003), in the patterns of the apatites studied the maxima (100), (101), (200) and (111) are better separated. Summing up, the studied apatites from bones, deposited in loess sediments, are more crystalline in comparison to bioapatites from recent bones but show considerably lower degree of crystallinity than hydroxyapatites. No differences in crystallization degree of bioapatites from various parts of skeletons: skulls, ribs, long bones were found.

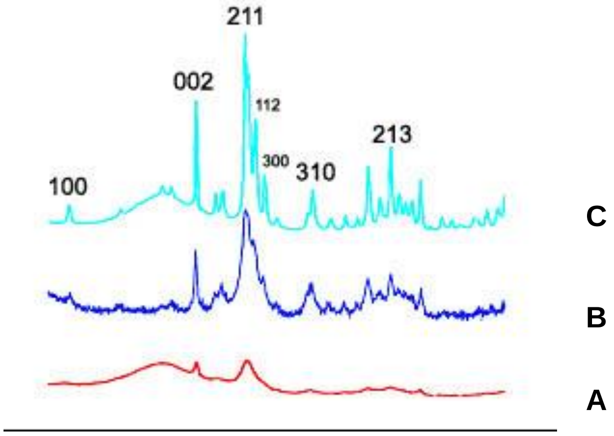

Fig. 2. Comparison of the diffractograms of bones of the foetus age individual (A), hydroxy-apatite (C) (Maneghini et al., 2003) and of the bones studied (B); scan range: 8-64º [º2θ].

In bioapatite the FTIR spectra the following bands 960, 468, 1040/1090, 604/ 562 cm^{-1} related with all four modes of PO_4 internal vibrations, were resolved. Moreover, these spectra exhibit the bands at 871-873, 1415-1419 / 1453-1459 cm^{-1}, connected with the presence of carbonate group CO_3^{2-}, occurring in the B-type carbonate substitution (CO_3-for-PO_4) (Rey at al. 1989).

The analysis of chemical composition of apatites using microprobe method has shown that the molar Ca/P ratio in them is variable and varies within the limits 1.82 - 2.15. Besides, these phases contain the admixtures of Na (0.2 - 1.1 wt. %) , Cl (0.2 - 0.6 wt. %), as well as of Mg, K and Fe but their contents do not exceed 0.5 wt. %. In hydroxyapatite the Ca/P ratio amounts to 1.67 whereas in bioapatites from bones it varies from 1.72 to 1.80 (LeGeros, LeGeros, 1984) and from 1,63 to 1,67

(Skinner, 2000). The formula of hydroxyapatite in which 1/6 of PO_4^{3-} ions was substituted by CO_3^{2-} is as follows: $Ca_5[OH/(PO_4)_{2..5}(CO_3)_{0.5}]$. The Ca/P ratio in it amounts to 2.0 and the CO_2 content is 4.6 wt.%.

High Ca/P ratio estimated in the apatites studied can result from their enrichment in Ca^{2+} or impoverishment in P. In the latter case it can be related to the displacement of PO_4^{3-} by CO_3^{2-} ions in the bioapatite structure. The precipitation of neomorphic calcite in pores and fissures of bones (the presence of source of Ca^{+2} and CO_3^{2-} ions), indicates that both these processes could be possible.

In sedimentary rocks the diagenetic processes and weathering processes are usually leading to a decrease of CO_3^{2-} content in carbonate apatites (McClelan, 1980). In the bioapatites studied the calcareous soil and loess, embedding the bones, formed conditions favouring the preservation of bioapatite and its recrystallization.

SUMMARY

Bioapatites from bones buried in loess sediments were subjected to transformation consisting on one side in negligible recrystallization and, on the other side, in the increase of Ca/P ratio when compared to bioapatites from fresh recent bones.

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MINERALOGIA POLONICA – SPECIAL PAPERS
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LOWER - MIDDLE ORDOVICIAN SHRIMP ZIRCON AGES OF LUBRZA METATRACHYTES FROM KACZAWA METAMORPHIC COMPLEX (WEST SUDETES, SW POLAND)

Abstract: Lubrza metatrachytes occur within the upper part of the Cambro-Ordovician volcanic succession, which forms the oldest part of the Palaeozoic Kaczawa Metamorphic Complex (KMC). Zircons separated from two samples of the acid metatrachytes from Bolków Unit of KMC were subjected to U-Th-Pb SHRIMP II microprobe dating. Sample BOLK representing very weakly deformed lava flow yielded an age 475 +/- 5,0 Ma and highly sheared KARCZ.1 sample an age of 468 +/- 3,1 Ma. Both data are interpreted as pointing out the Lower - Middle Ordovician lava extrusions followed by quick crystallisation and solidification.
Keywords: West Sudetes, Lower - Middle Ordovician, volcanic activity, geochronology, zircon, SHRIMP datings

INTRODUCTION

Palaeozoic Kaczawa Metamorphic Complex (KMC) is located in the West Sudetes constituting north-eastern prolongation of the Saxothuringian Zone within the Variscan belt. The KMC is built up of a few km thick volcano-sedimentary succession deposited in a marine basin from Cambrian to Lower Carboniferous. The basin infillings were finally stacked in Visean and presently form a highly complicated structure of Variscan accrecionary prism that includes folded thrust-sheets, slices and melange bodies (Baranowski et al. 1990, Collins et al. 2000, Kryza, Muszyński 2003). Within the KMC lithostratigraphic profile two main volcanic associations were distinguished: older – Cambro-Ordovician, composed of basic and acid eruptives showing geochemical signatures of within-plate, continental rifting setting and younger – Silurian, almost exclusively composed of E- to N-MORB metabasalts documenting mature stage of the basin development (Kryza, Muszyński 1992, Furnes et al. 1994).

The Cambro-Ordovician, spilite-keratophyre association, which locally reaches a thickness of 2-3 km, constitutes major parts of the Bolków and Świerzawa tectonic units of KMC (Kryza & Muszyński 1992). This association is mainly composed of

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greenstones and greenschists enclosing syn-depositionary interlayers: (i) voluminous bodies of the Wojcieszów limestones considered on the basis of problematic fossils as Cambrian (Gunia 1967) or not older than (Ordovican – Silurian (Skowronek, Steffahn 2000) and (ii) minor bodies of s.c. Gackowa volcanogenic sandstones containing detrital zircons not younger than 550 Ma (Kryza et al. 2007, in press). Amongst metabasites acid metavolcanics known as the Osełka metarhyodacites occur (Kryza, Muszyński 1992, Muszyński 1994, Furnes et al. 1994). They are of Cambrian age (zircon, Pb-Pb evaporation: Kozdrój et al. 2006).

The Lubrza metatrachytes (= "keratophyres") represent alkaline, bimodal suite of layered volcaniclastic deposits embedding oval bodies of massive lava flows and shallow subvolcanic intrusions (Piotrowski, 1988, Awdankiewicz 1992, Kryza, Muszyński 1992, Muszyński 1994, Furnes et al. 1994). Lubrza metatrachytes form up to a few hundred meters long, laterally inclined dome - like structures interfingering with metabasites or with thick sequence of grey slates believed to be the Ordovician flysch-like series (Baranowski et al. 1990).

METHODS

Zircon grains were hand selected and mounted in epoxy resin together with chips of the 91500 (Geostandart zircon) reference zircon. The grains were sectioned approximately in half and polished. Reflected and transmitted light photomicrographs and cathodoluminescence (CL) SEM images were prepared for all zircons. The CL images were used to decipher the internal structures of the sectioned grains and to target specific areas within these zircons.

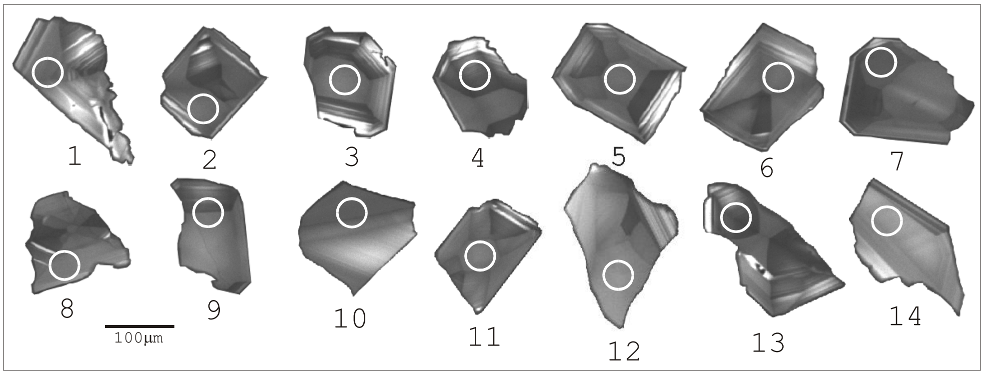
The U-Pb analyses of the zircons were made using a SHRIMP-II ion microprobe (Center of Isotopic Research, VSEGEI, St.Petersburg, Russia). Each analysis consisted of 5 scans through the mass range, spot diameter was about 20 μm, primary beam intensity was about 6 nA. The data have been reduced in a manner similar to that described by Williams (1998, and references therein), using the SQUID 13a Excel Macro of Ludwig (2000). The Pb/U ratios have been normalized relative to a value of 0.1791 for the $^{206}Pb/^{238}U$ ratio of the 91500 (Geostandart zircon) reference zircon, equivalent to an age of 1062 Ma (Wiedenbeck et al. 1995). Uncertainties given for individual analyses (ratios and ages) are at the one σ level, however the uncertainties in calculated concordia ages are reported at two σ level. The Ahrens-Wetherill (1956) concordia plot has been prepared using ISOPLOT/EX (Ludwig 1999).

RESULTS

The sample BOLK collected from an abandoned quarry 1.5 km NW of Bolków represents yellowish-brown, massive trachytic lava, which forms an oval, 200-300 m big body surrounded by (Ordovician?) tuffaceous – sedimentary rocks which in turn are locally in contact with Silurian black shales, cherts and Devonian silicious shales (Muszyński 1994). The investigated metatrachyte shows weakly pronounced web – like foliation. The main, light in colour, fine-grained rock mass of trachytic fabric is composed of dominating feldspars (albite), rare quartz grains, randomly distributed dark, short needles of pyroxene (possibly aegirine) and accessory ore minerals. Darker, anastomosing, irregular network of foliation planes is defined by chlorite bands and occasionally by amphiboles. Grains of epidote neoblasts often occur in chlorite zones.

The zircons dated from BOLK sample are mostly subhedral to anhedral (often fragments of larger crystals), mostly with oscillatory and sector zoning (Fig. 1A). They have similar U and Th abundances - 114-287 ppm and 74-324 ppm, respectively (Tab. 1). Fourteen dated zircons from BOLK sample yielded U-Pb concordia age of 475±5,0 Ma (Fig. 2).

A.



B.

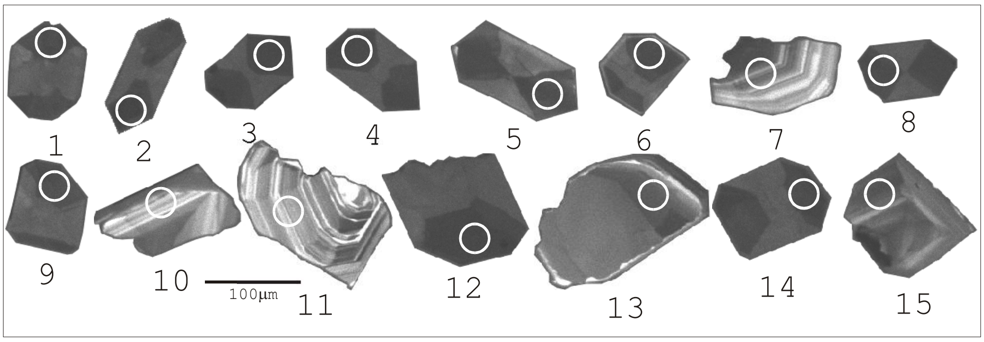


Fig. 1. Cathodoluminescence images of investigated zircons with marked analytical points from sample BOLK (A) and sample KARCZ.1 (B).

The sample KARCZ.1 was taken from the isolated rocky Karczmisko hill near Mysłów. The metatrachytes are grey-rose, distinctly foliated rocks produced by strong, ductile shearing of the lava flow of originally fluidal, laminated fabric. Enclaves of massive, resistant to shearing rocks are locally visible within the foliated matrix. The enclaves, from a few cm up to 1 m in diameter, are of fine- to medium grained fabric and cut by numerous quartz veins. They possibly represent detached blocks but under a microscope, most of them show fabric similar to the host rock (Muszyński 1994).

The sample KARCZ.1 exhibits well developed, mylonitic foliation. In very fine-grained matrix (feldspar, sericite, aegirine) consisting more than 90 % of the rock mass, foliation is defined by ubiquitous chlorite flakes. Ductile, rotational

Table 1. SHRIMP U-Th-Pb data for sample BOLK and KARCZ.1.

Spot	U (ppm)	Th (ppm)	$^{232}Th/^{238}U$	$\%^{206}Pb_C$	$^{206}Pb^*$ (ppm)	$^{206}Pb^*/^{238}U$	± %	$^{207}Pb^*/^{235}U$	± %	$^{207}Pb^*/^{206}Pb^*$	± %	$^{206}Pb/^{238}U$ Age (Ma)	$^{207}Pb/^{206}Pb$ Age (Ma)	% Dis-cor-dant
Sample BOLK.														
1.1	204	163	0.83	0.54	14.0	0.0796	2.1	0.583	9.0	0.0532	8.7	493.5 ±9.9	335 ±200	-32
2.1	191	151	0.82	0.28	12.8	0.0780	2.3	0.669	5.7	0.0622	5.3	484.0 ±11.0	682 ±110	41
3.1	183	145	0.81	1.10	12.7	0.0797	2.3	0.516	17.0	0.0469	17.0	494.0 ±11.0	46 ±410	-91
4.1	258	324	1.30	0.12	16.9	0.0760	1.9	0.598	3.3	0.0571	2.7	472.0 ± 8.7	495 ±59	5
5.1	205	151	0.76	0.09	13.6	0.0769	2.0	0.606	3.2	0.0572	2.5	477.7 ±9.2	497 ±55	4
6.1	218	180	0.86	0.00	14.2	0.0762	1.9	0.620	3.0	0.0590	2.3	473.2 ±8.9	568 ±50	20
7.1	287	176	0.63	0.21	19.4	0.0785	1.9	0.601	4.1	0.0555	3.7	487.1 ±9.0	432 ±82	-11
8.1	190	143	0.77	1.08	12.0	0.0726	2.2	0.484	15.0	0.0483	15.0	452.1 ±9.6	114 ±360	-75
9.1	244	272	1.15	--	16.0	0.0765	1.9	0.626	2.8	0.0594	2.1	474.9 ±8.8	582 ±45	23
10.1	270	249	0.95	0.14	17.2	0.0742	1.9	0.568	3.5	0.0556	2.9	461.2 ±8.5	436 ±65	-5
11.1	169	126	0.77	0.60	11.1	0.0762	2.1	0.552	9.8	0.0526	9.6	473.2 ±9.5	311 ±220	-34
12.1	133	92	0.72	0.15	8.8	0.0766	2.0	0.597	4.1	0.0565	3.5	476.1 ±9.3	472 ±78	-1
13.1	230	261	1.18	0.48	15.2	0.0767	2.0	0.575	7.8	0.0544	7.6	476.4 ±9.2	386 ±170	-19
14.1	114	74	0.67	0.65	7.5	0.0757	2.1	0.586	6.8	0.0562	6.4	470.4 ±9.5	458 ±140	-3
Sample KARCZ.1														
1.1	1581	1400	0.91	0.00	103.0	0.0760	1.1	0.605	1.8	0.0578	1.5	471.9 ±5.0	521 ±32	10
2.1	2744	3090	1.16	3.25	73.2	0.0300	1.2	0.234	6.3	0.0566	6.2	190.7 ±2.2	477 ±140	150
3.1	2072	2679	1.34	0.12	136.0	0.0765	1.1	0.587	1.8	0.0557	1.4	475.2 ±5.0	440 ±31	-7
4.1	1935	2715	1.45	0.01	126.0	0.0757	1.1	0.597	1.4	0.0572	0.9	470.4 ±5.0	498 ±20	6
5.1	1345	1969	1.51	0.20	87.1	0.0752	1.1	0.588	3.2	0.0566	3.0	467.5 ±5.0	478 ±67	2
6.1	1453	1859	1.32	--	93.2	0.0746	1.5	0.570	1.8	0.0553	1.0	464.1 ±6.6	426 ±23	-8
7.1	564	373	0.68	0.30	38.6	0.0794	1.2	0.578	3.5	0.0528	3.3	492.4 ±5.7	320 ±75	-35
8.1	1814	2169	1.24	0.05	118.0	0.0754	1.1	0.589	1.6	0.0566	1.1	468.9 ±5.0	477 ±25	2
9.1	1223	971	0.82	0.11	80.3	0.0763	1.1	0.596	2.2	0.0566	1.8	474.0 ±5.1	478 ±41	1
10.1	178	72	0.42	3.02	11.6	0.0738	2.0	0.340	35.0	0.0330	35.0	458.8 ±8.8	-860 ±1000	-287
11.1	180	82	0.47	0.24	11.2	0.0724	1.3	0.554	3.3	0.0556	3.1	450.3 ±5.5	435 ±69	-3
12.1	1848	2466	1.38	0.13	118.0	0.0741	1.1	0.574	1.7	0.0562	1.3	460.8 ±4.8	458 ±29	-1
13.1	563	301	0.55	0.31	36.3	0.0748	1.2	0.557	4.9	0.0540	4.8	464.7 ±5.3	373 ±110	-20
14.1	822	589	0.74	0.32	52.4	0.0739	1.1	0.584	3.1	0.0573	2.9	459.6 ±5.0	504 ±63	10
15.1	646	598	0.96	0.03	42.0	0.0756	1.1	0.591	1.7	0.0567	1.3	470.1 ±5.1	478 ±29	2

shearing is documented by long, stretched lenses composed of disintegrated albite grains (with preserved lamellae structures) sealed with chlorite flakes and epidote neoblasts.

Zircon crystals in KARCZ.1. sample can by classified into two populations. The first one is represented by rich in U (up to 2744 ppm) and Th (up to 3090 ppm), dark in CL imaging, euhedral to subhedral, short- to normal prismatic crystals with morphology dominated by {100} and {101} forms. According to classification by Pupin and Turco (1972), they represent D and J types. Sector zoning is a common feature of investigated individuals (Fig. 1B). The second group comprises subhedral to anhedral grains, often with terminated oscillatory zoning and sometimes overgrown by darker (in CL) zircon (Fig. 1B – zrn 10). They contain less U and Th and display significantly brighter CL in comparison to zircons of the previous population (Tab. 1, Fig. 1B - e.g. 7, 10, 11). The zircons of both groups show similar age pattern yielding mean U-Pb concordia age of 468±3.1 Ma (Fig. 2).

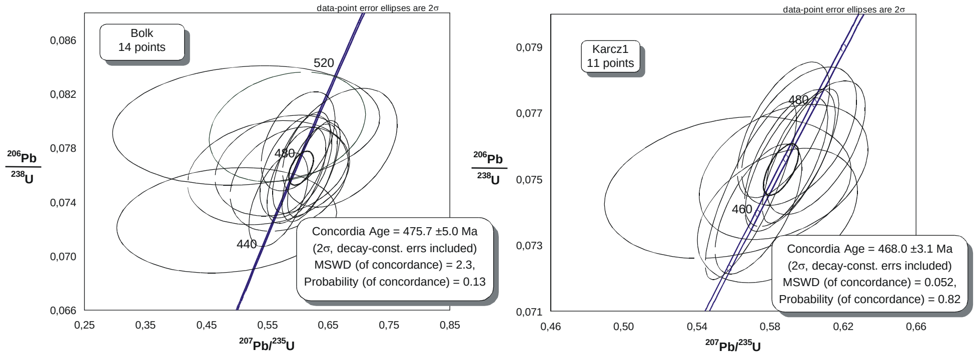


Fig. 2. $^{207}Pb/^{235}U$ v. $^{206}Pb/^{238}U$ plots showing concordia ages for BOLK and KARCZ.1 meta-trachyte samples.

CONCLUSIONS

New SHRIMP isotope data from Kaczawa Metamorphic Complex (KMC) indicate that the volcanic, extrusive activity, which produced the Lubrza trachytic lavas, is of the Early to Middle Ordovician age (from Arenigian to Darrivilian). These data suggest that the investigated volcanics are the youngest and form the top-most part of the spilite – keratophyre association in the Bolków Unit of KMC.

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MINERALOGIA POLONICA – SPECIAL PAPERS
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GADOLINITE FROM THE MICHAŁOWICE QUARRY, KARKONOSZE MASSIF, SW POLAND

Abstract: Gadolinite crystal 16 mm long was collected from a pegmatite in the quarry at Michałowice, in the northern part of the Karkonosze Variscan granitoid massif. The studied mineral is metamictic gadolinite-Y with only 0.14 vacancies, 0.32 (OH) and 0.04 F pfu. The content of total REE is 1.64 apfu and relatively high content of boron reaches 0.21 apfu. Homogenization studies of fluid inclusions in quartz coeval with gadolinite yielded temperatures 327-347°C; tentative determinations of pressure during the gadolinite crystallization gave values 1-1.2 kbar. The parent solutions were aqueous with ca. 15% NaCl, 3% KCl and 3% $CaCl_2$; carbon dioxide was present.
Keywords: gadolinite, pegmatite, fluid inclusions, temperature, pressure, Karkonosze

INTRODUCTION

Karkonosze Variscan granitoid massif, located in the north-eastern marginal part of the Bohemian massif (Mazur et al. 2007), contains numerous pegmatites consisting mainly of microcline, albite, quartz, biotite, muscovite, chlorite and hematite. The detailed list of the Karkonosze pegmatite minerals may be found in the paper published by Kozłowski & Sachanbiński (2007).

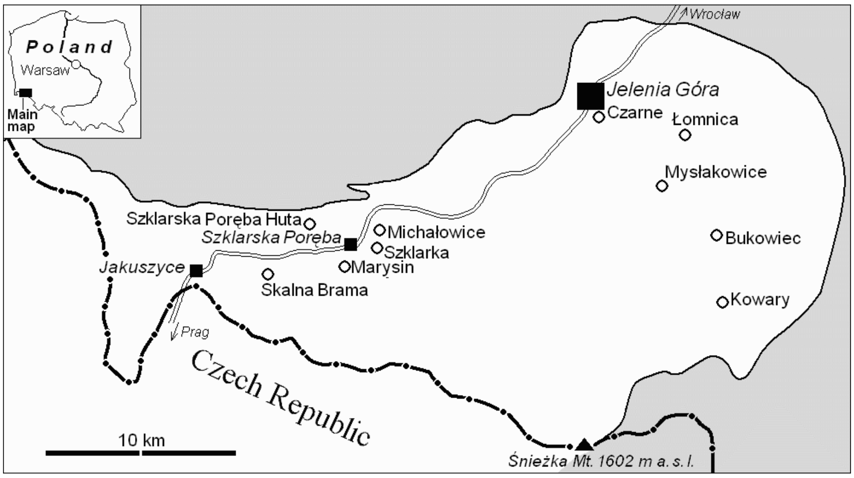

Fig. 1. Locations of the gadolinite-bearing pegmatites, marked as circles, in the Polish part of the Karkonosze granitoid massif.

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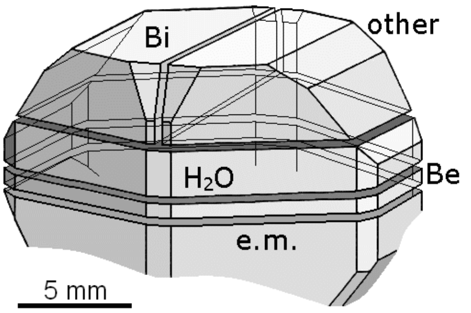
As the minor components, the pegmatites contain numerous minerals, the rare earth ones inclusively (*op. cit.*). Gadolinite apparently occurs relatively frequently (Fig. 1) and was noted from pegmatites found at Marysin in Szklarska Poręba, in the quarry at Szklarska Poręba Huta, in the rocks of Skalna Brama, in the Szklarka Creek valley, moreover at Czarna, Bukowiec, Łomnica, Mysłakowice, Kowary and Michałowice (*see* Kozłowski, Sachanbiński 2007, and the references quoted there).

THE SAMPLE

The investigated crystal of gadolinite was collected in 1977 in the granite quarry at Michałowice from a typical pegmatite nest ca. 55 by 43 cm in size. The crystal was euhedral, rich in faces (Fig. 2), and its largest dimension was 16 mm. Its colour was black, with tar lustre. The crystal formed between and on quartz, microcline and albite; in its lower part, hidden between the named minerals, large grain of magnetite closely contacted with gadolinite (Fig. 3).



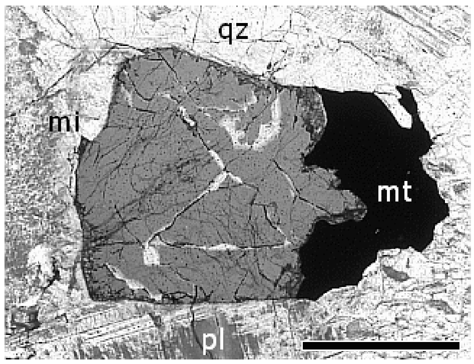


Fig. 2 (*left*). Habit of the studied gadolinite crystal, the parts cut off for various determinations are shown: e. m. – electron microprobe determinations, Be – beryllium determinations, H_2O – water determinations, Bi – bismuth determinations, other – other investigations.
Fig. 3 (*right*). Gadolinite (gray) in the preparation used for the electron microprobe investigations; mt – magnetite, qz – quartz, mi – microcline, pl – plagioclase (albite), scale bar 5 mm.

METHODS OF INVESTIGATIONS

Most of the elements, except for those named below, have been analysed in thin section by means of a Cameca SX 100 electron microprobe (in the Inter-Institutional Laboratory of Microanalysis of Minerals and Synthetic Substances, Faculty of Geology, Warsaw). The analytical procedure for most of elements was as follows: an accelerating voltage of 20 kV and a beam current 10 or 20 nA, natural and artificial standards.

The gadolinite slices for the special methods of the component determinations were cut off from the crystal (Fig. 2) by the tungsten wire micro-saw.

Beryllium was determined quantitatively by the colorimetric methods. The slice was divided into 7 pieces (samples), each piece was powdered, mixed with the

Na_2CO_3 flux, fused and dissolved with HCl. Four samples were analyzed for the Be content by the colorimetric alberon method in weakly acid solution, and the three samples – by the colorimetric berylon III method in alkaline solution. The average BeO content was 12, 21 wt. %.

The slice for the water determinations was split in 3 parts, washed by alcohol, dried at 105°C, powdered with K_2CrO_4 and fused in miniature Penfield tubes to determine the water content by weight. The average H_2O+ content was 0.62 wt. %.

Bismuth was determined by spectral emission method, the DFS-13 spectrograph with the 1200 lines/mm diffraction grid was used. The spectrum was recorded in the 2nd order, for the determination the longer-wave component of the Bi 3067,712 Å line was applied (with the detection limit 1 ppm). The powdered sample was mixed with the buffer: graphite 95%, Na_2CO_3 4,97% and Sb_2O_3 0,03% as internal standard. Natural epidote, with the same buffer and Bi_2O_3 sp. pure added, was used as the analytical standard. The average value of 7 determinations was 312 ppm Bi.

X-ray diffraction method was applied to check the structural properties of gadolinite. The fluid inclusions were investigated by the conventional heating-freezing microscope stage method.

RESULTS

The chemical investigations of the studied mineral yielded the gadolinite-Y composition (Table 1).

Table 1. Chemical composition and crystallochemical formula of gadolinite from the Michałowice quarry.

Component	Wt. %	Component	At. pfu	Component	Wt. %	Component	At. pfu
SiO_2	24.88	Si^{4+}	1.93	Dy_2O_3	1.08	Dy^{3+}	0.03
B_2O_3	1.61	B^{3+}	0.07	Ho_2O_3	0.17	Ho^{3+}	0.004
			0.14	Er_2O_3	1.34	Er^{3+}	0.03
BeO	10.21	Be^{2+}	1.90	Yb_2O_3	3.31	Yb^{3+}	0.08
ThO_2	2.53	Th^{4+}	0.04	Lu_2O_3	0.55	Lu^{3+}	0.006
UO_2	0.56	U^{4+}	0.01	CaO	3.72	Ca^{2+}	0.31
Y_2O_3	26.80	Y^{3+}	1.11	MgO	0.15	Mg^{2+}	0.02
La_2O_3	0.87	La^{3+}	0.02	MnO	0.70	Mn^{2+}	0.05
Ce_2O_3	4.38	Ce^{3+}	0.24	FeO	12.22	Fe^{2+}	0.79
Pr_2O_3	0.74	Pr^{3+}	0.02	H_2O+	0.62	OH^-	0.32
Nd_2O_3	2.27	Nd^{3+}	0.06	F	0.15	F^-	0.04
Sm_2O_3	0.53	Sm^{3+}	0.01	Subtotal	100.21	*Note*: total Fe as bivalent iron; Bi content 0.03 wt. %.	
Gd_2O_3	0.89	Gd^{3+}	0.02	- O = 2F	0.06		
Tb_2O_3	0.08	Tb^{3+}	0.004	Total	100.15		

The heavy horizontal lines in the column with the atoms pfu values separate the groups of elements occurring in the same crystallochemical sites. Other elements than these listed in the Table were below the detection limit.

The calculated crystallochemical formula:

$$(REE_{1.64}Ca_{0.31}Th_{0.04}U_{0.01})_{2.00}(Fe_{0.79}\square_{0.14}Mn_{0.05}Mg_{0.02})_{1.0}(Be_{1.90}B_{0.14})_{2.04}\rightarrow$$
$$\rightarrow[(Si_{1.93}B_{0.07})_{2.00}O_8O_{1.64}(OH)_{0.32}F_{0.04}]$$

indicates typical gadolinite-Y composition with small shift toward the hingganite field, shown by the 0.14 vacancies, 0.32 (OH) and 0.04 F pfu (Pezzotta et al. 1999). The high content of boron in part replaces beryllium, suggesting the admixture of the homilite end member. However, the content of boron is in excess with respect to the beryllium deficit, but silicon is lacking to the full 2 atoms pfu as well. Thus, we suppose the partial replacement of silicon by boron. The spectrum of the rare earth elements present in the studied gadolinite is rich, only few of them were under the detection limit (Tab. 1). Ce, Yb and Nd are the most abundant rare earth elements. Thorium distinctly prevails over uranium, but contents of the two elements are low. Calcium occupies only 15% of the large-cation sites.

Bismuth content (312 ppm), though generally low, is rather high when compared with concentrations of this element in the other gadolinite specimens, varying from 12 to 262 ppm (Gurney, Ahrens 1969). This element most probably replaces rare earth elements in the gadolinite structure. On the other hand, the structure was completely metamictised.

The investigated aqueous fluid inclusions in quartz coeval with the gadolinite yielded homogenization temperatures 327-347^{o}C; tentative determinations of pressure during the gadolinite crystallization on the basis of the carbon dioxide inclusion investigations gave values 1-1.2 kbar. The parent solutions were aqueous with ca. 15% NaCl, 3% KCl and 3% $CaCl_2$ dissolved. Thus, the correction caused by the influence of pressure, which should be added to the homogenization temperatures, is ca. 80 to 90^{o}C.

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PRELIMINARY SHRIMP ZIRCON AGE OF A BENTONITE FROM THE LOWER CARBONIFEROUS PAPROTNIA SERIES OF THE BARDO UNIT (SUDETES, SW POLAND)

Abstract: The Lower Carboniferous Paprotnia series of the Bardo Unit in the central Sudetes, composed predominantly of mudstones and yielding Upper Viséan palaeontological evidence, comprises several bentonite layers. The bentonites contain abundant zircons, which are in line with their volcanic derivation. The main population of the zircons yielded a SHRIMP U-Pb age of c. 335 Ma corresponding with the biostratigraphic data, and proving a volcanic activity in the surrounding region in Viséan times.
Keywords: bentonite, zircon, SHRIMP geochronology, Viséan, Bardo Unit, Sudetes

INTRODUCTION

The Paprotnia series in the western part of the Bardo Unit (central Polish Sudetes) is composed of claystones in its lower part, and mudstones and greywackes in its middle and upper parts. Carbonate intercalations are subordinate. The deposits contain rich fossils of benthonic fauna dominated by brachiopods and corals. Fossils of nektonic animals as goniatids and nautiloids are less numerous. The exposed section, 13.7 m thick, contains several thin (2–10 cm) bentonite layers (Haydukiewicz, Muszer 2002).

The sediments of this series were deposited in offshore to onshore conditions. The paleontological record indicates that the Paprotnia series belongs to the ammonoid *G. crenistria* zone which corresponds with the Asbian (regional substage) of the Upper Viséan (V3b) (Haydukiewicz, Muszer 2002).

Here we present preliminary results of our SHRIMP geochronological study of a bentonite from the Paprotnia series and discuss them within the context of biostratigraphic constraints.

METHODS

The mineral composition of the bentonites was analysed using X-ray diffraction and thermal (Derivatograph) analysis. The %S in the I/S minerals was measured using Środoń's technique (1984). Paleotemperatures were calculated based on Šucha et al. (1993).

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The bentonite samples from several bentonite layers collected for zircon separation, c. 1 kg each, were dispersed in water and sieved. Minerals were separated using the conventional heavy liquid (sodium polytungstate) procedure. Careful examination under the polarizing microscope (Jurasik 2006) helped to select one sample (A) for SHRIMP dating. Hand-picked zircons of this sample were mounted in epoxy resin, and a polished section was used for optical microscopy, CL imaging, and SHRIMP analysis.

RESULTS

Bentonites: mineralogical data

The major clay minerals in the bentonites are kaolinite and I/S mixed-layer mineral, both occurring in similar proportion. Chlorite, smectite and illite have also been detected in two of six bentonite layers. The measurements of %S in I/S (20-30%, ordering R1-R3) testify that the maximum diagenetic paleotemperatures in these rocks attained c. 120-135^{O}C (August 2006).

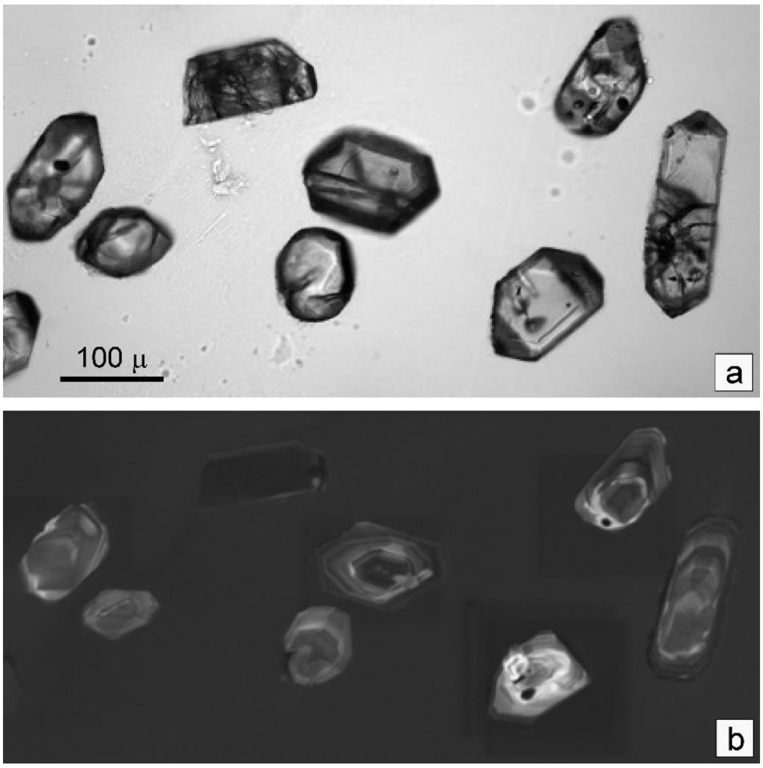

Fig. 1. Zircons from bentonite A. (a) transmitted plane polarized light, (b) CL image.

Zircon characteristics

The zircons in bentonite A are subhedral to euhedral, short- to normal-prismatic, colourless and transparent, with fairly common oval and needle-like inclusions (Fig. 1a). In cathodoluminescence (CL) images (Fig. 1b) they show regular "magmatic-type" zonation. ^{232}Th/^{238}U ratio is rather uniform, between 0.33 – 0.62, typical of igneous zircons. Portion of common ^{206}Pb is low, mostly between 0 and 0.7 %.

SHRIMP ages

Fifteen points in fifteen zircon grains have been analysed. Two points gave significantly older and fairly discordant (probably because of theirs low U content and high common lead: 0.7 and 2.2 %, respectively) ^{206}Pb-^{238}U ages of 405±10 and 413±14 Ma, and they apparently represent inherited materials. The remaining thirteen points (the main population) yielded ^{206}Pb-^{238}U ages scattered between 313±5 and 343±5 Ma (Fig. 2). The mean Concordia age calculated for nine points of the main population (excluding significantly younger and positively discordant one grain) is 334±4 Ma. An alternative interpretation is that the age of one single grain which is nearly perfectly concordant: 337±4 Ma (discordance D = –1 %) is the best approximation of the true magmatic age.

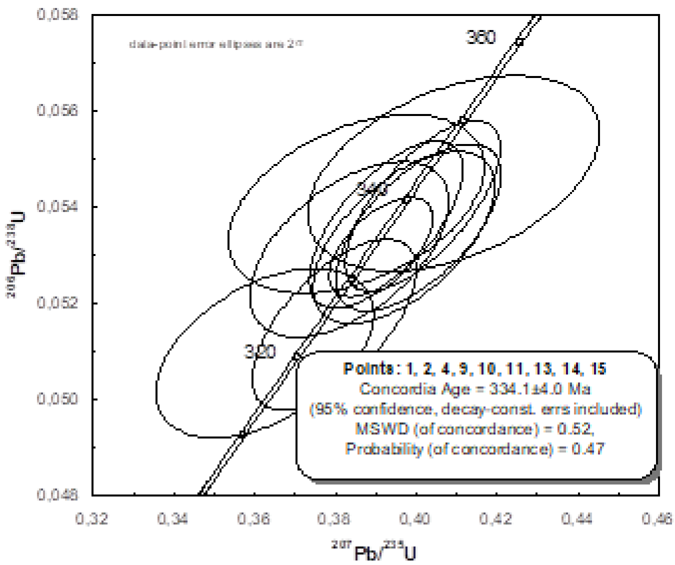

Fig. 2. Concordia diagram showing results of SHRIMP zircon analyses from bentonite A.

CONCLUSION

The preliminary SHRIMP ages of volcanic zircon grains from the bentonite studied fit well with the Viséan age based on biostratigraphic evidence. The radiometric ages for Upper Viséan (Asbian) in Central and West Europe have been derived mainly from ash layers, using U-Pb zircon IDTIM dating: 326.7± 5.2, and 325.6±4.3 Ma (Menning et al. 2000). Our data are fairly close, within analytical error, to those results. The new geochronological data from the bentonite further constrain volcanic activities in the region during Viséan times.

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SHRIMP U-Pb ZIRCON AGE FROM THE KARKONOSZE GRANITE

Abstract: The paper presents new results of dating by U-Pb high resolution ion microprobe technique, carried out on three zircon samples from the Karkonosze granite. The following ages have been acquired: 314 ± 4.5 Ma, 314.1 ± 3.3 Ma and 318.5 ± 3.7 Ma.
Keywords: Karkonosze granite, U-Pb SHRIMP dating, zircon typology

INTRODUCTION

The radiometric studies have been performed on the Karkonosze granite. Zircon grains have been selected from following five granite samples:

- medium-grained porphyritic granite (sample named MNA, taken from the "Fajka" rock in the area of Janowice Wielkie),
- fine-grained equigranular granite (KS1; "Huta" quarry in Szklarska Poręba – western wall),
- coarse-grained porphyritic granite (MSB; south of Radomierz),
- fine-grained equigranular "granophyric" granite (MSG; east of Góra Sokola and south-east of Trzcińsko),
- medium-grained equigranular granite (sample KM4B; granite from the heap in Miedzianka – the area of old drifts by the road Miedzianka – Ciechanowice).

The extracted zircons have been also subjected to typological analysis (Pupin, Turco 1972).

METHODS

The rock samples assigned for zircon extraction were carefully selected out of all the samples taken in the field, in order to assure representativity for several groups of rocks and different occurrence locations. The 22 samples of granitoids were chosen for zircon separation, including two granites from Miedzianka.

Isotopic dating of the chosen zircon grains from the five above-mentioned granitoid samples has been performed in the Research School of Earth Sciences ANU in Canberra. The ion microprobes SHRIMP II and SHRIMP RG were used for age determination. The zircon crystals, together with fragments of standard crystals

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FC1 and Sl13, have been mounted in epoxy resin. Each analysis consisted of six mass spectrum scans. The obtained results have been worked out by a procedure similar to described by Williams (1998), using SQUID Excel Macro programme (Ludwig 2001). The Pb/U value was normalized to 0.1859*$^{206}Pb/^{238}U$ in the FC1 standard and corresponds to the age of 1099 Ma (Paces, Miller 1989).

Extremely high content of uranium, thorium and radiogenic lead in majority of the zircon grains, turned out to be the basic problem in the analytical procedures. This factor made the dating process extraordinarily difficult.

RESULTS

Typological analysis of zircons and high amount of simple crystals, possessing only prism faces (the most frequently occurring morphotypes: P1, P2, P3, P4, G1) indicated sub-alkaline and high-alkaline environment of zircon crystallization (Pupin 1988).

The zircon dating by SHRIMP brought numerous problems. Their cause (in large number of grains) was too high concentration of uranium (reaching up to 4%) and also in some cases – increased content of ^{206}Pb. Thus, the reliable results have been obtained only for three of five assigned samples. For the zircons from the "Huta" quarry and the area to SE of Trzcińsko the analyses did not succeed.

Sample MNA – medium-grained porphyrytic granite (from „Fajka")

20 grains were selected from the sample. The majority of correct ages has been established from the central parts of the grains (cores of the crystals are usually not inherited) – with the highest U content. The measured points have been plotted on the Tera-Wasserburg concordia diagram (Fig. 1), at which one may, however, observe considerable point scattering. This effect is connected with the escape of radioactive lead. After exclusion of the analyses that did not fit to the concordia, the average $^{206}Pb/^{238}U$ age, which may be also interpreted as an age of the granite crystallization, has been calculated. **This age is 314.1±3.3 Ma.**

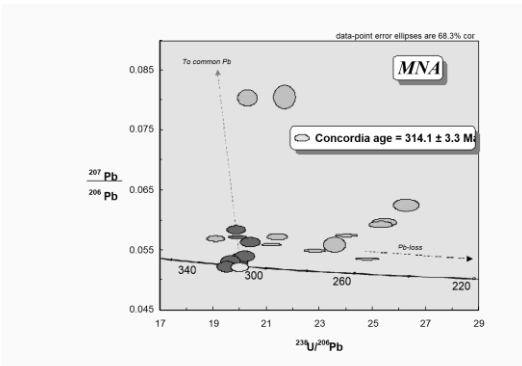

Fig.1 Tera-Wasserburg U-Pb concordia plot. The concordia age is shown as a white error ellipse representing the 95% confidence limit.

Sample MSB – coarse-grained porphyrytic granite (from Radomierz area)

The majority of zircons from this sample is characterized by magmatic zoning, however, visible mainly in the outer parts of the grains. It determined the location of the measuring points in the rims. More than 13 analyses have been performed, what allowed to establish the average age of the crystals as **318.5±3.7 Ma** (Fig. 2).

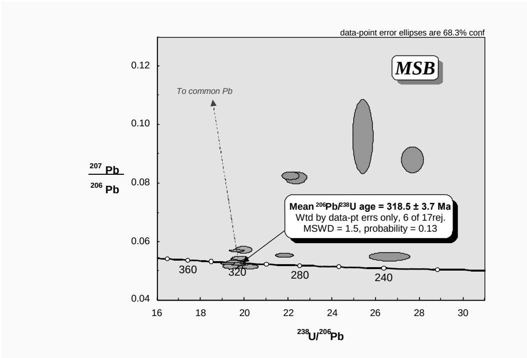

Fig. 2 U-Pb concordia plot of all zircon data from the sample MSB. The data are plotted uncorrected for common Pb.

Sample MNA – medium-grained equigranular granite (from Miedzianka)

The zircons from Miedzianka, similarly to the crystals from the former samples, are characterized by high concentration of uranium and numerous inclusions of opaque minerals. The measurements have been carried out on less alternated and brighter in the CL image cores of the grains and on, unfortunately, strongly changed and more rich in U rims. Extremely high content of ^{206}Pb resulted in the discrodance observed in more than 70% analyses (performed mainly at the grain rims) (Fig. 3). However, the correct results have been separately selected, what allowed for determination of the relatively consistent age of **314.9±4.5 Ma.** The correct analyses concern mostly the centres of the grains, what may cause some shift of the obtained age in the direction of (potentially) inherited material (Fig. 3).

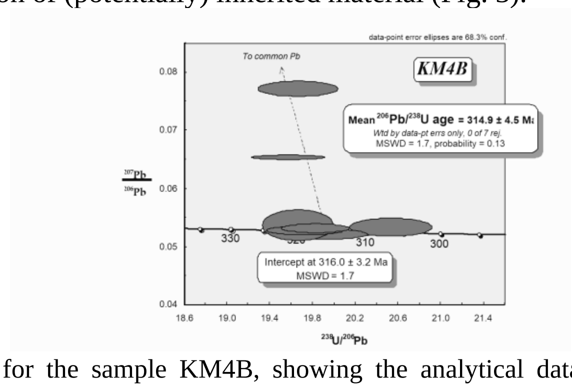

Fig. 3 U-Pb plot for the sample KM4B, showing the analytical data used to calculate a weighted mean U-Pb age as discussed in the text above. The data are plotted uncorrected for common Pb.

CONCLUSIONS

Despite the fact, that the reliable results have been obtained for the samples from the eastern part of the pluton, they correspond quite well with the ages obtained for the Karkonosze granite (including error limits) by the Rb-Sr isochrone (Pin et al. 1987, Duthou et al. 1991) and ^{40}Ar-^{39}Ar methods (Marheine et al. 2002). Referring to the unpresented here, abundant geochemical analyses (paper in progress), one may suppose that granites with considerable impact of mantle material (from the Radomierz area, 318.5±3.7 Ma) crystallized slightly earlier than the rocks rich in litophile elements. This thesis corresponds well with the earlier geochemical research in this area (Słaby, Martin 2005; Słaby et al. 2007) and the tectono-structural study of Mierzejewski (2002). Therefore, it draws the conclusion, that the northern and central parts of the pluton may be a little older than the south-eastern one.

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COMPILATION OF GEOTHERMOBAROMETRY AND THE KFMASH SYSTEM - AN EXAMPLE FROM WEDEL JARSLBERG LAND, SVALBARD

Abstract: Garnet-biotite geothermometer and GASP geobarometer were used to quantify P-T conditions of the metasedimentary Isbjørnhamna Group from the S part of Wedel Jarlsberg Land on Svalbard Archipelago. Results of geothermobarometry were compiled with KFMASH phase stability system. Such compilation allow for better understanding of rock forming P-T conditions.
Keywords: garnet-biotite geothermometer, GASP geobarometer, Spitsbergen

INTRODUCTION

The most useful tools of P-T estimations in metapelitic systems are well known garnet-biotite geothermometer and so called GASP (garnet-aluminosilicate-plagioclase) geobarometer. However, the use, of the over mentioned geothermobarometrical methods, is limited by presence of specific mineral assemblages in the investigated rock samples. In such cases, the use of quantitative petrogenetic grids is necessary. The aim of this paper was to present complementary use of geothermobarometry (calibrations of: Holdaway 2000 and Holdaway 2001) and the KFMASH system, proposed by Spear and Cheney (1989).

SAMPLES DESCRIPTION AND RESULTS

The Isbjørnhamna Group is composed of metapelites, paragneisses, calcite-mica schists and minor marble intercalations. Metapelites were chosen for geothermobarometrical investigations. Metamorphic zoning is clearly visible within the Isbjørnhamna Group metapelites. The lowest grade samples contain garnet and chloritoid but not biotite in the paragenesis. Second zone is distinguished by occurrence of garnet and biotite, and lack of any Al-saturated phases. Another zone is distinguished by presence of garnet, biotite and staurolite. Finally the highest grade samples reveal the presence of garnet, biotite, kyanite and somewhat staurolite. Such mineral assemblages are characteristic for relatively good quantified stability fields on the KFMASH petrogenetic grid.

To obtain more precise P-T conditions for some, of mentioned above metamorphic zones, garnet-biotite geothermometer and GASP geobarometer were used. Samples above chloritoid zone, but below staurolite zone yielded temperatures in range 530-550ºC. Samples from staurolite zone yielded temperatures in range

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580-600ºC. The most metamorphosed samples which contain kyanite in paragenesis yielded temperatures up to ca. 660ºC and pressures in range 8.7-11 kbar.

DISCUSSION

The use of both, geothermobarometry and the KFMASH system, allowed to precise the course of P-T paths of all paragenetic varieties of the Isbjørnhamna Group metapelites. It was assumed that samples collected from chloritoid zone were metamorphosed at temperature up to 520ºC and pressure up to ca. 6-7kbar. The same pressure but a little bit higher temperature (up to 550ºC) affected samples which contain garnet and biotite, but no Al-saturated phases. Samples with staurolite in paragenesis, but without kyanite had to be metamorphosed at temperature up to 600ºC and pressure around ca. 8-9 kbar. In contrast to the last zone, samples, in which kyanite was also found, had to form at the same pressure but at higher temperature (up to 650ºC). Finally, the samples which contain kyanite but no staurolite were metamorphosed under conditions of ca. 630-660ºC and ca. 11 kbar.

FINAL REMARKS

Complementary use of geothemobarometry and quantitative petrogenetic grids seems to be necessary in some specific cases, especially when mineral paragenesis does not allow using of unquestionable geothermobarometrical method. In such cases compilation of both provides more data about rock forming P-T conditions.

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MINERALOGIA POLONICA – SPECIAL PAPERS
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BIOMARKERS AND BIOMOLECULES PRESERVED IN THE MIDDLE JURASSIC FOSSIL CONIFER WOOD

Abstract: This work reports the occurrence of relatively high concentrations of aliphatic and polar abietanes and totaranes in a conifer woods: *Protopodocarpoxylon* and *Xenoxylon*, from the Middle Jurassic of Poland. The extracted phenolic abietanes like ferruginol and its derivatives (6,7-dehydroferruginol, sugiol, 11,14-dioxopisiferic acid) and phenolic totaranes (2-ketototarol), with simultaneous absence or a very small amount of tetracyclic diterpanes such as phyllocladanes, beyerane and/or kauranes, are characteristic for extant conifer families Cupressaceae s. l. and Podocarpaceae. The natural product terpenoids from the Middle Jurassic fossil woods are definitely the oldest polar biomolecules detected in geological samples.
Keywords: biomolecules, fossil wood, GC-MS, conifers, phenolic abietanes

INTRODUCTION

Polar terpenoids such as ferruginol, sugiol and other phenolic diterpenoids were reported predominantly from Tertiary conifers, sediments, resinites and lignites from different locations (e.g. Otto and Simoneit 2001). Here, we analyzed the extractable organic matter of the fossil woods *Xenoxylon phyllocladoides* Gothan from the Bathonian of the Polish Jura (south-central Poland) and Callovian of Łuków (eastern Poland), and *Protopodocarpoxylon* sp. from the Bathonian of the Polish Jura, where diverse fossil woods occur abundantly (see Philippe et al., 2006). Based on literature data, we compared this biomolecular composition with that of other fossil wood genera and modern conifer families.

MATERIALS AND METHODS

Ten fossil wood samples (nine from the Polish Jura and one from Łuków) were analyzed. Wood taxa were identified using normal transmitted light microscope and Hitachi S-800 scanning electron microscope. For organic geochemistry analyses, the

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fossil wood was pulverized and Soxhlet-extracted in pre-extracted thimbles with organic solvent (dichloromethane/methanol, 90:10 v/v). An aliquot of the total extract was converted to the trimethylsilyl derivatives by reaction with *N,O*-bis-(trimethylsilyl)trifluoroacetamide (BSTFA) and pyridine for 3 h at 70°C. Gas chromatography–mass spectrometry (GC-MS) analysis of the derivatized total extract was performed on a Hewlett-Packard model 6890 GC coupled to a Hewlett-Packard model 5973 quadrupole MSD. Separation was achieved on a fused silica capillary columns coated with DB5 (30m × 0.25 mm i.d., 0.25 μm film thickness) and DB35 (60m × 0.25 mm i.d., 0.25 μm film thickness). For GC-MS conditions see Marynowski et al. (2007).

RESULTS

The wood samples from Gnaszyn Dolny (Polish Jura) and Łuków are characterized by a very low range of maturity. The R_r for the samples from Gnaszyn are from 0.25-0.30%, and the vitrinite reflectance of the Łuków sample equals 0.33%. These values correspond to those of the brown coal maturity level. The extract of the Łuków and Gnaszyn samples of both *Xenoxylon phyllocladoides* and *Protopodocarpoxylon* wood specimens contains aliphatic lipids (*n*-alkanes, isoprenoids and *n*-fatty acids), sesquiterpenoids, diterpenoids, triterpenoids, steroids as well as aromatic hydrocarbons and polycyclic aromatic compounds. Major constituents of fossil wood extracts are diterpenoids of the abietane and totarane classes. Such polar diterpenoids as ferruginol, *2*-ketototarol or sugiol are common components of recent conifer resins (Otto, Wilde 2001) and the Palaeogene and Neogene brown coals (Otto, Simoneit 2001; Fabiańska 2007) but are rather sporadic in the Mesozoic wood and coals (Alonso et al. 2000; Marynowski et al. 2007). It is because they are thermally unstable and undergo further diagenetic transformations. The investigated *Xenoxylon* wood sample from Łuków is characterized by particularly rich composition of organic compounds of the diterpenoids group (Fig. 1). The main compound in the analyzed extract is ferruginol, the concentration of which is 39.3 μg/gTOC. Quantitatively significant are also dehydroabietane (14.3 μg/gTOC), hinokiol (9.8 μg/gTOC), 2-ketototarol (7.6 μg/gTOC) and sugiol (4.3 μg/gTOC). Such diterpenoids as dehydroabietol, 18-norferruginol, 12-hydroxysimonellite and hinokiol (Fig. 1) are described for the first time in such an ancient material, as the Middle Jurassic *Xenoxylon* wood samples (Marynowski et al. submitted). Among the sesquiterpenoids, cadalene (19.9 μg/gTOC) dominates. Slightly minor quantitative abundance of other sesquiterpenoids, as calamene (8.62 μg/gTOC), cadina-1(10),6,8-triene (8.64 μg/gTOC) and dihydro-*ar*-curcumene (1.01 μg/gTOC), are also noticed. In comparison to the Łuków wood sample, the Gnaszyn fossil wood samples are characterized by a worse preservation state of polar biomolecules. Nonetheless, in these samples, the same compounds occur as well, and sugiol is the main compound of the extract.

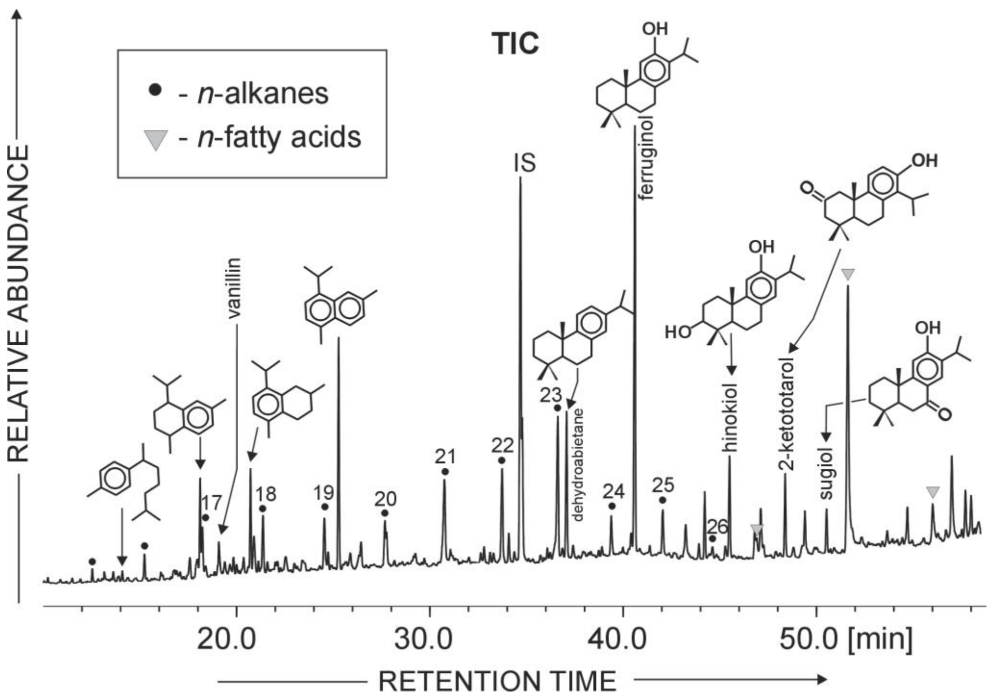

Fig. 1. Total ion chromatogram of solvent extract (TMS derivatives) of the Middle Jurassic *Xenoxylon phyllocladoides* wood from Łuków (Poland). Numbers indicate the number of carbons in the aliphatic lipid series. IS – internal standard.

DISCUSSION AND CONCLUSIONS

The majority of diterpenoids detected in the Middle Jurassic fossil woods *Xenoxylon phyllocladoides* (see Marynowski et al. submitted) and *Protopodocarpoxylon* sp. (Marynowski et al. 2007) are unaltered biomolecules, similar to those observed in extant higher plants. Such phenolic abietanes like ferruginol, 6,7-dehydroferruginol, sugiol, hinokiol or 2-ketototarol are produced currently only by distinct conifer families (Cupressaceae s. l., Podocarpaceae and Araucariaceae) and are used as their characteristic biomarkers. However, an araucarian affinity of the investigated woods may be ruled out, since Araucariaceae are characterized by the presence of tetracyclic diterpanes, such as phyllocladanes, beyerane and/or kauranes as major compounds (Hautevelle, unpublished data). The presence of totarane class biomarkers with a relative high abundance in the Łuków and Gnaszyn samples also attests that the Araucariaceae origin is unlikely, because totaranes have never been reported in Araucariaceae (Otto, Wilde 2001). As it was reported by Marynowski et al (2007) the natural product terpenoids from the Middle Jurassic fossil woods are definitely the oldest polar biomolecules detected in geological samples.

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MINERALOGIA POLONICA – SPECIAL PAPERS
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ORIGIN OF XENOLITHS FROM THE WINNA GÓRA BASALT (SW POLAND)

Abstract: Basalt occurrence on Winna Góra near Jawor originated during older episode of Tertiary volcanism in Poland. Chemical composition of minerals forming peridotitic xenoliths suggests complex history of ascending and/or metasomatism. Pyroxenitic and gabbro xenoliths may represent part of mafic layered body situated on the mantle – crust boundary. Clinopyroxenite and gabbro may also be cumulates from the host magma, the websterite might be a part of pyroxenitic vein from the upper mantle. Almost all types of xenoliths suffered from melting during ascent.
Keywords: Jawor, basalt, mantle xenoliths, mafic xenoliths

INTRODUCTION

Basalt occurrence on Winna Góra near Jawor (SW Poland) belongs to Bohemo – Silesian Belt of Tertiary Central European Volcanic Province (CEVP). Two main phases of volcanism occurred in the area of Lower Silesia: the older (33.7 – 31.3 Ma; Eocene/ Oligocene) and the younger (24.5 – 21 Ma; Oligocene/ Miocene; Badura et al., 2006). Age determinations of Birkenmajer et al. (2002) on basalt from Winna Góra gave 21.62 ± 0.93 and 21.96 ± 1.36 Ma.

In the Winna Góra basalt scarce, minute (< 5cm) xenoliths (dunite, harzburgite, lherzolite, websterite, gabbro and clinopyroxenite) occur.

PETROLOGY AND MINERAL CHEMISTRY OF XENOLITHS

Xenoliths from Winna Góra consist of olivine ± clinopyroxene ± orthopyroxene. They have protogranular texture sensu Mercier & Nicolas (1974), in some olivine crystals rare kink – bands occur. Elongated or oval pools (<200 μm) consisting of younger generation of clinopyroxene, spinel, plagioclase ± olivine occur between the primary phases. Clinopyroxene occurring in gabbro has spongy structure due to voids (<100 μm) filled with plagioclase and olivine.

The main constituent of dunite is olivine (Fo 89 – 82%, Ca < 300 – 1450 ppm, NiO 0.11 – 0.43 wt.%). In olivine occurring (together with spinel, clino- and orthopyroxene) in pools the Fo content varies from 82 to 85% (Ca 750 – 1800 ppm, NiO 0.19 – 0.35 wt.%). Clinopyroxene (#mg {[Mg/(Mg+Fe_{total})]*100} varying from 88 to 82) contains 20 - 23 wt.% of CaO, in orthopyroxene (Al_2O_3 0.5 – 0.6 wt.%) the #mg is about 86. The #cr ([Cr/(Cr+Al)]*100) in spinel is 74 – 78.

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Fo content in olivine forming lherzolite varies from 75 to 80 % (Ca< 300 – 1300 ppm, NiO 0.22 – 0.37 wt.%), #mg in clinopyroxene is 0.86 (CaO 23 wt.%) and in orthopyroxene 0.83 (Al_2O_3 0.6 – 0.74 wt.%). Spinel #cr is 0.73-0.76.

Olivine forming harzburgite contains 82 – 88% of Fo (Ca< 300 – 1700, NiO 0.2 – 0.5 wt%), the #mg in orthopyroxene is 85 – 87 (Al_2O_3 0.9 – 1.6 wt.%), #cr in spinel is variable from 0.5 to 0.7. Younger olivine (Fo 80 – 85, Ca 600 – 1500 ppm, NiO 0.09 - 0.3 wt.%) occurs in pools together with clinopyroxene (#mg 0.80 - 0.91, CaO 18 – 23 wt.%) and spinel (#cr 0.8 – 0.86).

Websterite consists of orthopyroxene (#mg 0.74 - 0.84, Al_2O_3 1.2 - 3.9 wt.%) and clinopyroxene (#mg=0.86, CaO 21 – 23 wt.%). Clinopyroxene occurring in pools together with olivine (Fo 71 – 78, Ca 1400 – 2300 ppm, NiO 0.01 – 0.06 wt.%) contains from 19 to 21 wt.% of CaO (#mg=0.86).

Clinopyroxene forming clinopyroxenite contains 23 – 24.5% of CaO, #mg is variable from 0.71 – 0.87.

Gabbro consists of clinopyroxene (#mg=68 – 74, CaO 19 – 22 wt%) and plagioclase (An 40 – 56%). An content in plagioclase occurring with olivine (Fo 64 – 70, CaO 1600 – 2200 ppm, NiO 0.02 – 0.09 wt%) in voids in clinopyroxene varies from 0 to 24%.

ORIGIN OF WINNA GÓRA XENOLITHS

The relationships between Al(IV) - Al(VI) in clinopyroxene suggest equilibration pressures characteristic for volcanic rocks, with the exception of websterite (Fig. 1a). Temperatures of primary clino- and orthopyroxene equilibration (Brey and Köhler algorithm) are 850-880°C (lherzolite, dunite) and 960-990°C (websterite).

Chemical composition of minerals forming xenoliths from Winna Góra is different than that typical for minerals which crystallized under mantle - conditions (eg. Fo and NiO content in Ol). Data from olivine from all the types of xenoliths fit well to cumulate (FeO/MgO)/NiO trend set for cumulate xenoliths from Carpathian – Pannonian region (Fig 1b; Kovács et al. 2004) despite relatively high content of Fo in olivine from peridotites. The content of Cr_2O_3 (Fig. 1c) in clinopyroxene forming the xenoliths is similar to those from Adak Island (after Kovács et al. 2004). Clinopyroxene forming dunite, harzburgite and lherzolite has Cr_2O_3 >1 wt.% and low TiO_2 and Al_2O_3 content which strongly suggest that the mineral is of mantle origin.

Composition of olivine and clinopyroxene from peridotites suggests that the xenoliths are of mantle origin, but record complex metasomatic or magma ascent history. The processes let to change in mineral composition and lowered estimated pressures and temperature of equilibration.

Gabbro and clinopyroxenite are cumulates of basaltic magma. Websterite may be a mafic cumulate too, but high temperatures and pressures of equilibration and presence of younger pools suggest that it rather represents pyroxenenite veins crystallised in upper mantle.

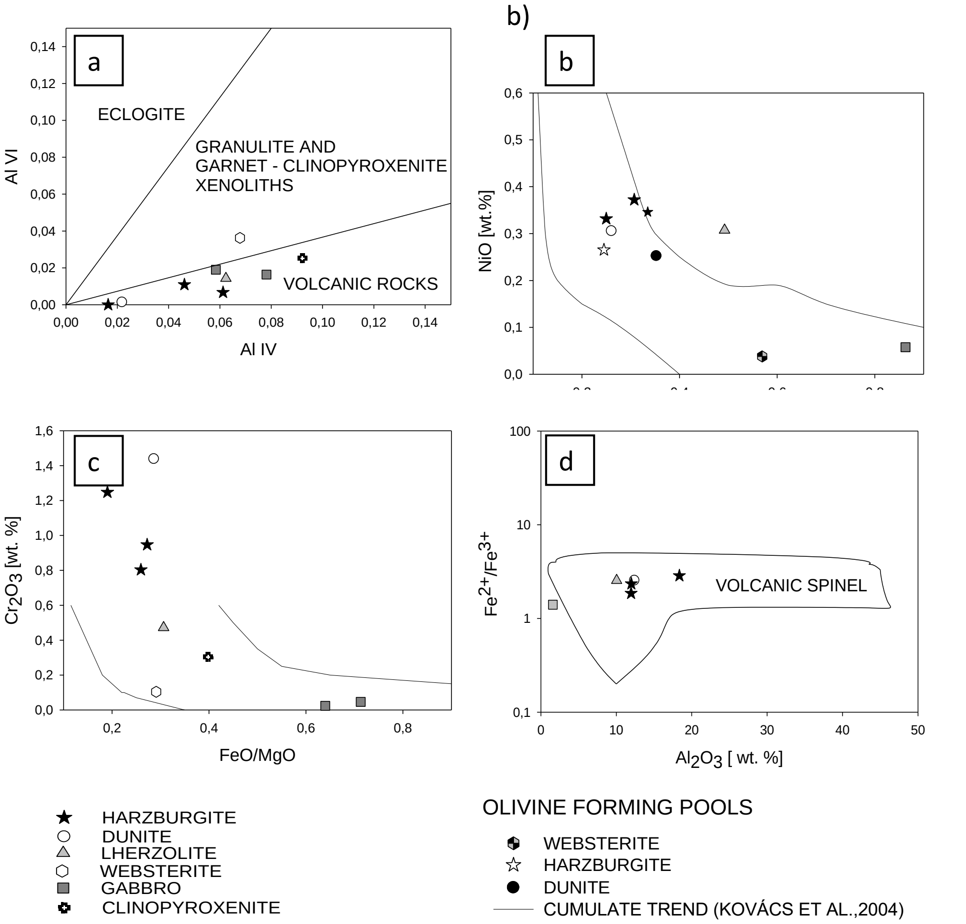

Fig.1 Chemistry of minerals forming xenoliths from Winna Góra: a) pressure estimation on Al (IV) – Al (VI) in clinopyroxene diagram (Aoki and Shiba 1973); b) composition of olivine on the (FeO/MgO)/NiO; c) composition of clinopyroxene on (FeO/MgO)/Cr_2O_3; d) composition of spinel on Al_2O_3/(Fe^{2+}/ Fe^{3+}) diagram (Kamenetsky et al. 2001).

Minerals occurring in pools have features which suggest their volcanic origin (ex. high, about 1000 ppm, Ca content in olivine, Al_2O_3/TiO_2 and $Al_2O_3/(Fe^{2+}/Fe^{3+})$ ratios in spinel; Fig.1d). The pools are probably an effect of xenoliths melting during the host lava ascent.

Peridotite xenoliths formed by minerals similar to those from Winna Góra have never been described in Lower Silesia.

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MINERALOGIA POLONICA – SPECIAL PAPERS
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THORIUM AND REE MINERALS IN PEGMATITE FROM PODGÓRZYN (KARKONOSZE MASSIF) – PRELIMINARY REPORT

Abstract: The investigation of pegmatite near Podgórzyn showed the presence of cheralite, xenotime and thorite. Cheralite occurs in two forms, varying from each other by the type of occurrence and the content of $CaTh(PO_4)_2$ end member. Thorite and xenotime are common accessory minerals in Karkonosze pegmatites, whereas from that localization cheralite was described for the first time. Analyses of all minerals described suggest that they are hydrated.
Keywords: cheralite, thorite, xenotime, pegmatite, Karkonosze, Podgórzyn, mineralogy

INTRODUCTION

Past researches of pegmatites found in Karkonosze granitoid were centered on Szklarska Poręba region and its neighborhood (Michałowice, Jakuszyce); sparse researchers did studies of pegmatites from other regions in Karkonosze massif (Karwowski, Kozłowski 1972). Kozłowski determined the homogenization temperature of inclusions un quartz from pegmatites in the studied area as cited: T_h=380-580 °C (Kozłowski 1978).

Pegmatites from Podgórzyn, near Jelenia Góra, are a relatively poorly known group of Karkonosze pegmatites. Formerly, similarly to other pegmatites from that area, were exploited due to their utility in the ceramic industry. After the exploitation was stopped in 19 th century, were completely forgotten and weren't an object of researches until recently.

The pegmatite, which derive minerals described below from, is formed as a socket with a few meters in diameter, situated in porphyrous granite. It mostly consists of K-feldspar, albite, quartz and biotite; zircon, rutile, ilmenite, thorite and REE phosphates are accessory minerals.

METHODS

The chemical composition of minerals was analysed by means of a CAMECA SX-100 microprobe in Inter-Institution Laboratory for Microanalysis of Minerals and Synthetic Substances at the Faculty of Geology, Warsaw University. Analyses of cheralite (Sn19 sample) and xenotime were done with 20 kV accelerating voltage and 20-50 nA beam current. Cheralite (Sn22 sample) and thorite samples were analysed under conditions of 15kV accelerating voltage and 10-20 nA beam current.

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RESULTS

Table 1. Electron microprobe data (in wt.%) REE-Y-Th minerals.

	Cheralite–(Nd)		Thorite	Xenotime-(Y)
Components	Sn19	Sn22	Sn13b	Sn21b
P_2O_5	25.80	23.56	4.17	33.54
SiO_2	0.45	0.89	14.60	1.16
ZrO_2	n.a.	2.64	5.78	n.a.
ThO_2	6.98	48.49	46.08	n.a.
UO_2	0.54		1.39	1.11
Al_2O_3	n.a.	0.66	0.71	n.a.
Y_2O_3	0.87	0.80	4.58	39.50
La_2O_3	13.46	2.24		
Ce_2O_3	12.18	n.a.		
Pr_2O_3	4.32		n.a.	
Nd_2O_3	15.19	2.62		0.33
Sm_2O_3	2.44	n.a.	n.a.	0.98
Gd_2O_3	1.10	n.a.	n.a.	3.67
Tb_2O_3		n.a.	n.a.	0.90
Dy_2O_3		n.a.	n.a.	6.59
Ho_2O_3		n.a.	n.a.	1.33
Er_2O_3		n.a.	n.a.	4.22
Yb_2O_3		n.a.	0.26	3.91
Lu_2O_3		n.a.	n.a.	n.a.
MgO	n.a.	n.a.		n.a.
CaO	5.27	5.89	1.38	n.a.
MnO	n.a.		n.a.	n.a.
FeO	n.a.	0.35		
PbO		n.a.	n.a.	
Total	88.57	88.13	78.92	97.24
$ThSiO_4$	0.020	0.043	0.805	0.039
(La–Sm)PO_4	0.678	0.089		
Y(Gd–Lu)PO_4	0.032	0.021	0.170	0.975
Th(Ca,U)$(PO_4)_2$	0.269	0.858		

Note: n.a. - not analysed; Zr, Al, Fe included into Th(Ca,U)(PO_4) member

Cheralite-(Nd)

Cheralite occurs in two forms:

(1) Euhedral grains of 20-30 μm found in mica. The mineral is a dominant member of monazite – cheralite system and consists 86 mole % of Th(Ca,U)$(PO_4)_2$ group. The studied crystal is probably metamictised, because it underwent destruction during the analyse, despite of use of a large beam spot. Metamictisation the mineral and the resulting hydratation is, as well as the presence of voids and microcaverns a probable reason for not reaching 100% in analysis. An approximate formula is:
$Th_{1.01}(Ca_{0.58}Zr_{0.12}Nd_{0.09}La_{0.08}Al_{0.07}Y_{0.04}Fe_{0.03})[(P_{0.91}Si_{0.04})O_4]_2$ (based on 8 oxygen atoms per formula unit; see: Sn22 sample).

(2) Random clusters of acicular crystals with its maximum size of 20 µm in mica. The investigated mineral formed fine intergrowths with mica, thus is very probable that the analyzed material was contaminated by the host one. The analysis didn't reach 100% as well, probably due the presence of mica intergrows.
$(Ca_{0.25}Nd_{0.24}La_{0.22}Ce_{0.19}Th_{0.07}Pr_{0.07}Sm_{0.04}Y_{0.02}Gd_{0.02}U_{0.01})(P_{0.95}Si_{0.02})O_4$ (based on 4 oxygen atoms per formula unit; see: Sn19 sample).

Thorite

The mineral as anhedral crystals of 20-110 µm, intergrown with zircon. The studied crystal is a solid solution of $ThSiO_4$–YPO_4 with the content of the $(Y,REE)PO_4$ (xenotime member) of 17 mole %. Microprobe analyses of thorite, due to difficulties in analysing, yield totals lower then 100%, as it was extensively discussed in references publications (e.g. Johan, Johan, 2005; Förster 2006)
That state is caused by various factors, from which probably the most important in the investigated case are: the presence of molecular water or hydroxyl groups substituting silicium and the presence of voids and microcaverns as well (Förster 2006). The approximate formula of the analysed thorite is:
$(Th_{0.58}Zr_{0.16}Y_{0.14}Ca_{0.08}Al_{0.05}U_{0.02})(Si_{0.81}P_{0.2})O_4$ (based on 4 oxygen atoms per formula unit; see: Sn13b sample).

Xenotime-(Y)

Xenotime is present as euhedral grains reaching 700 µm size, mostly included in K-feldspar or, less frequently, in quartz. Low totals suggest the hydratation of the analysed xenotime. The approximate formula of xenotime-(Y) is given below:
$(Y_{0.73}Dy_{0.07}Er_{0.05}Gd_{0.04}Yb_{0.04}Sm_{0.01}Tb_{0.01}Ho_{0.01}U_{0.01})(P_{0.98}Si_{0.04})O_4$ (based on 4 oxygen atoms per formula unit, see Sn21b sample).

CONCLUSIONS

Podgórzyn near Jelenia Góra is the first known occurrence of cheralite in the Karkonosze massif. It is present in two forms, varying in the chemical composition and type of occurcence. The two investigated grains have different chemical composition, the firs one close to monazite and the second one is almost pure $CaTh(PO_4)_2$, i.e. the presently discarded brabantite (Fig. 1).

Thorite and xenotime are common accessory minerals in pegmatites of the Karkonosze granitoid, mentioned in many works (e.g. Gajda 1960), though none detail chemical analyses weren't published until now. Most of the studied minerals REE-Y-Th are probably metamictised and hydrated.

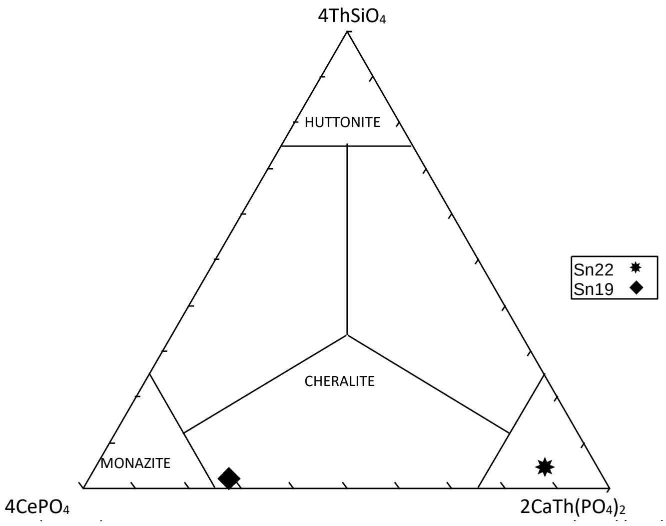

Fig. 1. The situation of studied samples in $CePO_4$-$CaTh(PO_4)_2$-$ThSiO_4$ system (based modified from Bowie & Horne, 1953). In calculating end-member proportions, the contents of other REE and Y are included into Ce amount, and the contents of U, Pb, Zr, Fe and Al are included into the $CaTh(PO_4)_2$ group (Förster 1998).

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MINERALOGIA POLONICA – SPECIAL PAPERS
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Štefan MÉRES[1], *Peter IVAN*[1]

NEW FINDINGS OF VANADIUM-BEARING MINERALS IN THE LATE PALEOZOIC CRYSTALLINE COMPLEX OF THE TATRIC UNIT (WESTERN CARPATHIANS, SLOVAKIA) AND THEIR PETROGENETIC SIGNIFICANCE

Abstract. The Late Paleozoic metamorphosed sedimentary rocks from the Strážovské vrchy Mts. (Tatric Unit, Western Carpathians) are represented by gneisses, graphitic gneisses and metacherts. Metacherts are primary enriched in V (~ 1000 ppm), U (~10 ppm) and HREE. The regional metamorphism of this V-rich sedimentary protolith produced in metacherts V-rich micas (roscoelite) and V-rich tourmaline. Occurrence of vanadium-bearing minerals and chemical composition of the metacherts indicate the deposition of metachert protolith under extremely anoxic conditions. Trace element distribution and common occurrence of metacherts with metabasites close to N-MORB type in the Strážovské vrchy Mts. indicate the ocean floor sedimentary environment for the protolith of the metacherts close to the active oceanic volcanic spreading centre producing basalts of N-MORB type.
Keywords: metacherts, roscoelite, vanadium dravite, Western Carpathians

INTRODUCTION

Micas are phyllosilicates and its simplified formula can be written as: I $M_{2\text{-}3}\,\square_{1-0}\,T_4\,O_{10}\,A_2$, where I is commonly Cs, K, Na, NH_4, Rb, Ba, Ca, M is commonly Li, Fe (di- or trivalent), Mg, Mn (di- or trivalent), Zn, Al, Cr, V, Ti, □ represents a vacancy, T is commonly Be, Al, B, Fe (trivalent), Si, and A is commonly Cl, F, OH, O (oxy-micas), S (Rieder et al. 1998). Dioctahedral mica with a dominance of V^{3+} replacing octahedral Al^{3+} is known as roscoelite ($K(V^{3+}, Al,Mg)_2AlSi_3O_{10}(OH)_2$; Roscoe 1877).

The tourmaline mineral group is a complex silicate of aluminium and boron, but because of isomorphous replacement (solid solution), its composition varies widely with sodium, calcium, iron, magnesium, lithium, vanadium, and other elements entering into the structure (Franklin, Rosenberg 1979; Deer et al. 1992). Tourmaline with a dominance of V^{3+} is known as vanadium dravite with formula $(NaMg_3V_6Si_6O_{18}(BO_3)_3(OH)_4$. The unusually vanadium-rich tourmaline coexisting with quartz, graphite, barium-vanadium muscovite, and biotite were found in the quartz graphite schist (Snetsinger 1966). An occurrence of V rich micas and V rich tourmaline we indentified in metacherts from the Pre-Alpine basement of the Strážovské vrchy Mts., near the village Chvojnica (Fig. 1).

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GEOLOGICAL SETTING

The geological setting of the Pre-Alpine basement of the Strážovské vrchy Mts. is illustrated on Fig. 1. Gneisses, graphitic gneisses and metacherts represent metamorphosed sedimentary rocks of this area. They underwent the Variscan regional metamorphism in amphibolite facies conditions (Hovorka, Méres 1991). The metachert occurrence is related to a metabasalts body in the Malá Magura Mts. Metacherts under study display schistose structures, dominantly granoblastic texture and are dark grey to black in colour. Quartz, metamorphosed organic matter, plagioclase, and white micas are common mineral components, tourmaline and ore minerals are relatively rare.

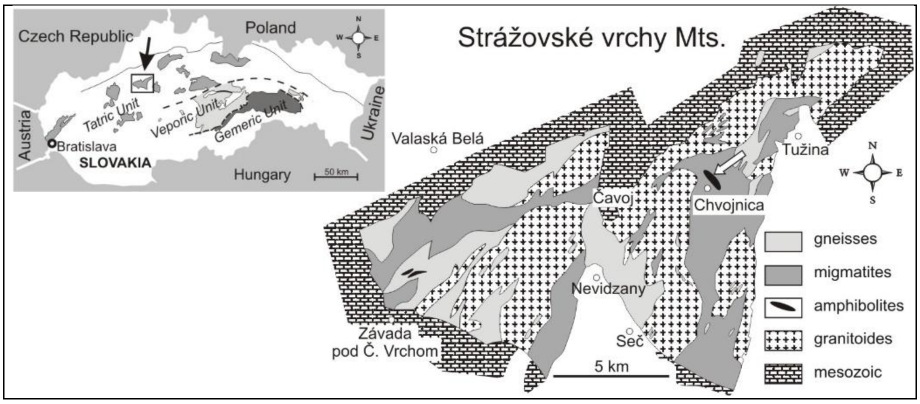

Fig. 1. Schematic geological map of the Strážovské vrchy Mts. with location (arrow) of the V-bearing mineral occurrence.

CHEMICAL COMPOSITION OF THE V-BEARING MINERALS

Roscoelite forms macroscopically identifiable aggregates with green pearly lustre and foliaceous to fibrous habit up to 2 mm in size in metacherts. Its appearance under microscope is light green in colour and displays yellow to pale-green pleochroism.

Vanadium contents in the micas from metachert vary from 1 to 21wt% and substitution V for Al is apparent (Fig. 2). Also elevated contents of Cr (up to 2.8 wt%) have been found in the V-rich sectors of micas. Vanadium-rich tourmaline is green in colour and yellow-green pleochroism is typical. Vanadium content in this mineral is about 3wt%. Compositional inhomogenity in both the V-bearing minerals is indicated by BSE images and quantitative compositional X-ray maps (Fig. 2, 3).

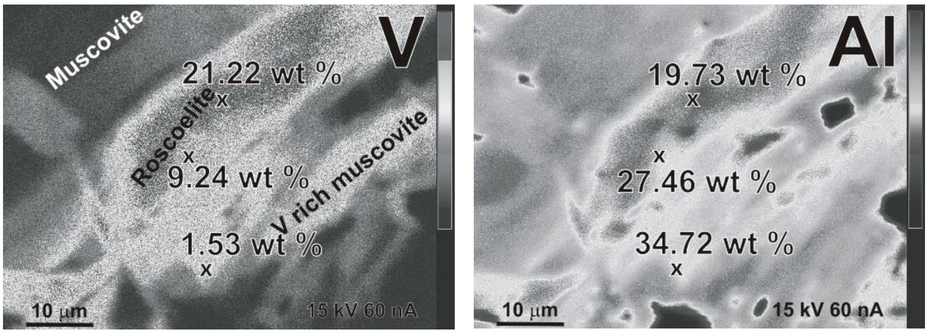

Fig. 2. BSE images and quantitative compositional X-ray maps of the Al and V in vanadium micas from Stražovské vrchy Mts.

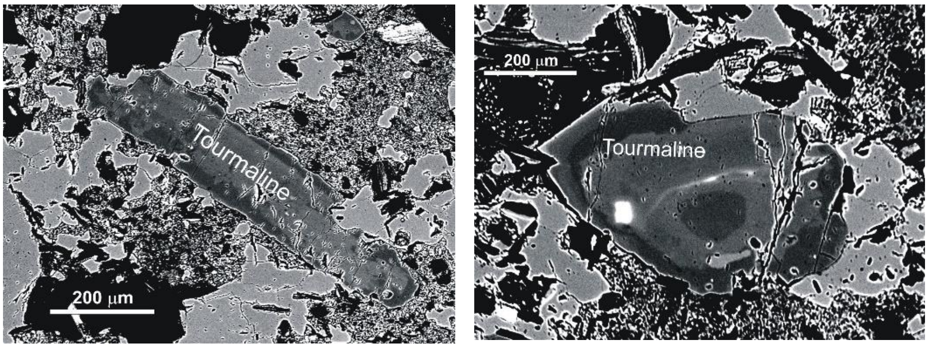

Fig. 3. BSE images of the zoned vanadium rich tourmaline from Stražovské vrchy Mts.

GEOCHEMISTRY OF THE METACHERTS

High contents of SiO_2 (~85 wt%) and C_{org} (8-10 wt%) as well as low contents of Al_2O_3 (~3 wt%), FeO (<0.3 wt%), MgO (<0.3 wt%), CaO (~0.01 wt%), Na_2O (~0.02 wt%) and K_2O (~1 wt%) are typical for metacherts. Primary enrichment in V (~1000 ppm), U (~10 ppm) and HREE together with low contents Ti and Sr are also characteristic for such type of rocks (Fig. 5).

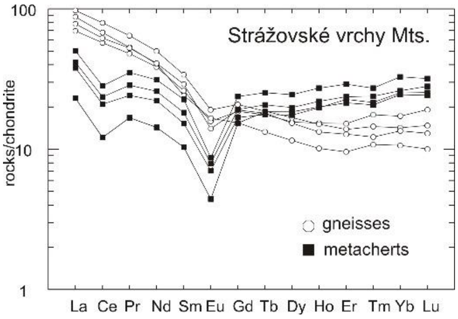

Fig. 4. The normalized REE patterns of the gneisses and metacherts.

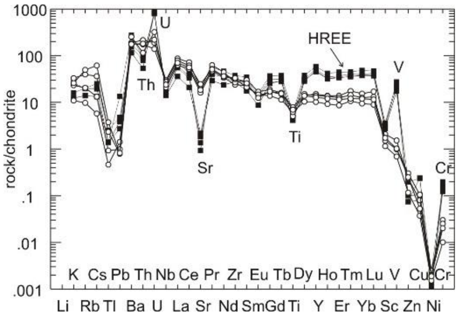

Fig. 5. The multiple elements normalized patterns of the same rocks as on the Fig.4.

Chromium content in metacherts is about 150 ppm. Chondrite normalized REE patterns display typical negative Ce anomaly, negative Eu anomaly, low La_N/Yb_N ratio and high contents of the HREE (Fig. 4). Considerably different REE distribution in metacherts and gneisses reflects differences in protolith and sedimentary environment for both rock types. The protolith of gneisses were greywackes/lithic arenites (Hovorka, Méres 1991).

RESULTS AND INTERPETATIONS

High vanadium content in mother rocks of micas provides important clues for evaluation of the original petrographic character and sedimentary environment of these rocks. Vanadium-rich micas and V-rich tourmaline were formed by regional metamorphism of originally V-rich sedimentary material. Occurrence of V-bearing minerals and U, Th, Cr and V enrichment in metacherts together with specific REE distribution (negative Ce anomaly) provides strong evidence for deposition under extremely anoxic conditions. Low Ti and Sr contents in metacherts suggest chemical/biochemical origin of their protolith. Common occurrence of metacherts and metabasalts of N-MORB type in the Strážovské vrchy Mts. and also some geochemical ratios (Th/U, La/Sc, La/Y, La/Ce, Th/Sc, Th/Yb, Ta/Yb) indicate that the original sedimentary environment of the metacherts was the ocean floor and that sedimentation was accompanied with rift volcanism producing basalts of N-MORB type. All mentioned geochemical results point to identical sedimentary environment for metacherts and metabasalts from Strážovské vrchy Mts. and from the Pernek Group in the Malé Karpaty Mts. (Méres 2005).

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Stanisław Z. MIKULSKI[1]

GOLD IN ARSENIC ORE FROM THE MIEDZIANKA COPPER DEPOSIT (RUDAWY JANOWICKIE MOUNTAINS)

Abstract: Gold was found in arsenopyrite ore from the Miedzianka copper deposit. Geochemical analyses revealed Au concentration in As-sulphide ore from 0.2 to 5.5 ppm, and its strong correlation with Co and As. In gold-bearing arsenic ore an increase of Co contents up to 0.3 % was determined. Massive, cataclased arsenopyrite is overprinted by base metal sulphides (mainly chalcopyrite and sphalerite) and carbonate. Microscopic gold occurs as very fine electrum inclusions within arsenopyrite, which contained constant Co admixtures up to 0.7 wt%.
Keywords: gold, arsenopyrite ore, Miedzianka Cu deposit, Rudawy Janowickie, Sudetes

INTRODUCTION

In the Western Sudetes gold was commonly extracted during metallurgical processes of arsenic ores (*e.g.* Złoty Stok, Radzimowice). According to Dziekoński (1972) arsenic was also product from the arsenopyrite-chalcopyrite ore from the Miedzianka-Ciechanowice metallurgical plants. However, no precise data about gold production from this ore district is known.

METHODS OF INVESTIGATION

Gold, arsenic and other elements were determined by application of the G/FASS (Au) and XRF methods in the Central Chemical Laboratory of the Polish Geological Institute. Microprobe analyses have been carried out in PGI in selected thin sections containing various ore minerals. The considered samples were analyzed by use of the Cameca SX-100 electron probe microanalyzer equipped with 3 wavelength-dispersive spectrometers. The operating conditions were: acceleration voltage - 20 kV, beam current - 100 nA and beam diameter – 2 μm. Natural and artificial materials have been used as standards (e.g. asp-57; asp-200).

THE MIEDZIANKA-CIECHANOWICE Cu MINING DISTRICT

In the northern part of the Rudawy Janowickie Mts. rich polymetallic sulphide mineralization dominated by copper ores occurred. Ore mineralization appears within numerous, but rather small quartz veins which cut Lower Paleozoic volcanic-metasedimentary rocks (Schneiderhőhn 1941; Zimnoch 1978). These rocks were metamorphosed first to amphibolite and later to retrograde green-schists facies condition. They are classified to various lithotectonic units (e.g. Teisseyre 1968; Kozdrój 2003). Four main vein systems are distinguished with different dip and strike directions. The directions of W-E and NW-SE are dominant. Veins are usually steeply deep (70-80°) to N, or to S and SE. They have variable

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thickness and length along the strike (<200 m), and along the depth (100-120 m). In most cases, veins are from 5 to 10-30 cm thick (max. 3 m). The main ore mineral was chalcopyrite. There also appear: chalcocite, bornite, covellite, malachite, tetrahedrite, bornite, arsenopyrite, sphalerite, galena, pyrite, pyrrhotite, uraninite, and nasturane and numerous rare minerals such as argentite or proustite (Schneiderhöhn, 1941; Zimnoch, 1978). Among the gangue minerals, quartz dominates, being associated with chlorite, hornblende, diopside, epidote, barite and calcite.

GEOCHEMICAL INVESTIGATION OF GOLD

30 samples were collected from the mining wastes in the Miedzianka area. In the mineralized and barren rock samples the arithmetic average of gold and silver content is 0.25 ppm (n = 30 samples; range <1 ppb to 5.5 ppm) and 17.4 ppm (range 0.5-230 ppm), respectively (Fig. 1). Gold-bearing As ores contain massive arsenopyrite which occurs as coarse-grained cataclased euhedral crystals, aggregates and single fine-grained euhedral crystals. An average ratio of gold to silver is very low (<1:1000). In ore samples with higher gold contents (>0.5 ppm) the Au:Ag ratios is from 2:1 to 1:25. In general, a higher Au concentration in the sample is correlated with higher Au to Ag ratios. Gold has a strong correlation with cobalt (r = 0.96), arsenic and CaO (r = 0.50 and 0.26, respectively). Gold has no correlation with bismuth. Bismuth revealed a positive correlation with Pb and Cu (r = 0.64 and 0.48, respectively) that indicates a presence of Bi-sulphosalts, what was earlier documented during microscopic studies by Zimnoch (1978). Silver has a positive correlation with Pb, Cu, Sr, Y, Zr and CaO. Total base metals content in sulphide ores may reach 20 %, however, Cu dominates over Zn and Pb content. Arsenic maximum concentration was *ca*. 16 wt % (arithmetic average – 1.9 % As for n = 30 samples).

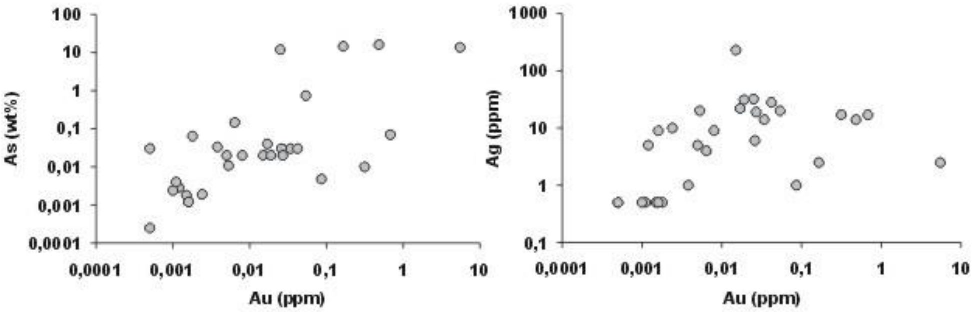

Fig. 1. The variation logarithmic plots of Au *vs.* As and Au *vs.* Ag in samples from the Miedzianka Cu deposit

MICROPROBE INVESTIGATION OF GOLD AND ARSENOPYRITE

Gold as electrum inclusions in arsenopyrite was found during microscopic studies under the reflected light. Electrum inclusions are rare and have sizes below 5 μm (Fig. 2A). Microprobe investigation of electrum indicates for its chemical composition of Au and Ag content from 60.7 to 63.4 wt % and from 34.8 to 36.3 wt%, respectively (table 1). Arsenopyrite coarse-grained euhedral crystals and of pile habit (*ca.* 0.5 mm in size) have As content from 45.1 to 47.9 wt %. An arithmetic average is 46.4 wt% As (n = 10) and is close to the stochiometric value.

Table 1. Arsenopyrite and electrum chemical compositions (in wt%) from the Miedzianka deposit

	Arsenopyrite		Electrum	
	Aver. Cont.	Range	Aver. Cont	Range
As	46.4	45.14–47.93	-	-
Fe	34.7	33.58–33.73	-	-
S	18.5	17.90–19.34	-	-
Co	0.5	0.17–0.74	-	-
Ag	-	-	35.3	34.75–36.31
Au	-	-	61.9	60.69–63.39

The characteristic features of auriferous arsenopyrite from Miedzianka are the following: strong cataclasis, base metal sulphides overprint and constant Co admixture (up to 0.7 % wt%). Beside, arsenopyrite may contain numerous inclusions of gangue minerals that formed its very characteristic poikilitic structure. Pyrrhotite, chalcopyrite, galena, and rarely bismuth minerals and electrum may also form inclusions within arsenopyrite.

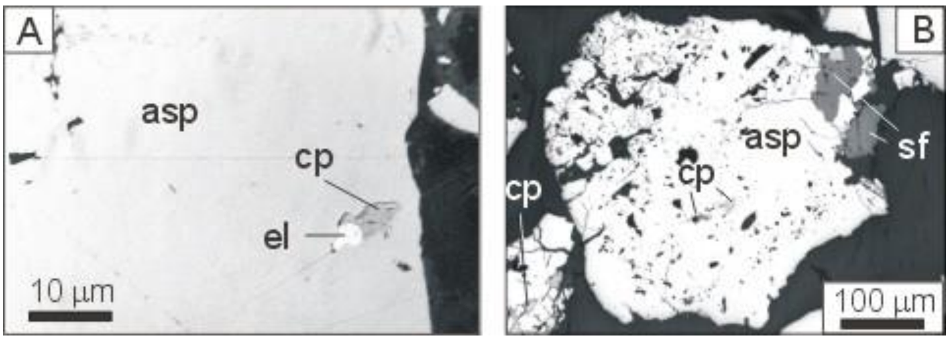

Fig. 2. Auriferous As-sulphide ore from Miedzianka. **A**. Electrum (el) and chalcopyrite (cp) inclusion within arsenopyrite (asp). **B**. Arsenopyrite (asp) with characteristic poikilitic texture. Note replacement of arsenopyrite by chalcopyrite (cp) and sphalerite (sf). Reflected light.

DISCUSSION AND CONCLUSIONS

At the Miedzianka deposit, gold was recognized for the first time resulting from geochemical and microscopic studies. Gold appears in the strong association with cataclased arsenopyrite ore. Gold occurs in the form of electrum inclusions in arsenopyrite with a constant Co admixture and probably in the arsenopyrite structure as a solid solution or chemically bound, or as submicroscopic inclusions (<1000 Å).

According to the mining records the arsenic ore from Miedzianka was a subject of metallurgical processing. About 2000 t of As produced (Dziekoński 1972) and at least about 0.1 t of Au was probably received from this Cu deposit.

The genesis of polymetallic sulphide-bearing quartz veins at the Miedzianka-Ciechanowice ore district was connected with the post-magmatic hydrothermal activities around the Karkonosze granite (Petrascheck 1933; Zimnoch 1978; Mochnacka 1982). Schneiderhöhn (1941) classified the Miedzianka Cu deposit as the "Copper chlorite formation". At the Miedzianka deposit the auriferous and cobaltoferous arsenopyrite is cataclased and overprinted by a younger generation of the base metal sulphides. Multiply stages of ore precipitation are the result of a successive hydrothermal fluid migration caused by the post-magmatic and tectonic activities from Upper Carboniferous to Lower Permian within the Intra-Sudetic fault zone in the north-eastern margin of the Karkonosze granite Massif.

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Krzysztof NEJBERT[1], *Danuta OLSZEWSKA-NEJBERT*[2], *Leszek MARYNOWSKI*[3]

VIVIANITE CONCRETIONS FROM THE WHITE CHALK (LOWER MAASTRICHTIAN) OF MIELNIK, EASTERN POLAND – PRELIMINARY REPORT

Abstract: The vivianite concretions found in the Lower Maastrichtian white chalk at the Mielnik quarry consist of vivianite, minor amount of clay minerals, calcite and framboidal pyrite. They originated during sedimentation of the overlying Paleogene deposits, as a result of downward migration of meteoric waters, enriched with Fe^{2+}, HPO_4^{2-}, and organic matter. The concretionary bodies are epigenetic in origin, and grown within the reduction/oxidation front developed during mixing of the Paleogene meteoric waters with the calcite saturated pore waters occurred within the white chalk deposits of Lower Maastrichtian age.
Keywords: vivianite, epigenetic concretion, genesis, Mielnik

INTRODUCTION

Vivianite /$Fe_3(PO_4)_2$*$8H_2O$/ is common in peat and bog iron deposits (e.g. Zieleniewski 1945; Kaczorek, Sommer 2003), lakes (e.g. Fagel et al. 2005), and iron/manganese deposits which undergo later diagenetic processes (Chukhrov, Ermilowa 1956; Kulczycki, Parafiniuk 1978; Bailey et al. 1998**).** Spectacular crystals of vivianite were also found in weathering zone of sulphide ore deposits as well as in low-temperature hydrothermal deposits and pegmatites (e.g. Rodgers et al. 1993).

Vivianite concretions, up to 2 cm in diameter, were found first time in the topmost part of the Lower Maastrichtian (*Belmnella lanceolata* Zone) white chalk deposits in the Mielnik quarry (Fig. 1). The white chalk was accumulated in a large epicontinental sea basin developed on the East European platform. In this paper we describe an unusual occurrence of vivianite concretions from the Maastrichtian marine white chalk of the Mielnik area, and present preliminary interpretation of their origin. The reference material, including large and well developed spherical concretions, has been stored at the Geological Museum of Silesian University in Sosnowiec, No. WNoZ/M/7/57.

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THE VIVIANITE CONCRETIONS

The vivianite concretions were discovered during the field work in the Mielnik quarry in 2005, where the Campanian and Lower Maastrichtian white chalk is still mined. In the upper part of the quarry, Lower Maastrichtian white chalk is overlaid by clays, muds, and glauconitic sands, which are regarded as Paleogene in age (Uberna 1981; Krzowski 1997). Within lower part of glauconitic sands, the characteristic horizon of phosphatic concretions, interpreted as residual lag deposit, were described (Uberna 1981; Olszewska-Nejbert, Nejbert 2005). The horizon enriched with vivianite concretions occurs in the topmost part of white chalk deposits, about 70 cm below the bottom of Paleogene deposits. It was recognized on the surface about 500 m^2 in the northern corner of the Mielnik quarry (Fig. 1). These occurrences are restricted to the areas where topmost part of white chalk forms shallow depressions, and overlaid Paleogene deposits, black in colour, are extremely enriched with organic matter. Partly decalcificated grey chalk (about 0.3 m thick) and completely decalcificated black residual clays (about 0.3 m thick) cover the white chalk with numerous vivianite concretions.

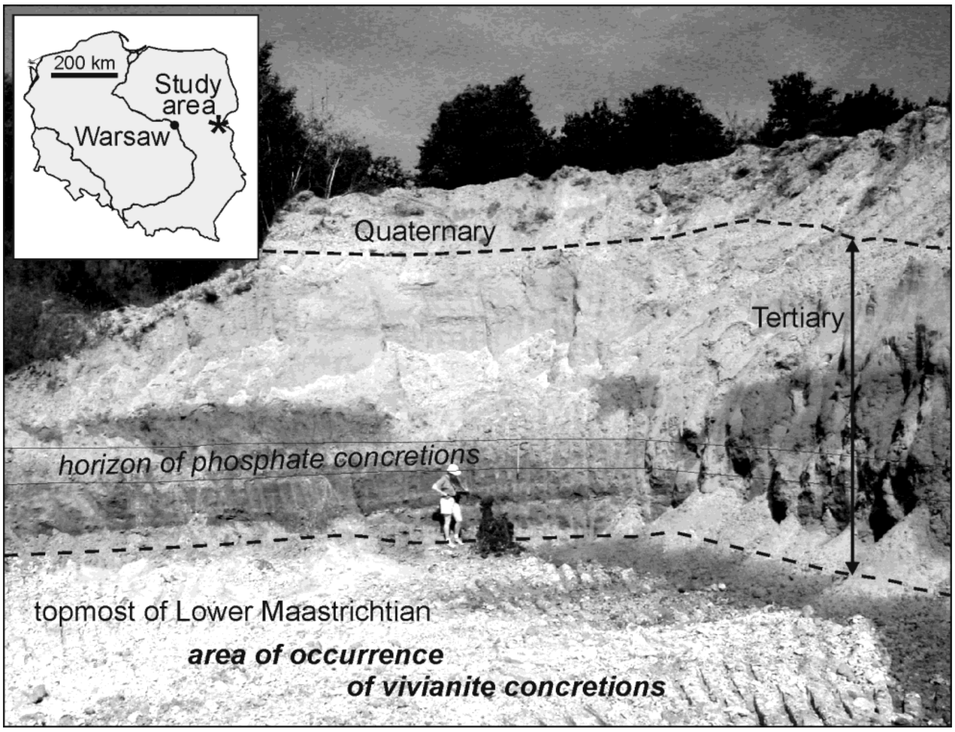

Fig. 1. The northern corner of the Mielnik quarry, general view the Lower Maastrichtian white chalk, Paleogene and Quaternary deposits. The vivianite concretion horizon occurs in the topmost part of white chalk (the photo was taken in 2005).

The vivianite concretions are different in size, from specimens of few mm up to 2 cm in diameter. They are frequently spherical in shape, with irregular surface formed by numerous convex bulges. Their texture resembles cauliflower-like forms (Fig. 2A). Other textural varieties of the concretionary bodies were also observed, including small plates composed of spherical aggregates of vivianite and irregular blebs with diffused borders at the contact with the host white chalk. A majority of concretions are intensive blue in colour; some of them display a yellow-brownish rim that surrounds the blue core. The concretions are strongly porous, slightly cemented and relatively soft. Vivianite is a major constituent of the concretions; beside the vivianite the concretions contain also minor amounts of clay minerals, calcite, and framboidal pyrite (Fig. 2B). The concretions grew from their centre to outside by progressive precipitation of platy-habit crystals of vivianite (Fig. 2C). The maximum size of (010) face of vivianite crystals is about 4 μm x 2 μm (Fig. 2D). SEM study revealed that vivianite concretions formed at open-space environment, and these open-spaces were developed simultaneously with the growth of the concretionary bodies.

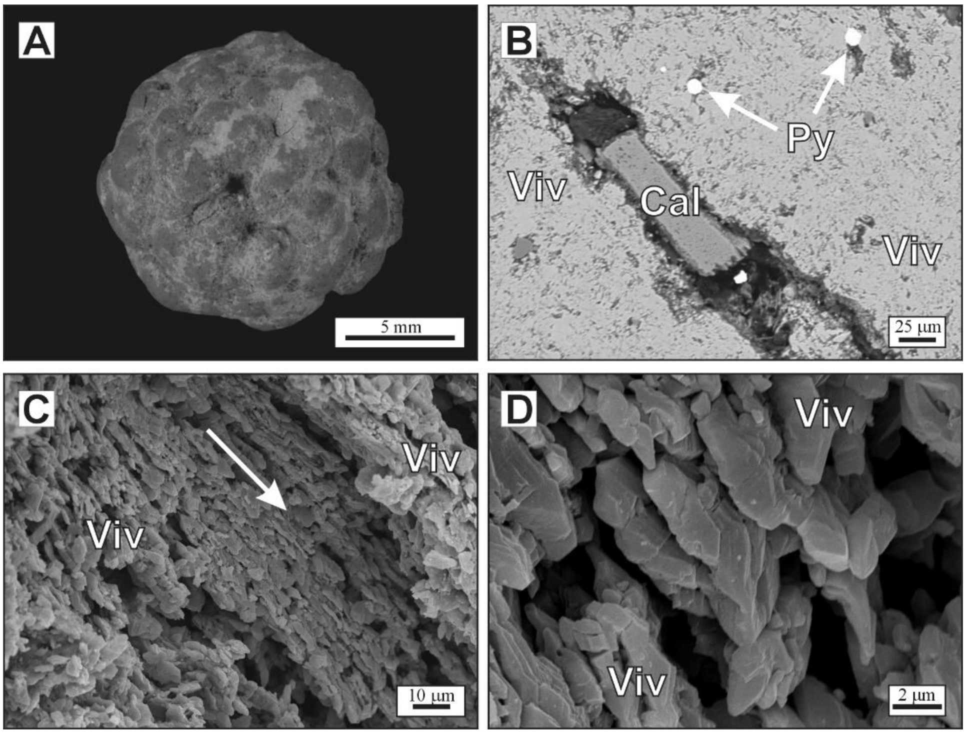

Fig. 2. Morphology and petrography of the vivianite concretions at Mielnik quarry. A – the example of the vivianite concretion, intensive blue in colour; B – back-scattered electron image of vivianite concretion (Viv) with intergrowths of calcite (Cal) and framboidal pyrite (Py); C – SEM image of close-up view within the vivianite concretion, the arrow indicate the direction of growth of the concretion; D – SEM image of aggregate of the platy-habit monoclinic vivianite crystals.

Chemical composition of vivianite in the concretionary bodies studied was determined by means of EPMA. Average contents of the FeO, P_2O_5, MnO and MgO, calculated from eighteen analyses, are close to 42.90 wt.%, 29.3 wt.%, 0.11 wt.%, and 0.14 wt.%, respectively. The amounts of the major elements are close to their contents in the stoichiometric vivianite. XRD study of the blue concretions confirms the presence of vivianite.

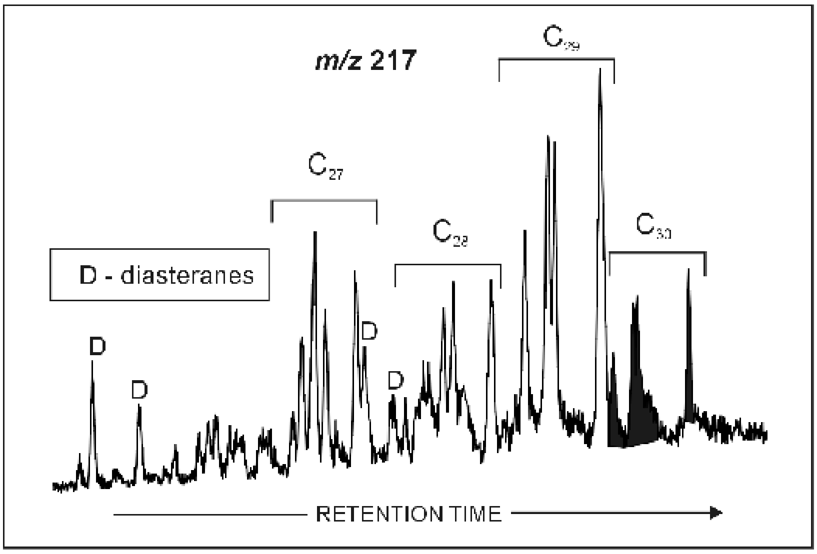

Fig. 3. Mass chromatogram of the Paleogene black clay showing distribution of steranes (*m/z* 217). C_{30}-steranes are marked as shaded peaks.

Samples of decalcificated grey chalk and black residual clay, both rocks developed during dissolution of Maastrichtian white chalk, and a sample of the sandy black clay of unquestionable Paleogene age, were analysed using gas chromatography-mass spectrometry method. All three samples characterized by uniform distribution of organic compounds (including biomarkers), which suggest the same source of organic matter (OM).

Taking into account the predominance of short chain *n*-alkanes (between n-C_{17} and n-C_{19}), the presence of C_{30}-steranes (Fig. 3, for identification see Moldowan 1984) and the lack of organic compounds characteristic of terrestrial OM, the marine source of OM is the most likely.

DISCUSSION AND CONCLUSIONS

Vivianite develops usually within terrestrial deposits that are rich in organic matter, e.g. lacustrine or peat deposits (e.g. Zieleniewski 1945; Kaczorek, Sommer 2003; Fagel et al. 2005). The occurrence of vivianite concretions within the white chalk in the Mielnik area that represents truly marine calcareous deposits accumulated within well oxygenated epicontinental sea of the Cretaceous age, is really unexpected. Thus, the origin of the vivianite concretionary bodies at Mielnik probably could be linked with deposition of the Paleogene organic-rich deposits, because the topmost part of decalcified white chalk (Maastrichtian) and overlaying black clays of Paleogene age have the same OM composition.

The Paleogene organic-rich deposits can be considered as a source of Fe^{2+} and HPO_4^{2-}, which were transported downward by meteoric waters. The vivianite probably precipitated during mixing of mildly reducing meteoric waters, derived from the overlaying Paleogene deposits, with the slightly alkaline calcite saturated pore waters, which occurred within the white chalk. Mixing of these waters resulted growing of vivianite concretions, thus, the studied concretionary bodies are epigenetic in origin. Vivianite concretions, similar to those occurring at Mielnik, were synthesized in laboratory during abiotic redox cell experiment (Zellibor et al. 1988, see Fig. 3d).

Textures of the studied concretionary bodies as well as their mineralogy indicate that precipitation of vivianite took place in open space environments (Fig. 2C-D), and origin of the vivianite concretions was not related to replacement of earlier pyrite nodules. Vivianite precipitation and simultaneous dissolution of the calcite around a growing vivianite concretion must be connected with a considerable lowering of pH of the pore waters. Thus, the vivianite growth can be shortly described by the reaction (for details see Nriagu, Dell 1974):

$$3\ Fe^{2+} + 2\ HPO_4^{2-} + 8\ H_2O = Fe_3(PO_4)_2{*}8H_2O + 2\ H^+$$

The intensive blue colour of vivianite concretions probably reflects later auto-oxidation processes (for details see Pratt 1997, Frost et al. 2004) occurring during changing of the environment into more oxygenated. Yellow rim surrounding blue core has developed during exposure of the concretionary bodies during recent mine works.

Acknowledgements: The authors thank for help Piotr Dzierżanowski, Lidia Jeżak, Grzegorz Kaproń, and Marek Wróbel. This research was supported by the Institute of Geochemistry Mineralogy and Petrology (Warsaw University) under Grant No. IGMiP-3-07.

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MINERALOGIA POLONICA – SPECIAL PAPERS
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Tomasz PAWLIK[1], *Michał SACHANBIŃSKI*[1]

APATITE-BEARING GNEISSES FROM ROŚCISZÓW IN SOWIE MTS. (SW POLAND)

Abstract: Homophanic gneisses near Rościszów (Sowie Mts.) host an inlier of apatite-bearing variety. The apatite is represented by two generations of fluorapatite of distinct composition and structure. The apatite-bearing gneisses originated from fine-grained sandstones and mudstones locally enriched in Ca-phosphates.
Keywords: fluorapatite, apatite-bearing gneisses, homophanic gneisses, Sowie Mts., WDS

INTRODUCTION

The 25 m long inlier of apatite-bearing rock occurs within gneissic rocks about 1-1.5 km west of Rościszów on the left bank of the Kłomnica stream. The rock is a mostly homophanic gneiss (migmatite) with locally preserved layering, medium- and coarse-grained, composed of oligoclase, biotite, quartz and apatite. Zircon, muscovite, ore minerals and garnet are present as accessory phases. The latter forms crystals up to 1 cm in diameter. Apatite content reaches 3 vol % while the amount of P_2O_5 is 1.8 vol % (Sachanbiński 1975). The apatite usually forms macroscopically discernible about 0.5-1 cm big green aggregates along feldspar-quartz boundaries. Rarely it is represented by 0.5-2 mm long single crystals and often constitutes minute inclusion in feldspar. The apatite crystals from the aggregates are isometric, oval or irregular, usually strongly fractured. The metamorphic conditions of the diatexite (homophanic gneiss) enclosing the apatite-bearing rock were estimated at 585±20°C (Grt-Bt geothermometer) or 610±22°C (Mu-Bt geothermometer) and 5.9-0.9 kbar (Mu geobarometer), (Budzyń et al. 2004). Geochronological investigations of zircons from the diatexites of this area were carried out by Kryza and Fanning (2007). The ages obtained cluster in three groups: from 1900 to 2300 Ma, from ~480 to ~518Ma and ~395Ma.

METHODS

Detailed investigations were focused on apatite from the homophanic gneisses. The WDS analyses and BSE images were obtained by means of a CAMECA SX-100 microprobe at the Inter-Institution Laboratory of Microanalyses of Minerals and Synthetic Substances at Warsaw University. Structural measurements were performed with a Jobin-Yvon T-64000 Raman spectrometer using an argon laser (λ=514.5 nm) at the Department of Molecular Physics, Technical University of Łódź.

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RESULTS

36 spot chemical analyses of the apatites from Rościszów were made. They revealed a presence of two chemically different varieties that could be distinguished on BSE images. First generation (apatite I) constitutes the main apatite volume whereas the other (apatite II) is noticeably darker in BSE and forms more or less regular zones developed along fracture planes in apatite I (Fig.1).

Tab. 1. Selected chemical electron microprobe analysis of apatites from Rościszów.

weight percent of oxides (based on 25 oxides)				
sample	**R2 apI**	**R6 apI**	**R5 apII**	**R9 apII**
SO_3	tr	0.03	0.004	tr
P_2O_5	41.965	42.231	41.978	43.044
SiO_2	0.024	0.024	tr	0.005
ThO_2	0.066	0.105	tr	0.033
UO_2	tr	tr	0.053	0.038
Al_2O_3	tr	tr	tr	tr
Fe_2O_3	0.131	0.318	0.001	0.09
Y_2O_3	0.267	0.375	0.071	0.143
La_2O_3	0.277	0.024	tr	tr
Ce_2O_3	0.095	0.114	0.142	0.058
Nd_2O_3	0.359	0.259	0.2	tr
MgO	0.023	0.051	tr	0.007
CaO	54.118	53.978	55.025	55.445
MnO	0.196	0.347	0.042	0.13
SrO	tr	tr	tr	tr
Na_2O	0.165	0.191	0.017	0.115
H_2O	0.729	0.703	0.647	0.871
F	2.137	1.953	2.349	2.237
Cl	0.13	0.081	0.061	0.062
total	100.682	100.048	100.590	100.134

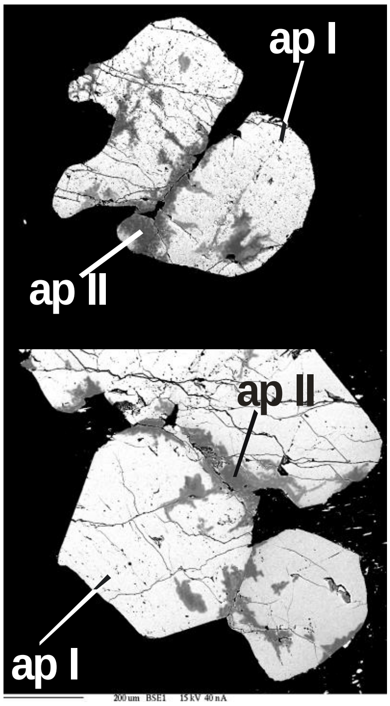

Fig. 1. Apatite from Rościszów: apatite I (ap I) and apatite II as veinlets (ap II).

The chemical composition obtained (amount of Ca, Na, P, Mn, Fe, Cl and F) corresponds with the one for fluorapatite from felsic rocks (Spear, Pyle 2002). The analyses show that apatite II contains less Y, La, Ce, Nd, Mn, Na, S, Si and Cl than apatite I (Tab. 1).

The presence of two apatite generations was confirmed by micro-Raman structural analyses. All the Raman spectra show bands at 430 cm^{-1} (E_{2g}: ν_2 [PO_4] bend), 580 cm^{-1} (E_{2g}: ν_4 [PO_4] bend), 605 cm^{-1} (E_{2g}, A_g: ν_4 [PO_4] bend) and 965 cm^{-1} (E_{2g}, A_g: ν_1 [PO_4] symmetric stretch). Weak bands at 448 cm^{-1} (E_{2g}: ν_2 [PO_4] bend), 590 cm^{-1} (E_{2g}: ν_4 [PO_4] bend), 1050 cm^{-1} (E_{2g}: ν_3 [PO_4] anti-symmetric stretch) and 1080 cm^{-1} (E_{2g}: ν_3 [PO_4] anti-symmetric stretch). Spectral positions of the bands correspond to the values for fluorapatites given by other authors (Penel et al. 1997; William, Knittle 1995). The spectra of apatite I and apatite II differ in the range of 580-610 cm^{-1}. Irrespective of apatite I crystal orientation there always appear two weak but clear and sharp bands ~580 and ~605 cm^{-1} (sometimes also weak ~590 cm^{-1}). These bands become weaker, broader and diffused to form a broad and weak feature in all the spectra of apatite II. The Ramana spectra of apatites from Rościszów are depicted on Fig. 2.

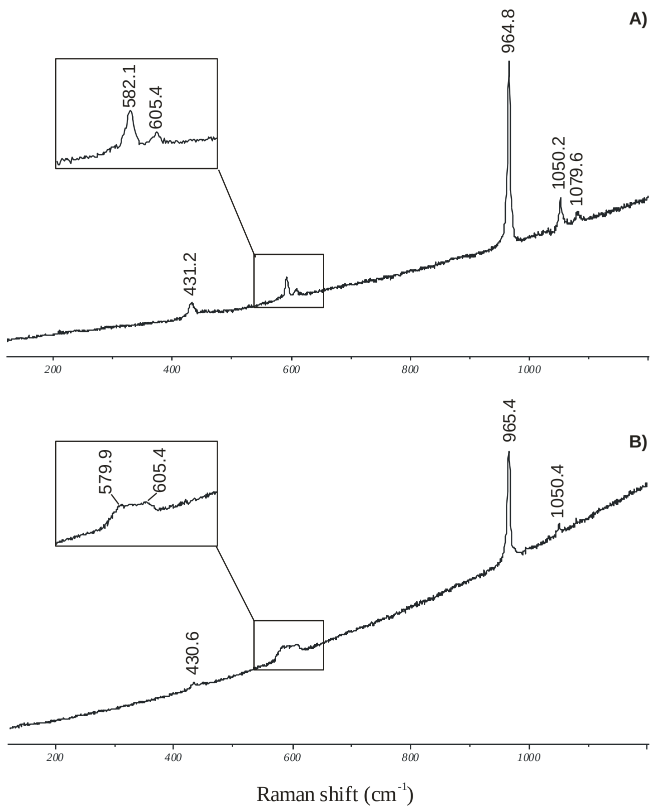

Fig. 2. Selected Raman spectra of apatite I (A) and apatite II (B).

CONCLUSIONS

Apatite-bearing gneisses from Rościszów may have been derived from locally Ca-enriched sandstones and/or mudstones. Metamorphic alterations led to structural rebuilding of Ca phosphates and enrichment in P_2O_5 and F at the expense of CO_3^{2-} and OH^- ions. As a result fluorapatites were formed. Chemical composition of the apatites from the Rościszów gneisses allows an attempt to reconstruct the metamorphic conditions. It is generally acknowledged that apatites from metamorphic rocks are characterised by small amount of Ba, REE, Na and Mn.

Rocks metamorphosed at high temperatures contain more of these elements as well as SiO_2 while SO_3, CO_2 and Cl decrease significantly (Kapustin 1987; Spear, Pyle 2002).

The differences in chemical composition and structural features of the apatites, manifested by higher concentration of Si, REE and Na in apatite I, may be explained by its crystallisation at higher temperature. The other generation was formed at lower temperature.

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MINERALOGIA POLONICA – SPECIAL PAPERS
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Maciej PAWLIKOWSKI[1], Ewa BENKO[2], Piotr KLIMCZYK[2]

HIGH PRESSURE AND HIGH TEMPERATURE TRANSFORMATION OF ETHERNITE AT LABORATORY CONDITIONS

Abstract: High pressure – high temperature (HPHT) transformation of ethernite into safe for life, not fibrous material have been investigated. Samples of powdered pure ethernite and ethernite with addition of 10 % of high alkaline granite were compressed under the pressure up to 8 GPa and then heat treated in the temperature range from 400 to 1350^{o} C. Depending on process parameters obtained various products were free of fibrous asbestos. Addition of high alkaline granite caused decreasing of pressure and temperature of transformation to 4 GPa and 800^{o} C respectively.
Keywords: ethernite, asbestos, high pressure – high temperature transformation

INTRODUCTION

The problem of cancerigenic asbestos is one of most important for life health (Skinner at al. 1988). Up to now there are not god technology concerning alternation of asbestos containing ethernite (mixture of cement and asbestos used for covering of house roofs) into not fibrous minerals.

The aim of publication is presentation of new technology of transformation of ethernite alternation into safe for life not fibrous material. The process was conducted at pressures up to 8 GPa and temperatures up to 1350^{o} C. Obtained various products are free of fibrous asbestos. Because of very high parameters (pressure and T temperature) necessary for modification of asbestos containing etherinte about 10 % of high alkaline granite was added to powdered ethernite. Next examination of ethernite alternation was performed at lower temperatures and pressure. As result of experiments the formation of new substance free of asbestos was obtained at temperature 800^{o} C and 4 GPa.

METHODS OF INVESTIGATION

Investigation were preformed using following methods:

- High pressure – high temperature apparatus,
- Polarizing light microscopy,
- X-ray diffractometry.

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High pressure – high temperature experiment

The powders of tested materials i.e. powdered ethernite or mixture of powdered ethernite and alkaline granite were mechanically mixed. Homogeneous mixtures were preliminary consolidated into pallets of the diameter of 15 mm and the height of 5 mm under the pressure of 200 MPa. The samples were received at high pressure (from 4 to 8 GPa) in the temperature range of 400 – 1350°C using a toroid type high – pressure apparatus. Duration of the process was from 60 to 120 s.

Microscopic examination

Microscopic examination of products of experiments at polarized light were performed with the use of Polmi A microscope. Observed phenomenon were documented as microphotographs.

X-ray diffractometry

X-ray examination of products of reactions were done using Dron 2.5 diffractometer and Cu radiation. X-ray patterns were determined with the use of Xrayan computer program.

RESULTS OF INVESTIGATION

Ethernite

Microscopic observation of ethernite conducted at polarized light shoved the fibers of asbestos disseminated at background composed of portlandite (Fig. 1A).

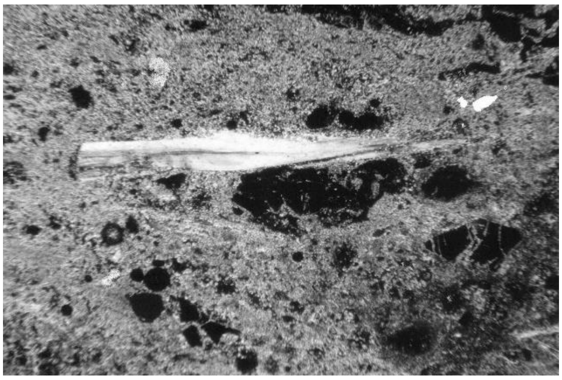

Fig. 1A. Fiber of asbestos at cement background – portlandite. Polarizing light, nicols X, 60 x.

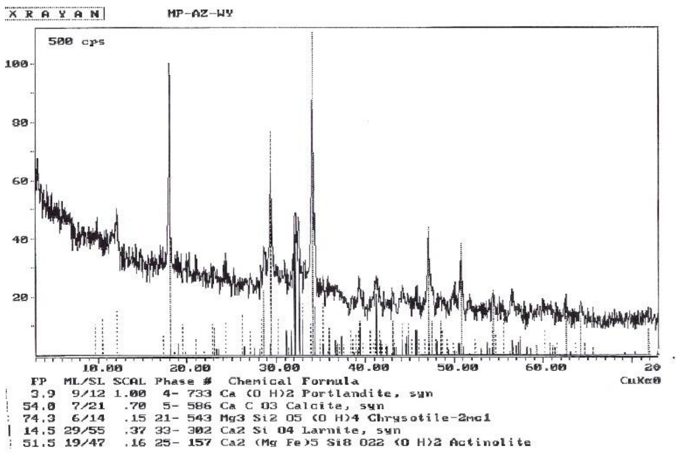

Fig. 1B. XRD pattern of natural ethernite. One can see weak peaks of chrysotile.

Transformation of ethernite without additions

Alternation of ethernite was conducted at conditions showed at Tab. 1.

Table 1. Conditions of alternation of ethernite.

Sample	Pressure (GPa)	Temperature (^{o}C)	Time (sec.)
1	6,5	1040	120
2	6,5	1350	120
3	8	1350	120

The growth of temperature and pressure lead to transformation of ethernite. Observations of products of alternation showed systematic changes of structure of ethernite. Mentioned phenomenon is confirmed by X-ray examination of products of transformation.

Event transformation of powdered ethernite performed at relatively low temperature and pressure (p – 6.5 GPa, T – 1040^o C) completely changed the structure of material. At polarizing light microscope one can see blastic structure where separate blasts of various shape are of about 100 – 200 μm. Observation confirmed (Fig. 2).

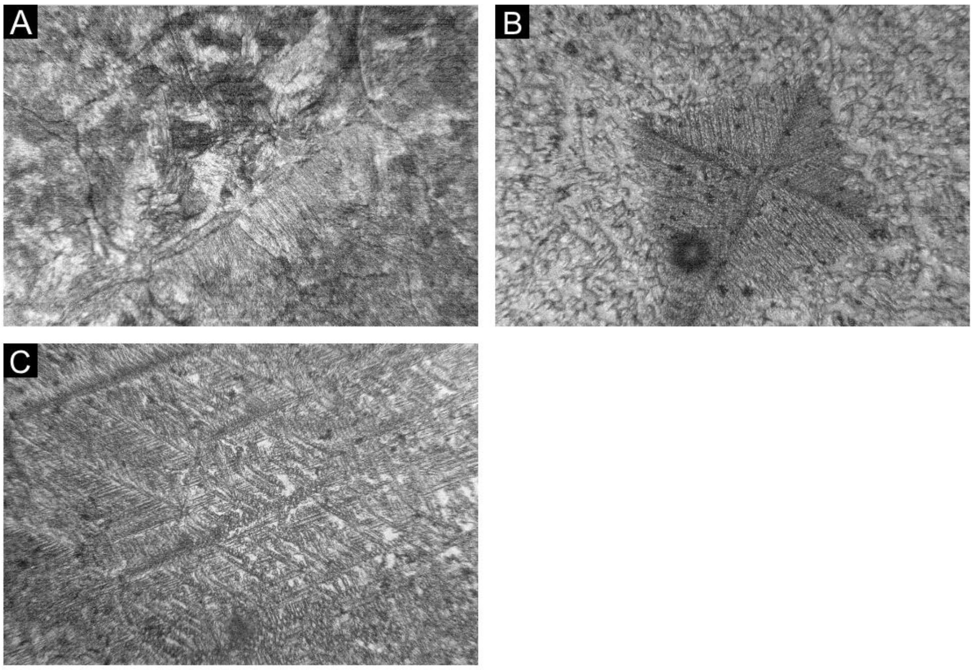

Fig. 2. Picture of transformed etherninte: A) p=6.5 GPa, T=1040^{o} C, t=120 sec; B) p=6.5 GPa, T=1350^{o} C, t=120 sec; C) p=8 GPa, T=1350^{o} C, t=120 sec. Polarizing light, nicols X, 80 x.

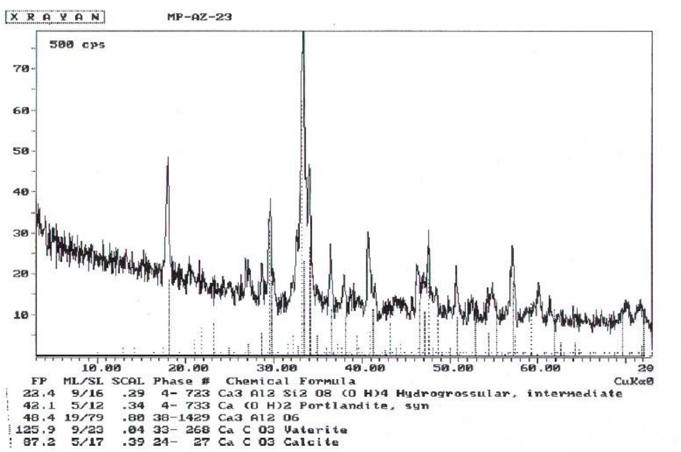

Fig. 2D. XRD pattern of transformed ethernite free of asbestos peak.

Major phases dominating in product of alternation of ethernite are represented by hydrogrossular and carbonates i.e. vaterite and calcite while portlandite is present as minor admixture.

Transformation of ethernite mixed with grinded alkaline granite

Due to high energetic process described before (very high temperature and pressure) the examination of phenomenon leading to transformation of ethernite was performed with admixture of 10 weigh % of grinded alkaline granite containing about 4 % of potassium (Orthoclase) from quarry located at Karpniki (Karkonosze granite). Experiments were conducted at conditions listed at table 2.

Table 2. Conditions of alternation of ethernite mixed with 10 weight % of alkaline granite.

Sample	Pressure (GPa)	Temperature (^{o} C)	Time (sec.)
4	4	400	60
5	4	600	60
6	4	800	60

Obtained data documents that there are not alternation of mixture at temp 400^o C and 600^o C and 4 GPa (Fig. 3A). Observation of products of alternation performed at temperature 800^{o}C and pressure 4 GPa shoved the mixture of ethernite with 10 % of alkaline granite is transformed to crystalline substance. Obtained structure is free of fibrous asbestos. Observed crystals are slightly elongated and have diameter up to 1.0 mm (Fig. 3B).

X-ray examination of substance obtained at 800^o C, pressure 4 GPa and time 60 sec. showed it represents mixture of crystalline scavitite, diopsyde, tylleite as well as siderophyllite and aragonite (Fig. 3C) and does not contain even traces asbestos. This means all fibrous crystals were altered into not fibrous phases.

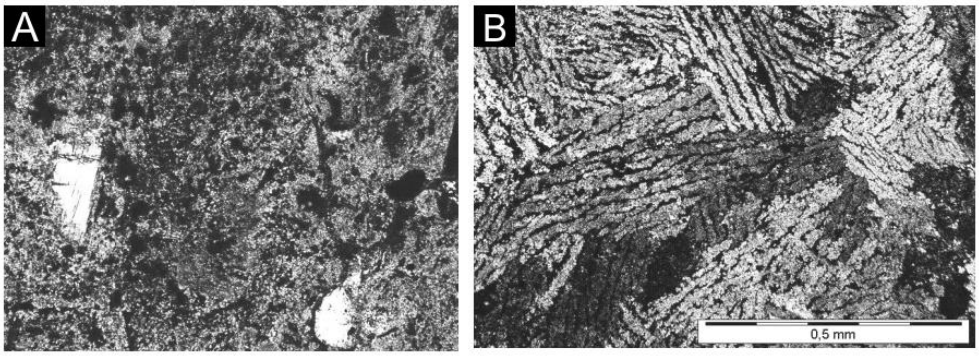

Fig. 3. A) microscopic picture of mixture ethernite + K-granite altered at 600 ^{o}C, 4GPa, 60 sec – no traces of alternation; B) microscopic picture of mixture ethernite + K-granite altered at 800 ^{o}C, 4GPa, 60 sec – mixture altered into crystalline scavitite, diopsyde, tylleite as well as siderophyllite and aragonite (Fig. 3C). Both photos-polarizing light microscope, nicols X.

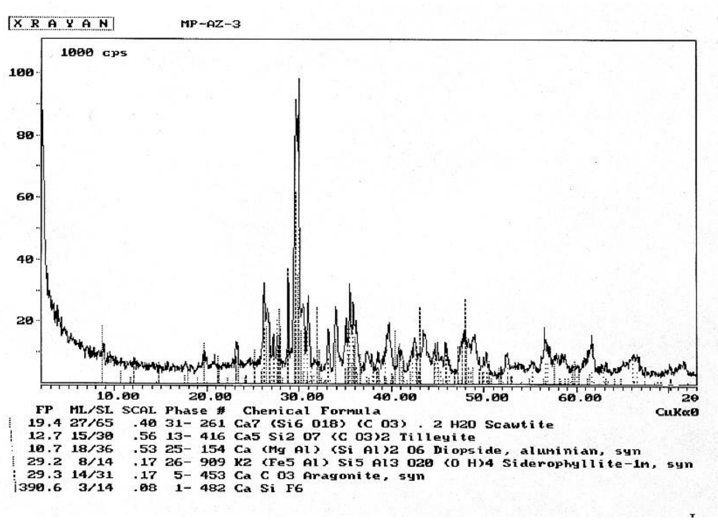

Fig. 3C. X-ray diffraction pattern of product of alternation of mixture powdered ethernite and alkaline granite.

The scavitite and diopside are dominating components. Other identified phases are accompanying in small amount.

CONCLUSIONS

Observed phenomenon of alternation of ethernite into asbestos free substance were described. Obtained data suggest that during heating of ethernite at high pressure the cement is melted. Fibrous asbestos is dissolved at melted cement (present at high temperature and pressure as liquid). Next during cooling products of alternation asbestos free secondary phases are crystallizing. They are various depending on composition of transformed material as well as on conditions of transformation. As products of transformation of pure ethernite (depending on conditions) the following phases were obtained: scavitite, diopside, tylleite, hydrogrossular, vaterite, calcite, portlandite and Admixture of alkaline granite to powdered ethernite was the reason of overing of temperature of transformation up to 800^{o}C and 4GPa. Following phases free of asbestos were obtained: scavitite and diopside. Other phases as tylleite, syderophyllite and aragonite are accompanying products of alternation. Described method is the way of alternation of asbestos containing substances as for example etherinte into asbestos free products safe for environment and health of Man. In comparison to other proposed methods (dissolution of asbestos, vitrification etc.) proposed method is cheap and save for environment. There is possible utilization of products of transformation of ethernite in industry (crushed material for road construction, admixture for concrete, etc.). Similar method is possible to use for transformation of pure asbestos.

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MINERALOGIA POLONICA – SPECIAL PAPERS
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Jacek PUZIEWICZ[1]

RELATIONSHIPS BETWEEN CLINOPYROXENE MEGACRYSTS AND PHENOCRYSTS IN THE KSIĘGINKI NEPHELINITE (SW POLAND, TERTIARY CENTRAL EUROPEAN VOLCANIC PROVINCE)

Abstract: The Tertiary Księginki nephelinite (SW Poland) contains three kinds of clinopyroxene phenocrysts and the megacrysts of the mineral. All are rimmed by thin layer of clinopyroxene of composition identical to that of the host nephelinite groundmass. The composition of phenocrysts suggests their crystallization at various stages of lava transport to the surface. Some of the phenocrysts might have originated under conditions similar to those of megacrysts crystallization.
Keywords: Tertiary alkaline rocks, Poland, clinopyroxene megacrysts

The alkaline lavas related to initial stages of continental extension originated in Central Europe in Tertiary, forming the Central European Volcanic Province. In the Variscan Orogen in Europe, whose crustal thickness commonly does not exceed 35 km, the sources Tertiary lavas are located few tens of kilometres beneath Moho. This means that the distance from magma source to the surface is long. Since the eruptive process is assumed to be fast, with magma migration speed in the range of kilometres per hour, the change of P-T conditions affecting the lava are changing drastically during eruption, affecting the crystallization of phenocrystic phases.

The alkaline lavas carry variable assemblages of phenocrysts dominated by clinopyroxene. In some occurrences the so-called "megacrysts" of clinopyroxene, of size reaching 10 cm, are common. The Księginki nephelinite in SW Poland fits well this characteristics, containing both the various kinds of clinopyroxene phenocrysts and megacrysts. Thus, it offers the opportunity to analyse the origin and relationships between them.

Chemical composition of minerals, reported in the following, was studied by a CAMECA SX100 electron microprobe at the laboratory of the Institute of Mineralogy, University of Hannover, Germany, working under standard conditions (acceleration voltage 15 kV, sample current 15nA, counting times 10 or 20 sec, natural silicates and synthetic oxides as standards, PAP correction procedure; counting times were enlarged to achieve high detection limits of Ni (800 ppm), Cr (200 ppm). The pyroxene classification scheme of Morimoto (1989) is used.

The phenocrysts of clinopyroxene are subhderal to euhedral, up to few millimetres in size. Three kinds of phenocrysts occur. The first one contains large diopsidic core surrounded by rim of subsilicic titanian diopside (Fig. 1).The second one contains inner spongy core (Fig. 1), whereas the third one consists of large

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spongy core surrounded by thin rim. Decomposed glass or analcite occur as intergrowths in spongy parts of grains.

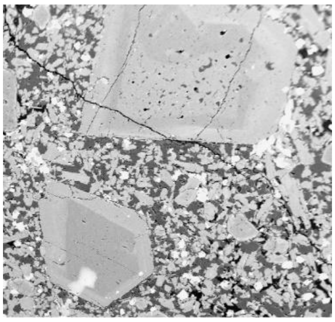

Fig. 1. Clinopyroxene phenocrysts in the Księginki nephelinite. The upper one contains inner spongy core, whereas the lower one has the homogeneous diopsidic one.

The outermost part of the rims has composition of subsilicic titanian diopside, identical to that of fine (< 50 μm) clinopyroxene forming the groundmass of nephelinite together with nepheline (Fig 2).

Clinopyroxene megacrysts, typically 2 – 5 cm long, occur scarcely in the nephelinite. The megacrysts more than ten centimetres in length were described by Kozłowska-Koch (1981). The megacrysts are subhedral to anhedral and have rounded edges. They consist of clear core, spongy rim and thin clear margin. The cores and spongy rims have the composition of diopside and the margins – of the matrix clinopyroxene. The clear cores occur only in larger megacrysts and the spongy rims are patchy.

The content of Ca in clinopyroxenes is variable. Those occurring in the matrix are highly calcic (approximately 0.95 atoms of Ca pfu – per formula unit, O^{2-} = 6), whereas the cores of megacrysts contain approximately 0.80 atoms of Ca pfu. The cores of phenocrysts contain amounts of calcium which are transitional between those two extremes (Fig. 2). The composition of megacryst cores is constant, suggesting that they originated under similar conditions and were in chemical equilibrium (Fig. 2). The cores of phenocrysts have more variable composition, probably due to their crystallization at different stages of lava evolution, and most of them are more calcic than the megacryst core. Textural relationships show that the phenocrysts are the early phases crystallizing at depths from the host lava. There should be a compositional overlap of the megacrysts and porphyrocrysts, if the megacrysts originated due to crystallization in a magma chamber from which the lava erupted. The chemical data are, however, unequivocal: the contents of Ti (Fig. 2), Na and Cr (not depicted) are overlapping, whereas those of Al (Fig. 2) are not. Probably more detailed study is necessary to asses if the megacrysts can be genetically related to the host magma. The spongy rims of megacrysts consist of patches of variable composition, from those chemically similar to cores to those similar to matrix clinopyroxene. Both the structure and composition are indicative of readjustment of the mineral composition to changing conditions, probably with some melt production. The inner spongy cores of phenocrysts have the appearance similar to that of spongy margins of megacrysts, but their composition is highly variable and mostly different (Fig. 2). Thus, their compositional evolution was supposedly different than that of megacrysts.

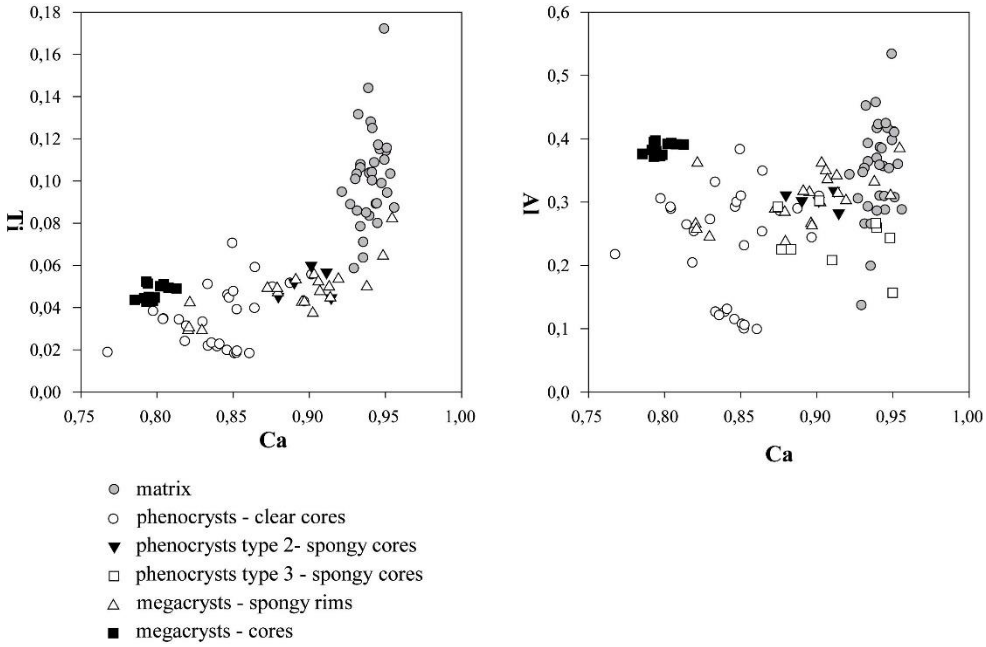

Fig. 2. Relationships between Ca, Cr and Al content in clinopyroxenes occurring in the Ksieginki nephelinite (matrix, phenocrysts and megacrysts).

The megacrysts of clinopyroxene occurring in alkaline volcanic rocks are commonly interpreted as products of high-pressure host- or genetically-related lava crystallization. (for recent review see Woodland, Jugo 2007). The chemical data presented for the megacrysts occurring in the Ksieginki nephelinite suggest similar origin. The variation in composition of clinopyroxene phenocrysts indicates that they crystallized at various stages of host lava evolution, and that they may record the injections of lava into the transient magma chamber before eruption.

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MINERALOGIA POLONICA – SPECIAL PAPERS
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GEOCHEMICAL INSIGHT INTO SASNAVA FORMATION (LITHUANIA)

Abstract: Data on paleontological and geochemical investigations of four core samples from Sasnava formation, Lithuania, were compared with the Zechstein Kupferschiefer in Poland. Positive correlations between respective microfacies were confirmed, however, polysulfide mineralization in Sasnava formation is scare. Biomarker assemblage preserved in kerogen of the Sasnava rock resembles the stagnant water column with photic zone anoxia during sedimentation. Maturity of organic matter remains at early diagenetic stage.
Keywords: Kupferschiefer, Sasnava formation, microfacies, biomarkers, maturity

INTRODUCTION

The north-eastern part of European Southern Permian Basin extends into Lithuania. It forms a bay on Paleozoic (Silurian – lowermost Carboniferous) depression in the region. The Polish Kupferschiefer relates to Lithuanian Sasnava formation, witch thickness ranges from 0,4 to around 3 m. The Sasnava shales are underlaid by sandstones of Kalvarija formation and overlaid by limestones of Naujoji Akmene formation. Sasnava floor transition (between shales and sandstones) is well marked, while roof transition (between shales and limestones) is often not clearly distinct. The elevated concentrations of metal sulfides (Cu, Pb, Zn), with no economical importance, are found only in points (Kadunas 2001). The Sasnava formation extends to central part of Polish-Lithuanian depression, and links to Polish Kupferschiefer *via* basin narrowing close to Mazury complex. In the dark sediments presence of the fossils is accompanied by kerogen. Here we present data on paleontological and molecular fossils in the Sasnava formation.

MATERIALS & METHODS

The examined core samples represent four boreholes of Lithuanian Sasnava formation derived from Vievis core stock near Vilnus. The Sasnava formation thickness of the Virbialiskiai 434, Pajavonys 13, Girdżai 51 and Nida 44 boreholes was 0.5, 1.0, 1.4 and 2.3 m, respectively. On the cores paleontological and microscopic investigations, analyses of thin sections and XRF elemental analyses were performed. The geochemical indices on kerogen contained in the rocks were achieved from the GC-MS analyses of nonpolar fraction of the Soxhlet extracts.

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RESULTS

In the investigated, finely laminated (0.1 – 0.5 mm) shales, are observed fossils of inarticulate brachiopods (*Lingula credneri* Geinitz) and ichthyolites – mainly fish scales of order Palaeonisciformes. The brachiopods are preserved as single, disarticulated, but not disintegrated shells. In the shales no signs on bioturbation were found, which suggest limited accessibility of oxygen into the sediment as well as closely above it. The thin sections show wavy lamination, which is manifested by mineral orientation and grains of microdetrituous organic matter. Lamination has rarely a lenticular form. Slightly rounded quartz and feldspar grains, plates of muscovite and laminas of carbonates are major mineralogical constituents in the shales. In Virbialiskiai-434 (depth 341.1m) and Pajavonys-13 (depth 740.0 m) shales elevated concentrations of the Cu (302 and 46 ppm, accordingly), Pb (118 and 73 ppm), Zn (181 and 16 ppm), Ni (252 and 86 ppm), Mo (20 and 124 ppm) and Sr (2833 and 86 ppm) are present.

Molecular assemblage of the selected biomarker compounds present in kerogen of the Sasnava shales provides insight into paleoenvironment conditions during accumulation of the strata and post-depositional organic matter transformation. The bimodal distribution of *n*-alkanes (Fig. 1) is characterized by prominent Gaussian homological profile over *n*-C_{12} – *n*-C_{19} range resembling higher maturity source, while a pronounced odd-over-even carbon number predominance of long chain *n*-alkanes within *n*-C_{20} – *n*-C_{34} range (CPI around 1.7; *n*-C_{27} and *n*-C_{29} most abundant) resembles low maturity organic matter source.

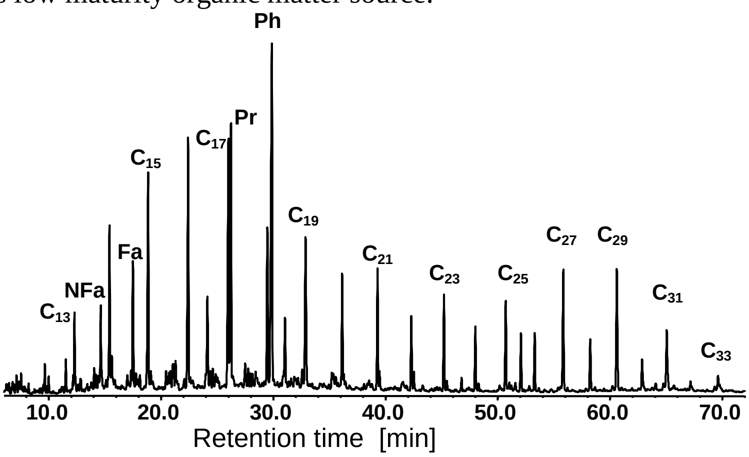

Fig. 1. Homological composition of *n*-alkanes and isoprenes in Nd1 sample (Nida 44 borehole of Sasnava shale). *Legend:* *n*-alkane chain length is indicated by C_x, Ph – phytane, Pr – Pristane, Fa – farnesane, NFa – norfarnesane.

The hydrocarbons representing lower molecular range of the *n*-alkanes, as well as *n*-alkylbenzenes represented by lower C_{12} – C_{18} range homologues (not shown), are probably the migration products from underlying formations. Prominent isoprenoid hydrocarbons (Fig. 1) are represented by phytane (Ph) and pristane (Pr), as well as farnesane (Fa) and norfarnesane (NFa), which may originate from chlorophylls (*Chlorophyceae*, green algae) and bacteriochlorophylls (*Chlorobiaceae,* green sulfur bacteria), respectively. Coexisting of algae and green sulfur bacteria families require stratification of the water column within photic zone, as *Chlorophyceae* require oxic conditions, while *Chlorobiaceae* are exclusive anaerobes. Utilization of the Shunmugam and Obermayer charts (Figs. 2a and 2b, respectively) indicate marine depositional environment and the type II kerogen accumulation during formation of the Sasnava strata.

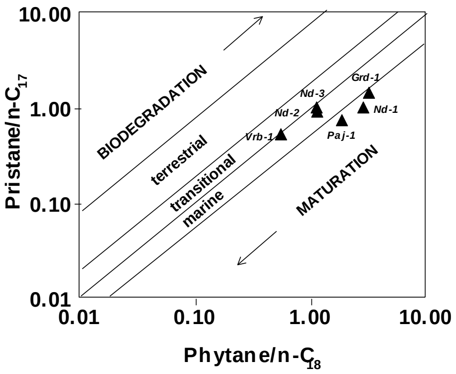

Fig. 2a. Depositional environment of Sasnava shales (Shunmugam chart).

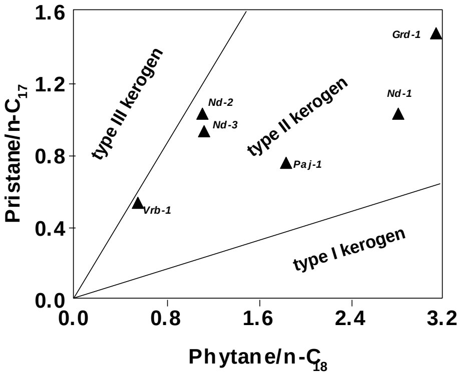

Fig. 2b. Kerogen type in Sasnava shales (Obermayer chart).

Boreholes assignment: *Nd* – Nida 44, *Gd* – Girdžai 51, *Paj* – Pajavonys 13, *Vrb* - Virbialiskiai-434

Very close values of Ph/Pr and Fa/NFa ratios above 1.4, suggest anoxic conditions at the sedimentation bottom. Evidence for the anoxic conditions extension into the photic zone comes from presence of the C_{13} – C_{23} aryl isoprenoids (not shown), early diagenetic products derived from isorenieratane, the aromatic carotenoid produced by *Chlorobiaceae*. Presence of these organisms, which are source of steranes in organic matter (Volkman, 1986), is confirmed by the abundant (20R)-5α(H),14α(H),17α(H) C_{27} - C_{30} steranes (Fig. 3), where the C_{29} is the most prominent.

Small amount of C_{30} 24-propyl-(20R)- 5α,14α,17α(H)-cholestane confirms marine sedimentary environment (Moldowan et al. 1990). Only partial transformation of thermodynamically unstable steranes with biological (20R)-5α(H),14α(H),17α(H) stereochemistry to (20R)-5β(H),14α(H),17α(H) counterparts additionally evidences low maturity of the kerogen. Domination in the C_{30}, C_{31} and C_{32} hopanes of the thermodynamically unstable (22R)-17β(H),21β(H) series and neohop-13(18)-enes further complements low maturity of kerogen in the Sasnava formation.

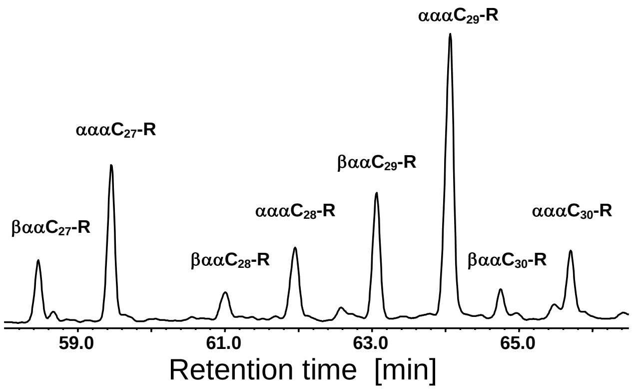

Fig. 3. Homological composition of steranes in Nida 44 borehole (Sasnava shale).

CONCLUSIONS

The Sasnava formation in Lithuania represents regional type of Kupferschiefer. It contains much lower concentrations of ore minerals. In cases with elevated metal concentrations (mainly sulfides) their assemblage is similar to that present in the Kupferschiefer. Microlithofacies of Sasnava shale are very similar to those distinguished in Kupferschiefer (Oszczepalski 1988) with one exception, i.e. lacking of type *A* facie (horizontally laminated shales with much elevated content of organic matter). Also in the Sasnava shales content of carbonates (calcite, dolomite) is higher as compares to typical Kupferschiefer from Fore Sudetic Monocline. The fossil assemblage in both regions is similar.

The kerogen biomarkers assemblage in the Sasnava shales provide consistent data on: (i) water column stratification in marine depositional environment, where oxygenated photic zone was followed by anoxic bottom enhancing the preservation of organic matter (ii) diverse primary source community of a photosynthetic green sulfur bacteria and algae, as well as partial contribution of allochtonous, terrestrial origin, organic matter, (iii) immature stage of organic matter in sediment, (iv) migration of low molecular weight chain hydrocarbons (*n*-alkanes, *n*-alkylbenzenes) from underlying strata.

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MINERALOGIA POLONICA – SPECIAL PAPERS
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MINERAL COMPOSITION OF AMD PRECIPITATES IN THE ŁĘKNICA REGION (THE MUSKAU ARCH, WESTERN POLAND)

Abstract: In the Łęknica region Neogene lignite deposits were exploited up to the end of the 80-ties of the 20th century. Oxidation of sulphide-containing lignite leads to formation of acidic waters, precipitating ochreous sediments. The waters are characterised by very high Fe and SO_4 concentrations. The main mineral constituents of the precipitates are schwertmannite, goethite, jarosite and gypsum. Such mineral association is typical for AMD environments. Sulphate concentrations and pH determine which ferric phase is formed.
Keywords: acid mine drainage, schwertmannite, goethite, jarosite

INTRODUCTION

The Muskau Arch, a 40 km long horseshoe-shaped belt of frontal and push moraines, which originated during the Mid-Polish Glaciation, extends from Klein Kölzig in Brandenburg, via Saxony, to Tuplice in Poland (Fig. 1). Neogene lignite and clay deposits, which occur within the push moraines, were exploited up to the end of the 80-ties of the 20th century. Abandoned excavations are recently filled with water, thus forming large anthropogenic lake district. Due to unique geological and biological value, as well as educational and geoturistic attraction, creation of trans-boundary geopark on this area is planned (Kasiński et al. 2004). Oxidation of sulphide-containing lignite, leads to the generation of abundant quantities of sulphuric acid. Therefore many of these lakes, especially at the Łęknica area, are of acidotrophic type characterised by very low pH values (usually < 4.0). As a consequence of iron oxidation and hydrolysis, numerous ochreous precipitates form. They occur on the pond banks, streambeds and sometimes built up spring bowls. The aim of this study was mineralogical characteristics of these sediments.

MATERIALS AND METHODS

Fifteen ochreous sediment samples were collected in the area SE of Łęknica. In most cases, the waters precipitating these sediments were also sampled. Mineral composition of the sediments were identified using X-Ray diffractometry (Philips X'Pert) and scanning electron microscopy (FEI QUANTA 200 FEG coupled with EDX). Electrolytic conductivity and pH values of sampled water were measured in situ. For main cation (Ca, Mg, Na, K, Fe, Mn) and anion (sulphate, chloride, bicarbonate) analyses, standard methods were used (AAS, turbidimetry and titration).

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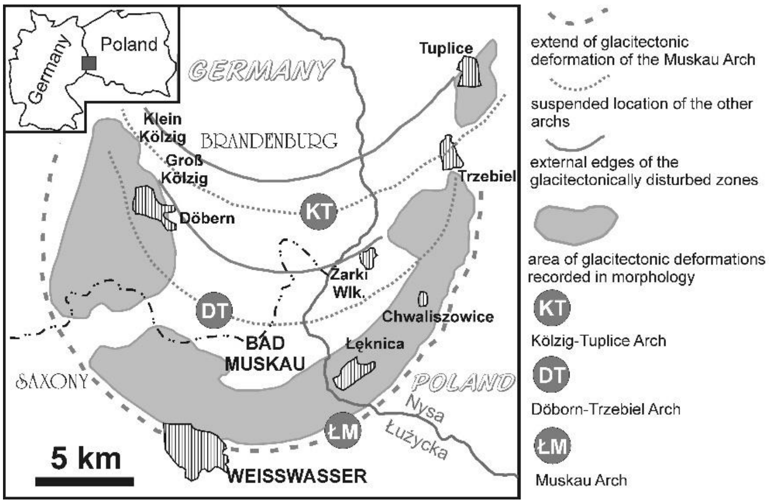

Fig. 1. Sketch-map of the studied area (after Kasiński et al. 2004, simplified).

RESULTS

The analysed waters are highly mineralised, acidic (pH 2.5-4.0) and characterised by very high iron and sulphate concentrations, reaching 495 i 1880 mg/dm^3, respectively (Tab. 1). Electrolytic conductivity ranges from 750 up to 2800 μS/cm. Rather high manganese levels of up to 3,4 mg/dm^3 are also noteworthy. Calcium and magnesium contents reach 280 mg/dm^3 and 80 mg/dm^3, respectively. Concentrations of sodium, potassium and chloride are relatively low (usually few mg/dm^3). Bicarbonate is absent due to very low pH values.

Table 1. Chemical composition of the sampled waters. EC – electrolytic conductivity [μS/cm].

ion/parameter	concentration range [mg/dm^3]	ion	concentration range [mg/dm^3]
pH	2.49–4.00	Fe_t	1.1–495
EC	749–2790	Mn_t	0.91–3.38
Ca^{2+}	38.5–283	HCO_3^-	0.0
Mg^{2+}	15.2–82.7	SO_4^{2-}	480–1881
Na^+	4.99–13.97	Cl^-	5,0-23,0
K^+	3.45–12.93		

The precipitated sediments are reddish-brown and orange in colour. In most cases white, yellowish or transparent gypsum crystals (up to 1-2 mm in size) cover the sediment surface. Very high porosity, diversified surface morphology and the presence of numerous plant remnants (leaves, stalks etc.) are typical for the precipitates. Bacteria-derived structures are also common. The main mineral constituents are iron oxides and hydroxysulphates: goethite α-FeOOH, jarosite $KFe_3(OH)_6(SO_4)_2$ and schwertmannite $Fe_{16}O_{16}(OH)_{12}(SO_4)_2 \cdot nH_2O$. Rarely, the presence of ferrihydrite $Fe_5HO_8 \cdot 4H_2O$ is also apparent. The most characteristic and most common ferric phase in the precipitates is schwertmannite. It usually forms hedgehog-like aggregates of small (< 2 μm long) needle-shaped crystallites (Fig. 2a) which is typical for this hydroxysulphate. XRD-patterns show only six very broad bands indicating poor schwertmannite crystallinity. The second hydroxysulphate, jarosite, is much more crystalline. A few millimetres in size, pyramidal or platy crystals are common (Fig. 2b,c). They appear together with schwertmannite, or form compact masses. Small needle-like, fibrous or platy goethite particles occur in structureless aggregates. Rarely, characteristic fan-like structures formed by elongated crystallites are seen (Fig. 2d) Goethite in the precipitates usually contains silica, aluminium and calcium as well as sulphate impurities (up to a few wt. percent). XRD patterns indicate rather poor crystallinity of the oxyhydroxide.

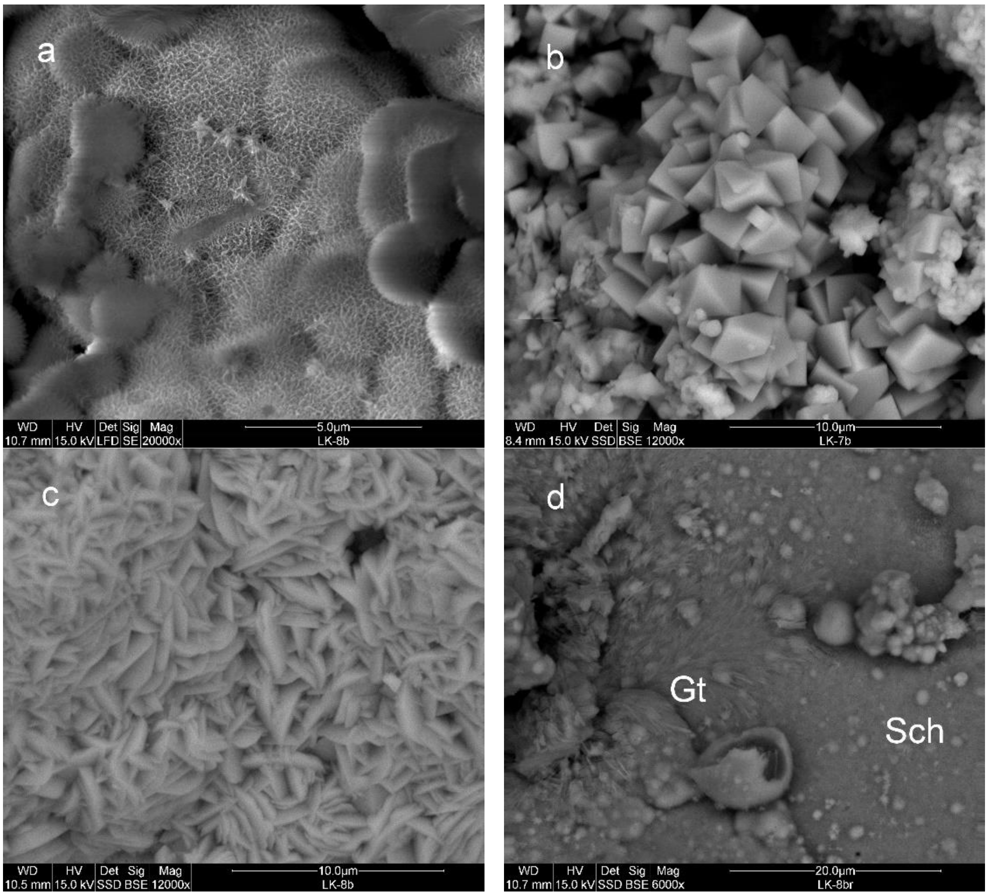

Fig. 2. SEM micrographs of the precipitates. a) hedgehog-like schwertmannite aggregates b) and c) jarosite crystals d) fan-like goethite aggregate (Gt) within schwertmannite (Sch) mass.

DISCUSSION AND CONCLUSIONS

Mineral association of the precipitates in the Łęknica region, including schwertmannite, jarosite, goethite and gypsum, is typical for acid mine drainage (AMD) environments. After Wieściszowice and Radzimowice in Western Sudetes (Parafiniuk, Siuda 2007), this is the third occurrence of schwertmannite in Poland. Origin of ochreous precipitates is related to ferrous sulphide oxidation. Sulphate concentration and pH determine which ferric phase is formed. At the lowest pH (< 3) and highest [SO_4^{2-}], jarosite is preferentially formed. When pH is getting slightly higher (3–4) and sulphate concentration is getting lower, schwertmannite precipitates (Schwertmann et al. 1995, Bingham, Nordstrom 2000). Both these phases are unstable with respect to goethite, so the latter can be a product of the hydroxysulphates transformation. However, direct precipitation of goethite is also possible, but in less acidic conditions (Murad, Rojik 2005). Because of very slow Fe^{2+} oxidation rate in an acidic environment, the precipitation of ferric compounds is probably microbially controlled. The presence of numerous bacterial remnants in ochres supports this admission. Coexistence of various Fe-bearing phases may reflect fluctuations in chemical composition of the waters and overall weathering conditions. Nevertheless, the dominance of schwertmannite in the precipitates is in a good agreement with common pH values as well as sulphate concentrations of Fe-rich waters in this area.

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MODEL OF MAGMA GENERATION AND DIFFERENTIATION IN PERMIAN VOLCANIC ROCKS FROM CRACOW AREA

Abstract: Isotope data on bimodal volcanic suite gave evidence on different magma sources for the intermediate and for the acid rocks. Geochemistry of the rocks point to a partial melting as a process responsible for their evolution. Metasomatized mantle has been melted giving rise to intermediate rocks formation. Crustal amphibolites are supposed to be a source for acid magma. Magmas from both sources occasionally mixed. Originating from this process blobs are of intermediate composition, although enriched in silica.
Keywords: bimodal volcanic suite, magma evolution, partial melting, mixing, fractional crystallization, Permian magmatism

INTRODUCTION

The geochemical composition of Permian volcanic rocks from Cracow area presents bimodal high K to shoshonitic calc-alkaline suite ranging from intermediate to acid composition. The intermediate rocks are: basalts-trachybasalts-trachyandesites; the acid ones: dacites-trachydacites. The most evolved items display ryolitic composition. The volcanism shows collisional geotectonic setting affinity and can be related to Małopolska Terrane and Upper Silesian Terrane collision (Pharaoh 1999; Żaba 1999).

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ORIGIN OF MAGMAS - PREVIOUSLY PUBLISHED IDEAS

The origin of magmas and their evolution were subjects of many research works. Rozen (1909) assigned all the volcanic rocks to one series of magma differentiation. Bolewski (1939) related magma origin to two different sources. Due to his opinion two compositionally different magmas have been generated calc-alkaline and high potassium – alkaline ones. This result was questioned by Słaby (1987) due to recognition of wide scale of secondary adularization and albitization processes, which could account for rocks enriched in alkalis. Bukowy and Cebulak (1964) correlated the differences in the rocks geochemistry with magma mixing processes, where the end-member magmas are of mafic and felsic composition. This idea was not continued by (Harańczyk 1989), who supposed four different types of magmas reflected in four types of rocks: diabase, ryodacite, trachyte and lamprophyre. Due to (Czerny, Muszyński 1997) only three types of magmas are responsible for all rock formation respectively: diabasic, lamprophyritic and ryodacitic. The trace elements variation in low silica (intermediate) rocks they explained by variable degree of mixing between mafic and lamprophyritic melts. Rospondek et al. (2004) proposed fractional crystallization as a petrogenetic mechanism causing intermediate magma evolution into acidic one. Finally Gniazdowska (2004) and Falenty (2004) show magma differentiation in both more basic and more acidic rocks using major elements and selected trace element concentrations in the rocks. They revealed, that the magmas have been evolved by fractional crystallization. They haven't found the mafic and felsic rocks co-magmatic. Consequently intermediate magma evolution into felsic magma was, according to their research results, not possible.

NEW DATA AND RESULTS

Twenty samples, collected by Gniazdowska (2004) and Falenty (2004) for their research work, have been selected for trace elements analyses, where five of them with distinct signature of intermediate and acid composition have been additionally selected for isotope analyses (Sm-Nd and Rb-Sr).

The progress in magma differentiation has been investigated using three differentiation indexes: # Mg, Th and SiO_2. Mostly both, intermediate and acid rocks, don't show co-magmatic evolution. Using SiO_2 as differentiation index, at many Harkers, the intermediate rocks show almost perpendicular trends. Acid rocks data plot as a cluster. REE present smooth patterns without any Eu anomaly (intermediate rocks) or with very weak Eu anomaly (acid rocks). Spider diagrams display some anomalies. Detailed analysis of the relation between the element showing anomaly and the surrounding them other elements revealed, that the anomalies resulted from the geochemical characteristic of the magma source and they are not a result of magma differentiation triggered by fractional crystallization.

New trace element analyses and isotopic data allowed performing extended geochemical modelling using full set of data. It seems, that magma for all the rocks is generated from two different sources, metasomatized mantle and crust ($\varepsilon Nd(t)$ respectively ~ +4 and ~0, $\varepsilon Sr(t)$ respectively ~ +28 and +19). New geochemical models (performed using set of major and 30 trace elements) show, that the variability in geochemical composition of the basalts-trachybasalts-trachyandesites can be related to various degree of partial melting as well as to compositional heterogeneity of metasomatized mantle. Dacites-trachydacites-ryolites are derived from crust-related magma and are not evolved from mafic melt. Crustal amphibolites are supposed to be a source for the acid magma. Mixing hypothesis suggested by Czerny and Muszyński (1997) as well as Bukowy and Cebulak (1964) have been not verified positively taking under consideration their assumptions. All the same new contamination models have been developed using parental intermediate and acid magmas. These models explained the origin of some silica enriched, intermediate magma blobs.

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ATOLL GARNETS FROM STRUHÁR COMPLEX (NÍZKE TATRY MTS.); MINERALOGY AND PETROLOGY

Abstract: Recently, there have been found occurrences of garnet-amphibole gneisses containing atoll-like garnets in the Struhár complex (Nízke Tatry Mts.). The garnets contain a high amount of almandine (Alm – 70), rather increased amounts of grossular (Grs – 15) and pyrope (Prp - 12), and a low amount of spessartine. The amphiboles are of two generations and correspond to ferrotschermakite or ferrotschermakitic hornblende. We suppose that the atoll-like shapes of the garnets are a result of replacing the central (less stable) parts of primary zoning garnets by biotite, amphibole, plagioclases, and/or quartz under changing PT conditions of metamorphosis. Atoll-like garnets are typical of polymetamorphic regions.
Keywords: atoll-like garnets, composition, Struhár complex, Nízke Tatry Mts

INTRODUCTION

Atoll-like garnets represent a specific type of garnets whose genesis has not been unambiguously resolved yet. They occur mainly in medium to higher-grade metamorphic complexes. There are known occurrences of atoll-like garnets from the Bohemian Massif (Krušné hory – Satran 1957, Klápová 1990; Zbraslav complex – Fediuk, Fediuková 1997), Ireland (Donegal – Smellie 1974, Homan 2003), China (Dabie Shan Mts. – O´Brien, Carswell 2006), Russia (SE Tuva, Ushakova, Usova 1990) and other complexes. Garnets of this type were also found in garnet-amphibolite gneisses in the Struhár complex of the Nízke Tatry Mts.

GEOLOGY

The southern slopes of the Ďumbier part of the Nízke Tatry Mts. are divided into four tectonic zones (Bezák, Klinec 1980) with typical rock filling. The Struhár complex is considered a separate tectonic unit overfaulted on its northern foreland formed by the complexes of Zámostská hoľa (hybrid granodiorites and nebulites) and Špíglová hoľa (stromatitic and nebulitic migmatites). In general, the Struhár complex is petrographically variable. Beside typical orthogneisses (Bezák, Klinec

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1980; Spišiak, Pitoňák 1990), also more basic varieties of gneisses, amphibole gneisses up to amphibolites, as well as banded migmatite-type rocks occur here. It is supposed that this lithological type is a member of LAK (leptyno-amphibolite complex, Hovorka et al. 1994). A part of this complex is made by garnet-amphibole gneisses containing atoll-like garnets.

MINERALOGY

Atoll-like garnets from garnet-amphibole gneisses are specific in composition. They contain high amounts of almandine (Alm 71–75) and rather low amounts of grossular (Grs 14–16) and pyrope (Prp 8–12), and/or low amounts of spessartine. Tiny (non-atoll-like) grains are slightly zonal. It is the so-called normal continuous zoning, where Mn and Ca are high in the core and Fe and Mg are increasing from core to rim. The central parts of atoll garnets are replaced by biotite, rarely amphibole, plagioclase and quartz. The atoll-like garnets from the Struhár complex are similar in composition to atoll-like garnets from other metamorphic rocks (Spišiak, Hovorka 2003, Homan 2003, O´Brien, Carswell 2003 etc.).

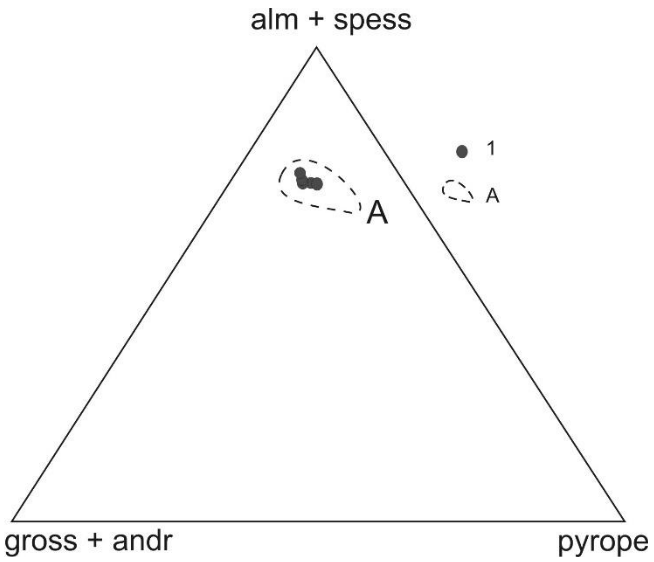


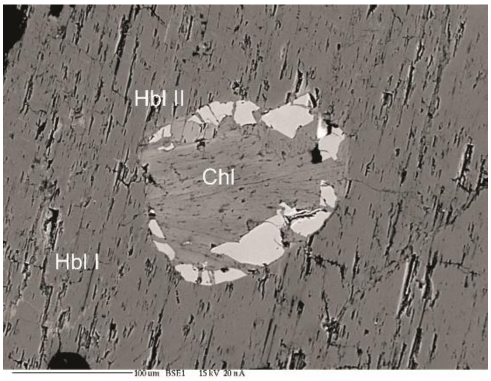
Fig. 1. Ternary diagram gross+andr : alm+spess : pyrope for the studied garnets. 1 = atoll-like garnets from Struhár complex, A = atoll-like garnets from eclogite (Spišiak, Hovorka 2003)

The amphiboles are of two generations and correspond to ferrotschermakite, and/or ferrotschermakitic hornblende (according to Leake et al. 1998). Other minerals represented are plagioclase An_{35-40}, quartz, biotite and secondary minerals (epidote and chlorite).

DISCUSSION

Atoll garnets occur in metamorphic rocks of various types (regional and contact metamorphosed rocks). Their most characteristic feature is normal zoning, i.e. Mn and Ca are high in the core, and Fe and Mg are increasing from core to rim (Smellie 1974; O´Brein, Carswell 2006 and others). According to O´Brein, Carswell (2006) this zonality was the reason why the rims of garnets have been preserved (higher stability of the rims in mineral reactions) and thus atoll texture formed. Another possible origin of atoll texture is formation to a skeletal growth at a short-time temperature increase in contact aureole (Ushakova, Usova 2003**)**

It is supposed that in the Struhár complex atoll-like shape originated during the retrograde phase of metamorphism when the central parts of garnets were replaced by others minerals (mainly biotite, amphibole, plagioclase). However, locally there are also observed occurrences of probably skeletal growth of atoll garnets. In this case, atoll garnets grow irregularly through different mineral phases (hornblende and plagioclase).



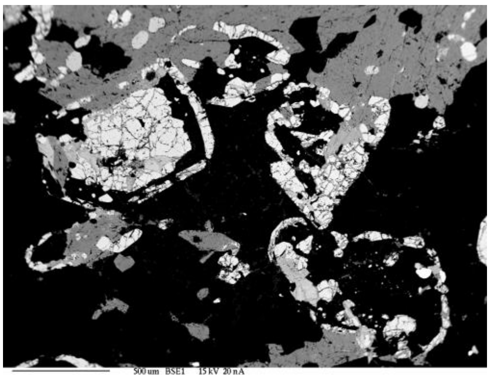


Fig. 2, 3. Back scattered electron image of atoll garnets.

CONCLUSIONS

- Atoll-like garnets are garnets typical of medium to high-grade metamorphosed complexes.
- Atoll-like garnets are similar in composition in variou types of rocks. They have an abundant almandine (Alm 72) component, rather large grossular (Grs 15) and pyrope (Prp 10) components and a poor spessartine component.
- The presence of atoll-like garnets points to a polymetamorphic character of the rocks in which they occur.

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LOWER-CRUSTAL COMPLEXES IN THE PRESENT SURFACE OF THE WESTERN CARPATHIANS

Abstract: There are two complexes recrystallized under the conditions of low continental crust (granulite facies); Leptynite-amphibolite complex (LAC) and Struhár complex in the Central Western Carpathians. The complexes have undergone a complicated geological process, when uplifted to higher parts of the continental crust they were retrogressively recrystallized under the conditions of amphibolite and greenschist facies.
Keywords: leptynite-amphibolite complex, lower crust, petrology, Western Carpathians

INTRODUCTION

In the recent years, there have been reported metamorphic complexes where top P-T conditions match to the conditions of granulite facies, i.e. conditions of the lower continental crust, in the central zone of the Western Carpathians (when divided transversally into three basic zones: externides, centralides and internides). Hovorka et al. (1994, 2004) included this bi-modal banded complex, made by light quartz-feldspar ± garnet rocks and amphibolites ± garnet, to the leptynite-amphibolite complex of Western European Variscides (Santalier et al.1998). By defining this complex (= LAC) he laid a basis for classification of metamorphic pre-Upper Carboniferous complexes of the Western Carpathians according to their original position (= top P-T conditions of their generating) in the vertical profile of the continental crust. This newly-defined complex together with prevailing metamorphites of the greenschist and amphibolite facies completes the conception of rock types of the continental crust in vertical section in the space of the Western Carpathians.

More recently, there has been reported a heterogenous polymetamorphic supracrustal complex (Struhár complex; Hovorka, Spišiak, in print) on the southern slopes of the Ďumbier Nízke Tatry Mts.. The top conditions of metamorphic recrystallization of this compex match the top P-T conditions of granulite facies, i.e. lower continental crust.

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The lower-crustal metamorphic complexes under consideration represent also a connection between Western European Variscides and Variscan complexes underlying Alpine-type Europe. In the following part, we will present a description of both lower-crustal complexes that occur in the set of pre-Upper Carboniferous substrate of the Western Carpathians.

LEPTYNITE-AMPHIBOLITE COMPLEX OF CENTRALIDES OF THE WESTERN CARPATHIANS

Leptynite-amphibolite complex of centralides (LAC) occurs in most core mountains of the Western Carpathians and in north-Veporic metamorphic units. It has the following typical features:

- LAC has a strongly tectonic setting and it is seated on metamorphic greenschist as well as amphibolite facies rocks. It was uplifted from the lower crust to the upper parts of the continental crust during the Variscan orogeny along the main Variscan thrust fault (Hovorka 1994);
- Dip and strike of this complex are different from those in adjacent metamorphic complexes. Locally, (north Veporicum – Pohronská Polhora and Jasenie areas in the Nízke Tatry Mts.) LAC has a virtually vertical position, which can be well documented in exploration drifts near Jasenie in the Nízke Tatry Mts.
- The basic lithotypes of the complex studied here are light bands, greatly varied in thickness (from milimetres to metres). The second basic lithotypes are different varieties of amphiboles. The have similar thickness as light bands
- LAC has undergone a number of metamorphic processes, of which local hydratation recrystallization and anatectic melting had the biggest impact on it. That resulted in the formation of hydrous minerals (muscovite, biotite), recrystallization of basic silicate minerals, larger mineral grains and others. The resulting anatectic melts only scarcely left the space of LAC.

The effect of the subsequent process is intense retrograde recrystallization of LAC with the originating of different varieties of greenschist (chlorite-albite-actinolite) and quartz-albite-sericite schists.

In some places (mountains, units), the lower parts of LAC contain bodies of retrogradely recrystallized eclogites (Hovorka et al. 1994), and very seldom also metabasites with preserved omphacite (Janák et al. in prep). There can be also found small bodies of antigorite serpentinites (or their recrystallized varieties of tremolite-talc rocks), gabbros and troctolites. All these types are bodies uplifted by LAC from the lower continental crust to their current geological position.

In some places, antigorite serpentinites are typical for disseminated mineralization of Fe-Cu-Ni sulphides (Pohronská Polhora), which together with locally preserved palimpsestic textures, point to a gabbro-peridotite protolith, with antigorite serpentinites representing hydrated and metamorphosed varieties of peridotites of this protolith.

THE STRUHÁR COMPLEX OF THE NÍZKE TATRY MTS.

Bezák and Klinec (1980) divided metamorphic and magmatic members of the pre-Upper Carboniferous substrate of the Nízke Tatry Mts. into several SW – NE zones.

In recent years, the authors of this paper have done field and laboratory research of the rocks of the Struhár complex (Hovorka, Spišiak, in print) and summarized these issues as follows:

- The Struhár complex has a tectonic position to its surrounding complex, which is emphasized by a band of Permian-Triassic sediments at its contact with a more-to-the-north Špiglová zone.
- The basic (most widespread) rock types of the Struhár complex are light medium- to fine-grained rocks of orthogneiss type. In most occurrences micas contents are very low and both muscovite and biotite are present in variable amounts. Light orthogneisses have only slightly planparallel fabric, which is clearer in places with higher amounts of micas.
- Bodies of amphibolic gneisses to amphibolites as well as bodies of muscovite to quartzite gneisses follow the course of the foliation. The thickness of these inlays in the basic complex type is greatly varied.
- A typical petrological phenomenon is the presence of atoll-like garnets in all these rock types. We see these structures of garnet porphyroblasts as a result of replacing of pyrope-rich central parts (and thus the least stable under lower P-T conditions) of garnets by newly-formed silicate minerals (most often biotite, quartz and feldspar).

CONCLUSIONS

We consider both the above-mentioned rock complexes of Western Carpathians centralides (LAC and Struhár complex) as complexes recrystallized under the conditions of lower continental crust (= granulite facies).

The complexes have undergone complicated geological processes, when uplifted to higher parts of the continental crust they were retrogradely recrystallized under the conditions of amphibolite and greenschist facies.

The current position of this complex (at the contact with lower-metamorphosed rocks – Špíglová zone) is a result of the Alpine orogeny.

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Wojciech STAWIKOWSKI[1]

GEOCHEMISTRY OF POST-ECLOGITIC AMPHIBOLITES FROM THE ŚNIEŻNIK METAMORPHIC COMPLEX (WESTERN SUDETES)

Abstract: The preliminary geochemical investigations of post–eclogitic amphibolites reveal their significant enrichment in Si and alkalis comparing to high-pressure predecessors, what was probably connected with the influx of those elements from the surrounding gneisses during retrogression. For the first time the post-HP metabasites from Strachocin and Stronie Śl. have been interpreted. Similarly to the granulites from Stary Gierałtów, they reveal signals of calc-alkaline affinity. Simultaneously, they are distinct from the metabasites in the remaining regional units, what may suggest the tectonic melange as the possible environment of the eclogite occurrence in the Śnieżnik Complex.
Keywords: Śnieżnik Metamorphic Unit, eclogites, retrogression, geochemistry

INTRODUCTION

Numerous lensoid bodies of eclogites suspected to experience ultra-high pressure metamorphism occur in the Śnieżnik Metamorphic Complex (ŚMC). They are surrounded by the rocks recording lower metamorphic conditions: the orthogneisses traditionally divided into the Gierałtów and Śnieżnik types and the paragneisses of the Stronie group. All those felsic rocks display the evidence of metamorphic peak in the amphibolite facies conditions and traces of migmatisation. The outer parts of the eclogitic lenses or sometimes the whole bodies were subjected to intensive retrogression, resulting in the formation of amphibolites.

The geochemical studies of the fresh eclogites revealed their strong geochemical diversity connected with regional arrangement (Bakun-Czubarow 1998). Considering 4 orthogneissic units distinguished in the ŚMC, the eclogites from the Międzygórze and Radochów U., have MORB signature, while those from the Śnieżnik U. and HP granulites from the Gierałtów U. show calk-alkaline affinity.

The present study is focused on geochemical effects of the eclogite retrogression, shaped by interaction with the surrounding rocks of acidic composition. Locally, the problem was studied by Bakun-Czubarow (1968), who shown increase in K and Ba.

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SAMPLING STRATEGY AND METHODS OF INVESTIGATION

Ten samples of post-eclogitic amphibolites were taken at 8 exposures. All the units of the ŚMC were represented, although not evenly. Half of the specimens came from the Gierałtów Unit (GU), in which the HP metabasites are the most poorly recognized. In case of Strachocin, full trace element analysis had not been applied yet, while the metabasites from Stronie Śl. were so far treated as members of the middle-pressure Stronie Group. However, petrologic observations (i.e. high-Mg garnet and zoisite relics, poikiloblastic texture) revealed their analogy to the post-HP metabasites from 2 km distant Strachocin (Stawikowski 2005).

The major and trace elements (incl. REE), have been studied using inductively coupled plasma techniques. The ICP-MS has been applied for trace elements, while the ICP-OES for major elements. The analyses were performed at the ActLab. Ltd.

RESULTS

Major element analyses reveal the diversified geochemical reaction of the metabasites on retrogression. The smaller part of the amphibolites does not show significant differences in composition related to fresh eclogites, while the majority displays relevant changes. The comparison of major elements content reveals the enrichment in *Si* and *alkalis* due to retrogression. It is clearly visible at the TAS classification diagram (Fig. 1), which includes, apart from the amphibolites, the analyses of fresh eclogites from Smulikowski (1979). The retrogressive processes resulted in shift of the metabasites from basalts towards basaltic andesites. The second field is occupied mainly by the rocks from the GU. The rocks from Strachocin frequently contain *Pl* and *Qtz* in their HP paragenesis (Smulikowski 1967), what is reflected by higher amount of SiO_2 (>52%). However, there is still a significant increase in *Si*, *K* and *Na* in the products of their retrogression.

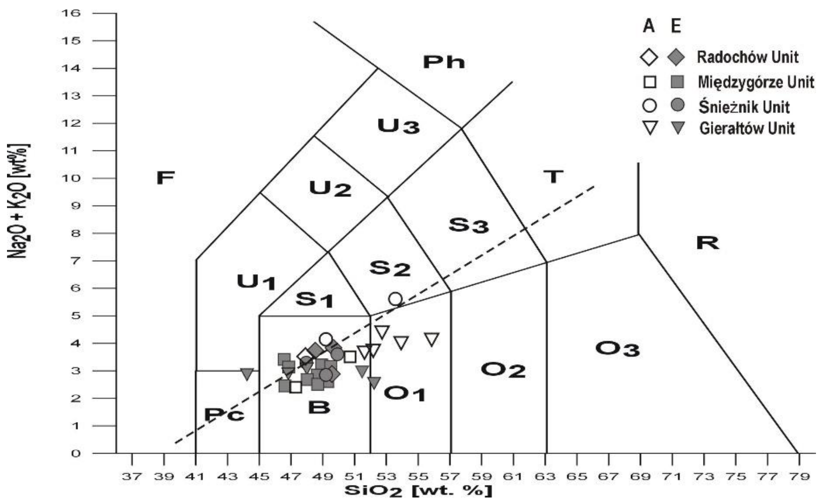

Fig. 1. Post-eclogitic amphibolites (A) and fresh eclogites (E) at the TAS diagram. B – basalts, O_1 – basaltic andesites, S_2 – basaltic trachyandesites, Pc – picrites. Dashed line: division to alkaline (above) and subalkaline rocks (below the line).

The increase in *K* content in the amphibolites implies the enrichment in strongly mobile LIL elements (*Rb, Ba, U, Th*), reflected by their high values at the spider diagrams (Fig. 2). There is no possibility to compare the results to eclogites. However, they can be confronted with the Stronie Group amphibolites (Floyd et al. 1996), what is important regarding the possibility of misinterpretation: the SG metabasites may sometimes, like the amphibolites from Stronie Śl., be retrogressed HP rocks. Despite similarity of the trends for all the samples, some distinction of the GU amphibolites patterns can be observed. They display stable down-slope trends, whereas in the rest of the units, HFSE segments of the curves are more flattened.

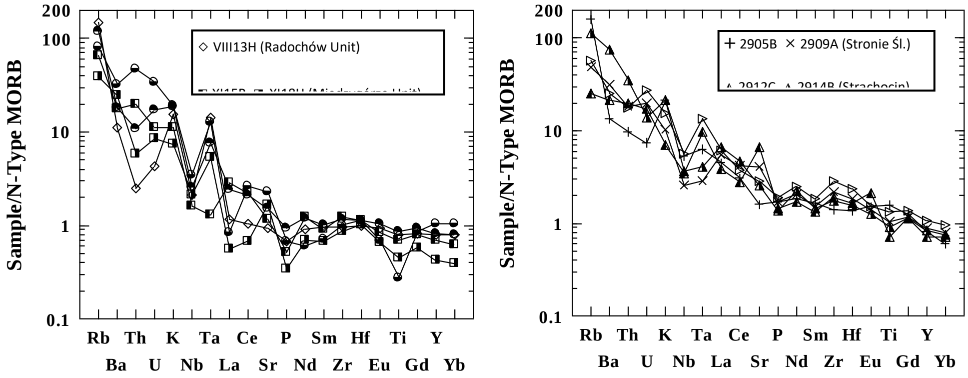

Fig. 2. Spider diagrams of post-eclogitic amphibolites. Normal.: Sun&McDonough (1989).

The distinctness of the GU metabasites is confirmed by the REE diagrams (Fig. 3). They possess negative patterns, with conspicuous enrichment in LREE. The samples from the other units either have more flattened sloping or do not show the LREE enrichment. While the negative REE trends (GU) suggest island arc environment, the bell-shaped curves (XI18H, MU) are linked with MORB affinity (Biino 1995).

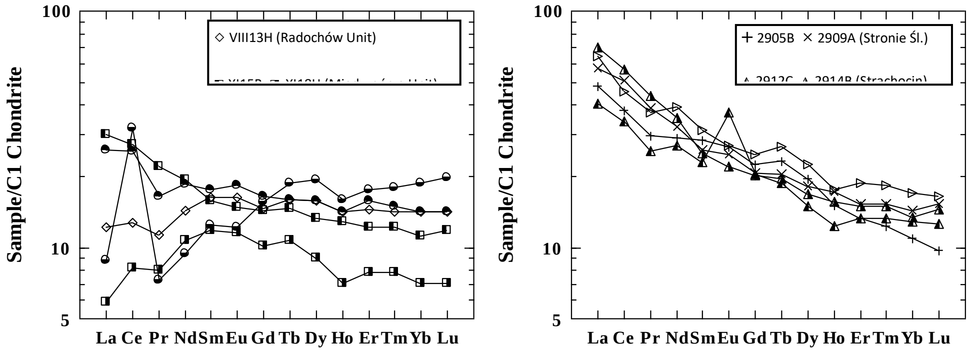

Fig. 3. REE diagrams of post-eclogitic amphibolites. Normal.: Sun & McDonough (1989).

With caution due to limited applicability of the method for metamorphic rocks, the discrimination diagrams were used (Fig. 4). The elements (Ti, Y, Sr) were chosen, with respect to acceptable correlation with *Zr*. The GU metabasites tend to group in the fields of calk-alkaline rocks (in agreement with HP granulites). However, some other diagrams suggest contradictory provenance (Stawikowski 2005), what indicates reserve to protolith geotectonic interpretation of the studied rocks.

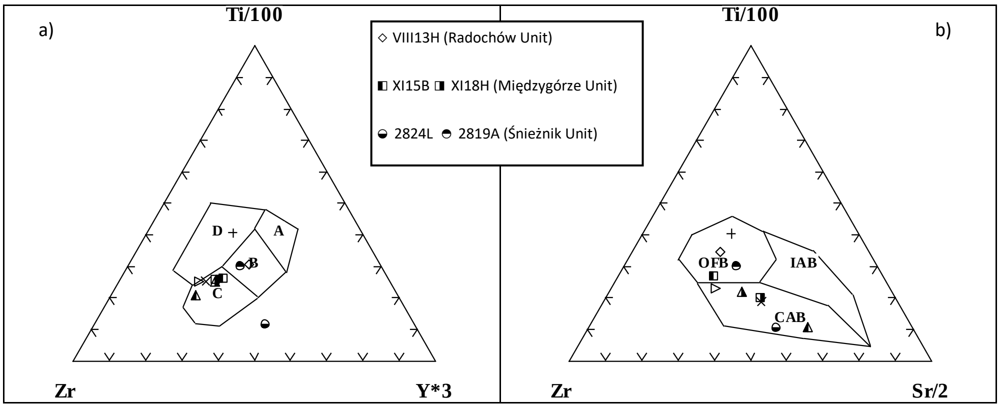

Fig. 4. Post-eclogitic amphibolites at the basalt diagrams of Pearce & Cann (1973). a)*Ti-Zr-Y*: A–island arc, B–MOR, island arc and calc-alkaline, C–calc-alkaline; D–within-plate; b) *Ti-Zr-Sr:* OIB–ocean island and MOR, CAB – calc-alkaline; IAB – island arc.

CONCLUSIONS

Post-eclogitic amphibolites from the ŚMC significantly depart in chemical composition from their predecessors. They reveal higher content of *Si* and alkalis, probably connected with the element influx from the surrounding gneisses. Such exchange could be facilitated by migmatisation, which affected the contacting rocks. The most detailedly studied amphibolites from the GU reveal calc-alkaline affinity. They differ from the metabasites in the other units. It suggests conception of tectonic melange as explanation to strong diversity of the HP rocks in the Śnieżnik Complex.

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MINERALOGIA POLONICA – SPECIAL PAPERS
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Milan SÝKORA[1], Štefan MÉRES[2], Peter IVAN[2]

DETRITIC GARNETS AND SPINELS IN SEDIMENTARY ROCKS OF THE GOSAU GROUP (WESTERN CARPATHIANS, SLOVAKIA): THEIR COMPOSITION AND PETROGENETIC SIGNIFICANCE

Abstract: The detritic garnets and spinels from conglomerate matrix and sandstones of the Gosau Group in the area Dobšinská Ľadová Jaskyňa village were studied. Chemistry of the garnets and spinels indicates that they were derived: (1) from such rocks as gneisses, amphibolites, metagabbros, metamafic rocks and eclogites which are parts of the leptynite-amphibolite complex in the pre-Alpine basement of the Western Carpathians; (2) from the Triassic and Jurassic ophiolites of the Meliata Unit, (3) from Carboniferous conglomerates of the Gemeric Unit.

Keywords: spinels, garnets, provenance analysis, Late Cretaceous – Paleocene, Western Carpathians

INTRODUCTION

Sediments of the Late Cretaceous to Paleocene age in area Dobšinská Ľadová Jaskyňa (DLJ) village, are regarded as an equivalent of the Gosau Group sediments of the Northern Calcareous Alps (Mello et al. 2000). Sequence of clastic sediments – conglomerats, sandstones, marls and limestones of the above mentioned Group are fillings a small basinal relic (approximately 3 x 1 km). Pebbles and clasts of rocks of a complete ophiolite association have been found in some outcrops of conglomerates (Ivan et al. 1998). Garnets and spinels have been found in the conglomerate matrix and in the sandstones (Fig. 1). Magnetite, zircon, rutile and apatite were also identified.

GEOLOGICAL SETTING

The sediments of the Gosau Group in the studied area are in transgresive position on the Triassic carbonate sediments of the Silicic Unit or Jurassic melange of the Meliatic Unit (Mello et al. l.c.). Sediments of the Gosau group near DLJ village are composed by two sequences. (1) Sequence of brownish marly slates and marls contains thin coal beds in its lower part. Freshwather limestones with alga *Munieria grambasti* BYSTRICKÝ alternate in some parts with marls. (2) Upper part of the Gosau group is represented by polymict conglomerates. Pebbles of Triassic and Jurassic limestones, radiolarites, ophiolites, blueschists, porphyroides, freshwater limestones were found in conglomerate bodies (Ivan et al. 1998). Conglomerates alternate with brown – reddish sandstones and lithic greywackes.

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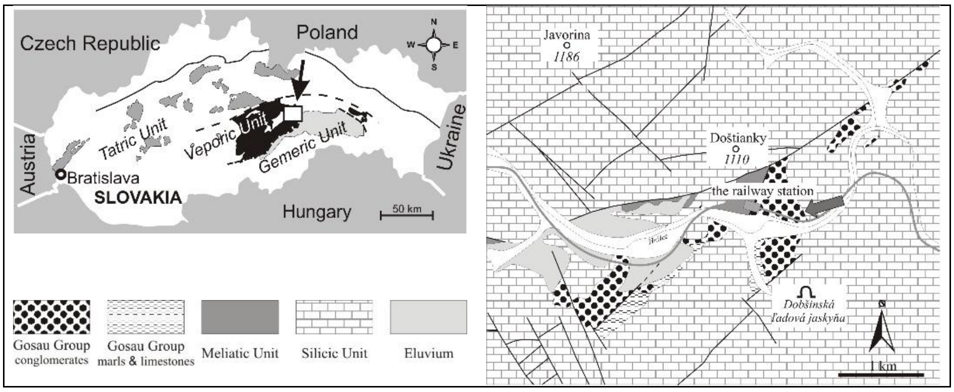

Fig. 1. Schematic map of position study area – left; simplified geological map with location (arrow) of the occurence sedimentary rocks of the Gossau Group containing detritic garnets and spinels - right.

RESULTS AND INTERPETATIONS

The variability of composition of the detritic garnets (Grt) is in the Fig. 2.

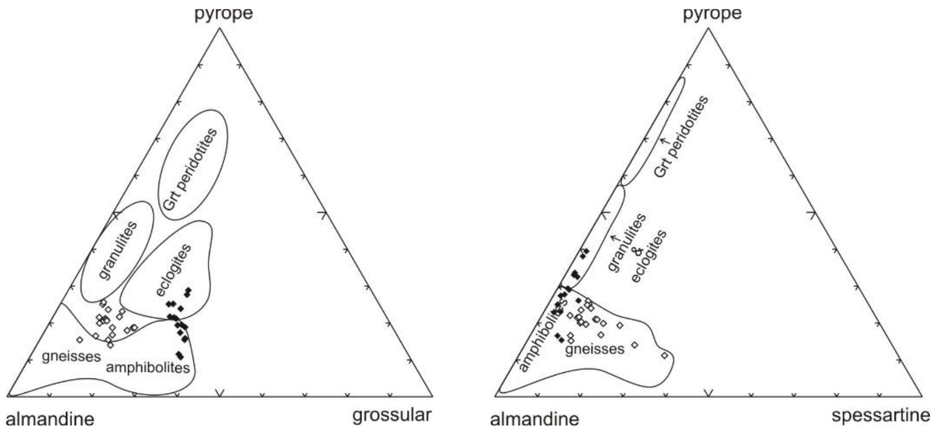

Fig. 2. Composition of the detritic garnets from the studied Gosau Group sequences. Fields of diagrams see Aubrecht & Méres 2000.

Two main groups of Grt have been recognized according to their composition: **(1)** first group with relatively high content of grossular component (black filled diamond on the Fig. 2) derived from the mafic metamorphosed rocks and **(2)** second group with lower content of grossular component derived from acidic metamorphosed rocks (white diamond on the Fig. 2). According to composition and possible source rocks Grt can be divided into four groups (Fig. 2): **(1)** Grt coming from mafic granulites or high-grade amphibolites. They have relatively higher content of pyrope component (20-25 mol %) in comparison to the Grt from gneisses. Also high content of almandine (50-60 mol %), low proportion of grossular (~ 30 mol %) and very low content of spessartine (~ 2 mol %) are typical. **(2)** Grt coming from eclogites. These Grt display pyrope content higher than 25 mol %, almandine content of 40-50 mol %, grossular content of 25-30 mol % and spessartine less than 1 mol %. They differ from the group 1 by higher proportion of the pyrope component (>25 mol %). **(3)** Grt coming from gneisses have high almandine content (~ 55 mol %), low pyrope (< 10 mol %) and higher content of spessartine (10-27 mol %) than Grt from granulites. Content of grossular is less than 10 mol %. **(4)** Grt coming from amphibolites metamorphosed in epidote-amphibolite to amhibolite facies conditions. They differ from the group 2 by lower proportion of the pyrope molecule (< 20 mol %) and by spessartine content < 10 mol%, grossular content < 10 mol % and relatively high content of almandine (50-60 mol %). Continual transition of Grt composition in both above mentioned main groups (Fig. 2) reflect a dominance of one source area composed of rocks metamorphosed in the amphibolite to granulite facies. Such rock complex in the pre-Alpine Western Carpathian basement is represented by leptynite-amphibolite complex (LAC, Hovorka et al. 1997).

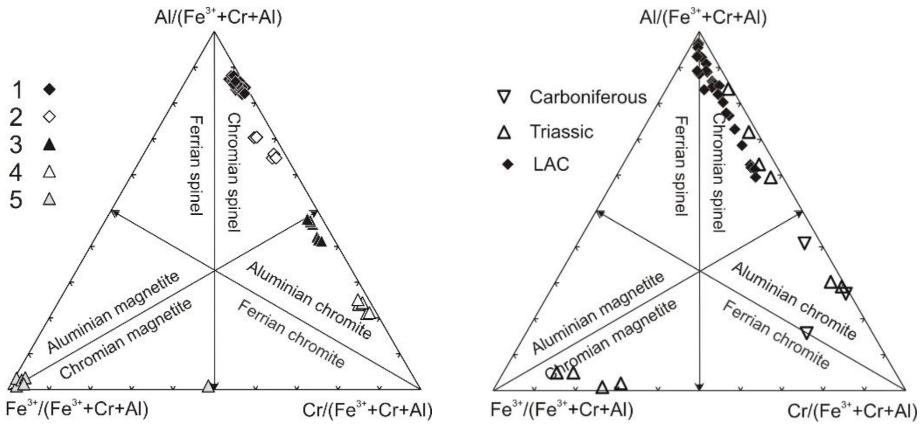

Fig. 3. Composition of the detritic spinels (on the left) and spinels from metamafites of the LAC, spinels from ultrabasic bodies in the Carboniferous sequences (Ochtiná, Rudňany) and spinels from ultrabasic bodies in the Triassic sequences (Rudník, Jasov, Jaklovce, Dobšiná, Danková; data from Rojkovič et al. 1978 - on the right).

The nearest outcrop of LAC is in the Dobšiná area (Klátov group) and in the surrounding of Helpa village (LAC in the pre-Alpine basement of the Veporic Unit of the Nízke Tatry Mts).

Some garnets with relatively elevated content of the grossular and spessartine component indicate the second possible source rocks metamorphosed under low temperature (enrichment in spessartine component) and relatively higher pressure (enrichment in grossular component) conditions. This source could be probably related to metamorphic rocks of the Meliatic Unit.

As follows from microprobe analyses of detritic spinel grains their composition vary from alumianchromite to chromian spinels (Fig. 3). Source rocks of spinels plotted in the chromian spinel field (Fig. 3; 1 and 2 group) were ultramafics rocks, metamorphosed into granulite to eclogite facies. Identical spinels were described from the metamafic rocks of the LAC in the Veporic Unit (Méres et al. 2006). The spinels plotted in the aluminian chromite field (Fig. 3, 3 and 4 group) are typical for ultramafic rocks. Spinels of same compositions were described from the ultramafic rocks of the Meliatic Unit (Fig. 3, Triassic). These rocks are considered as the second possible source rocks of spinels under study. Also Carboniferous conglomerates of the Gemeric Unit could be take into account as another possible source rocks of the detritic spinels (see Fig. 3).

CONCLUSIONS

Detritic garnets and spinels from the clastic sequences of the Gosau Group near Dobšinská ľadová jaskyňa village were probably derived from two different sources: (1) the first source could be gneisses, amphibolites, metagabbros, metamafics and eclogites correlated with the leptynite-amphibolite complex in the pre-Alpine basement of the Western Carpathians, (2) the second source rocks were probably the Triassic and Jurassic ophiolites of the Meliatic Unit and (3) the third possible source rocks were Carboniferous conglomerates of the Gemeric Unit.

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MINERALOGIA POLONICA – SPECIAL PAPERS
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Jacek SZCZEPAŃSKI[1]

PSEUDOSECTION ANALYSIS FOR METAPELITE FROM THE BYSTRZYCKIE MTS., SUDETES: PRELIMINARY RESULTS

Abstract: A quantitative phase diagram in the MnNCKFMASH system was calculated for one metapelitic sample from the southern part of the Bystrzyckie Mts. in the PT range of 1-15 kbar and 350-700°C. The investigated metapelite was collected from garnet zone. The previously published peak P-T conditions (564±26°C at 6.3±1 kbar) are confirmed by the present study. Additionally based on the Si content in muscovite as well as pyrope, grossulare and spessartine contents in garnet a part of the PT path recorded by the investigated rock was reconstructed.
Keywords: metapelite, phase equilibria, isopleth thermobarometry, metamorphic petrology, Bystrzyckie Mts, Orlica-Śnieżnik Massif

INTRODUCTION

Rocks of the Stronie formation in the Bystrzyckie Mts. (western part of the Orlica-Śnieżnik Massif) form four separate outcrops described by Dumicz (1964) as individual tectonic units. From the NE to SW and from bottom to top of the structural sequence they are: Równia Łomnicka, Mostowice-Jagodna, Gniewoszów-Kamieńczyk and Niemojów-Czerwony Strumień units. In the Gniewoszów-Kamieńczyk unit peak mineral assemblages are related to the main deformation episode and form a typical Barrowian type sequence with biotite, garnet and staurolite zones (Szczepański 2003). Estimated temperatures yields values of 435 - 490°C for biotite zone, 580 – 588°C for garnet zone and 615°C for staurolite zone at pressures of 4.9 - 6.4 kbar (Szczepański 2003). In spite of the fact that peak PT conditions for those rocks are well estimated, garnet and staurolite devoid of any inclusions (apart from quartz) preventing from construction of PT path for metapelites using conventional geothermobarometry. Therefore, a quantitative phase diagram technique is necessary to reconstruct at least part of PT path using mineral composition and whole-rock chemistry.

METHODS OF INVESTIGATION

A quantitative phase diagram in the MnNCKFMASH system was calculated using PERPLEX software (Conolly 1990) for metapelite (sample s82) collected from garnet zone. The calculations were based on an updated version (2002) of the internally-consistent thermodynamic data set of Holland and Powell (1998) and solid solution models incorporated into the software package. Major composition of the bulk rock sample was determined using ICP-emission spectrometry following a lithium metaborate/tetrabortate fusion and dilute nitric digestion.

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RESULTS

In the studied sample the major minerals are phengite, biotite, garnet, plagioclase and chlorite. Garnet, forming porfiroblasts up to 2 mm in diameter, contains sigmoidal inclusion trails composed mainly of quartz. Chlorite often forms asymmetric pressure shadows around garnet grains. Plagioclase grains are normally flattened and elongated parallel to the main foliation plain suggesting that at least its rims grew syn-kinematically. Both phengite and biotite define the main fabric of the rock. Thus, Chlo+Ms+Pl+Grt+q represent a mineral assemblage formed during the main deformation episode recorded by the investigated sample.

A typical composition of most important minerals constituting the investigated sample can be detailed for phengite (3.08-3.12 Si p.f.u.), plagioclase (An 1.2) and garnet (core: Alm - 63, Grs - 15, Py - 5, Sps – 18; inner rim: Alm - 72, Grs - 8, Py - 6, Sps – 13; outer rim: Alm – 76.5, Grs – 4.5, Py – 7.4, Sps – 11.7). Moreover cores of the analyzed garnets are characterized by slightly bell-shaped spessartine and grossular content. Rims of the analyzed garnets are characterized by noticeable drop of both grossular and spessartine contents.

A main feature of the presented pseudosection (Fig. 1) is defined by stability of garnet under pressures exceeding c. 4.0 kbar at 550-700ºC. The lower limit of biotite stability is about 420ºC, whereas plagioclase and phengite are stable almost over the entire range of PT conditions. The stability range of mineral assemblage Ms+Bio+Chlo+Grt+Pl+q observed in the rock is 540ºC at 4.0 kbar up to 630ºC at 12.5 kbar. Further narrowing of the PT range recorded by the sample is possible using Si isopleths for phengite (Fig. 1). Intersection of Si 3.08, 3.10 and 3.12 isopleths with the stability field of the observed mineral assemblage gives a fairly narrow PT range of 5.0-8.3 kbars at 540-590ºC. This result resembles PT conditions calculated using conventional geothermobarometry (564±26ºC at 6.3±1 kbar). The advantage of the MnNCKFMASH system is the ability to model a composition of garnet in the PT field. Thus, the combination of presented data with garnet isopleths allows partial reconstruction of the PT path for the investigated sample (Fig. 1). As no relics of zoisite are observed in the sample the PT path must have left a Chlo+Ms+Pl+q field and during pressure and temperature increase entered a field of Chlo+Ms+Pl+Grt+q. The initiation of garnet growth occurred at pressure of about 10 kbar. After the pressure peak (at c. 11 kbar) investigated sample must have underwent c. 4.5 kbar pressure drop under increasing temperature. Surprisingly, the PT path finishes in the field Chlo+Ms+Pl+Grt+q at 6.5 kbar and 550ºC where biotite is not a stable mineral phase. It might be due to the calculation error or less probably it means that the deformation responsible for the development of penetrative foliation must have continued until the PT path finally entered the field Ms+Pl+Chl+Bio+Grt+q. The second explanation seems improbable as both garnet-biotite and garnet-muscovite thermometry yields the same temperatures for garnet and mica rims. The temperature could not exceed c. 570ºC at 6.5 kbar as no staurolite is observed in the investigated sample.

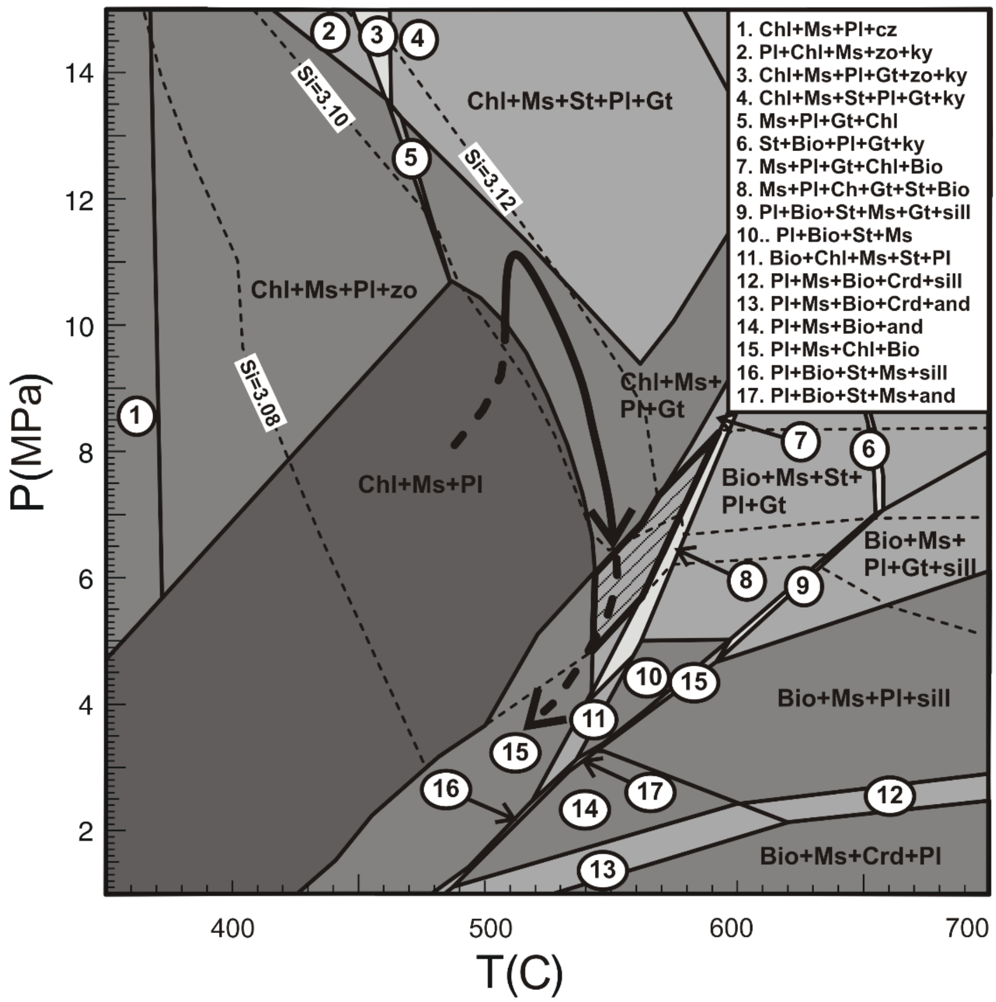

Fig. 1. PT pseudosection calculated for sample s82 with quartz and water in excess. The broken lines mark Si isopleths with Si content given in white rectangles Thick line marks the supposed PT path for the investigated sample. Its part outside the garnet stability field is marked by broken lines as no other data than mineral assemblages define it. MnO-0.09;Na_2O-0.66;CaO-0.14;K_2O-4.73,FeO-7.19;Al_2O_3-19,33;SiO_2-65.47; on weight percent basis in MnNCKFMASH system. Estimated P-T conditions are marked by dashed field in the Ms+Pl+Gt+Chl+Bt+q stability field.

CONCLUSIONS

The peak PT conditions calculated with conventional thermobarometric methods (564±26°C at 6.3±1 kbar) are confirmed by the PT stability range of mineral assemblage Ms+Pl+Chl+Grt+q obtained from the MnNCKFMASH pseudosection. The mineral composition isopleths for silica content in white mica combined with garnet isopleths for grossular, spessartine and almandine contents allowed reconstruction of part of the PT path recorded by the investigated sample. The reconstructed PT path can be divided into two sectors. The first is characterised by pressure increase at almost stable temperature with peak P at 11 kbar and 510ºC. The second reflects decompression undergoing at increasing temperature with thermal peak at ca. 550ºC and 6.5 kbar. The reconstructed PT path is typical of Barrovian type metamorphism which is normally related to thickening of continental crust (England, Thompson 1984) due to thrusting and folding. Recently, a border zone between the Nové Město Unit and the western part of the Orlica-Śnieżnik Massif was interpreted as a suture separating two crustal-scale units – Tepla-Barrandien to the west and Moldanubian to the east (Mazur et al. 2005). Consequently, it is suggested that the whole western part of the Orlica-Śnieżnik Massif (including the Bystrzyckie Mts.) may represent a pile of nappes tectonically assembled during this collision.

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MINERALOGIA POLONICA – SPECIAL PAPERS
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Krzysztof SZOPA, Patryk DUBIEL, Aleksandra GAWĘDA,[1]

MAFIC SCHLIEREN AND ALKALI FELDSPAR MEGACRYSTS – ARE THERE ANY GENETICAL RELATIONS?

Abstract: Two types of schlieren and associated alkali feldspar porphyrocrysts were investigated. The Afs zonation and temperatures of structure equilibration differ in both types of schlieren, as being an effect of two different mechanisms involved. The chemical monazite age around 300 Ma pointed out the equilibration of xenoliths with the granite. The age at 255 Ma suggest the presence of the Permo-Triassic tectono-thermal event.
Keywords: schlieren, alkali feldspar megacrysts, High Tatra granitoids.

INTRODUCTION

Many granitoid plutons are characterized by the presence of elongated trails of mafic minerals, sometimes with gradational margins, called schlieren. According to the very general definition given by Vernon (2004) schlieren are "*layers or streak-like concentrations, typically of relatively coarse-grained mafic minerals, with or without K-feldspar megacrysts and microgranitoid enclaves in intrusive rocks, especially granites; mostly formed by sorting during magmatic flow*". The origin of schlieren was discussed by several authors, which represent contradictory theories. Alkali feldspar megacrysts are observed in many granitoid intrusions, and are sometimes bounded to schlieren. Chemical patterns of alkali feldspars are indicators of magma mixing/mingling processes and, in consequence, changes in magma temperature (Hibbard 1981, Słaby et al. 2007), decompression during felsic magma ascent (Nekvasil 1991) and/or changes of water activity in the magma (Long, Luth 1986). The aim of this paper is to discuss the possible genetic inter-relations between the schlieren formation and crystallisation of zoned alkali feldspar megacrysts, found in several localities in the High Tatra granite.

GEOLOGICAL SETTING & SAMPLING

The crystalline basement of the Tatra Mts. comprises a polygenetic granitoid intrusion (Gawęda 2007) and a metamorphic envelope preserved mostly in the western part of the massif. The composite granitoid body forming so called High Tatra Mts. is a major point of interest. In the High Tatra Mts. two petrographic types of granitoids predominates: biotite and biotite-muscovite granodiorite-granite, in place porphyritic, called the common Tatra type and equigranular biotite granodiorite - monzogranite, called High Tatra type (314 Ma, Kohut, Janak 1994, Poller et al. 2001, Fig. 1). The typical feature of High Tatra granite is the presence

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of enclaves, represented by: hybrid quartz diorites (341 Ma), metapelitic and calc-silicate xenoliths, MME and plume-related mesoladogites (Pawlica 1918, Gawęda 2006, Gawęda 2007). Schlieren in the High Tatra granites are usually spatially connected to xenoliths and surrounded by Afs phenocrysts. For the purpose of this study we sampled schlieren associated with Afs-phenocrysts from four localities: Gerlach (1), Kończysta (2), Velicka Valley (3), Mięguszowieckie Mnich, nearby the Kazalnica overthrust (4), Mały Kościelec (5) and Mały Kozi Wierch (6).

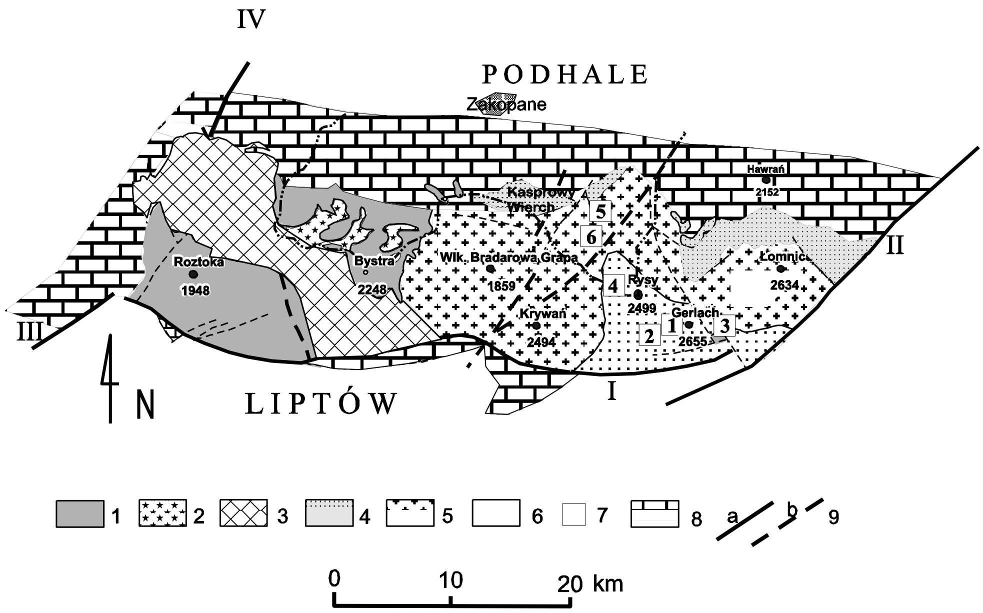

Fig. 1. Simplified geological map of the Tatra Mountains (compilation after Kohut, Janak 1994, Bac-Moszaszwili 1996, Gawęda et al. 2005). 1 – metamorphic cover, 2 – alaskites, 3 – Rohače Granite, 4 – Goryczkowa Granite, 5 – porphyritic granite, 6 – biotite monzogranite, 7 – samplig points, 8 – sedimentary cover, 9 – main faults: a – identified, b – assumpted. I – Subtatric Fault, II – Ružbachy Fault, III – Choč Fault, IV – Krowiarki Fault.

EXPERIMENTALS

Microscope observations were carried out in the Faculty of Earth Sciences, University of Silesia, using Olympus BX-51 microscope. Microprobe analyses of minerals, with a special care of alkali feldspar and monazite analyses were conducted on a CAMECA SX-100 electron microprobe in the Inter-Institution Laboratory of Microanalysis of Minerals and Synthetic Substances, Warsaw using sets of natural and synthetic standards. For monazite analyses the operating conditions were as follows: acceleration voltage 20 kV, beam current 50 nA, beam diameter 2 um, counting times 200 s (2 x 100), 400 s (2 x 200), and 600 s (2 x 300) for peak and background positions respectively. The monazite U-Th-common Pb chemical ages were calculated using Montel et al. (1996) procedure. The compositions of alkali feldspars with coexisting plagioclase were used to determine the temperature using the ternary feldspars procedure proposed by H. Nekvasil (1992) and SOLVCALC computer program.

SCHLIEREN PETROGRAPHY & MINERALOGY

Two types of schlieren were investigated:

1. Gradational bedding with visible physical sorting of feldspars, biotite, opaque minerals and accessories (Mz + Zr) and Afs phenocryst (usually corroded) located at the border between the light and dark layers. Quartz content is almost stable through the schlieren profiles. The biotite orientation changed in the profile: from the mostly disoriented in the lighter part of the layer to highly oriented in the bottom of each layer. Biotite is characterised by ***fm*** ratio in the range of 0.542 - 0.685 and Ti content between 0.315 and 0.351 [a.p.f.u.]. Muscovite show the features of magmatic white mica, with Ti [a.p.f.u.] = 0.123 – 0.117. Hipidiomorphic to idiomorphic plagioclase, composing 21 to 25 % vol. of the rock is an almost unzonal oligoclase (An_{18}-An_{20}). K-feldspar in matrix is xenomorphic, showing no internal zonation, while the Afs phenocrysts, concentrated at the bottom of gradual layer, show chemical internal zonation, expressed by Ba (celsjan molecule) content. Afs phenocrysts are oriented horizontally, parallel to the main magmatic foliation. This situation is observed in many granitoid massifs (Büttner 1999, Vernon et al. 1988). U-Th-Pb chemical dating of monazite crystals condensed in the mafic "base" of the gradational bed (as the inclusions in biotite and ilmenite) revealed the age of 255±5 Ma.

2. Thin (up to 2 cm thick) streaks of biotite with subordinate muscovite, opaque minerals and accessories (Mz + Zr + Xe), deformed by unstrained Afs and plagioclase phenocrysts, located nearby the bigger metapelitic xenoliths portions. The schlieren orientation is parallel to the xenoliths foliation. Biotite flakes show high degree of orientation, they defined the schlieren. The deformation of the mica-related fabric is visible only around the rigid Afs and Pl phenocrysts. Biotite is characterised by ***fm*** ratio in the narrow range 0.645-0.632, Ti content in the range 0.385-0.415 [a.p.f.u.] and is similar to the chemistry of biotite from the nearby xenoliths, while muscovite chemistry is typical of magmatic white mica (Ti = 0.13-0.20 [a.p.f.u.]). Assuming the original chemistry of biotite is preserved the Ti-in biotite temperature of 648-690^{o}C was calculated (according to Henry et al. 2005). U-Th-Pb chemical dating of monazites from the 2nd type schlieren showed the age of 300 Ma.

ALKALI FELDSPARS CHEMISTRY AND TEMPERATURE CALCULATIONS

In the 1st type schlieren the Afs megacrysts with corrosive borders contain zones of oligoclase, albite and quartz inclusions, attached by synneusis mechanism (Vernon 2004). The Ba in Afs shows normal distribution in the core-mantle profile: Celsjan molecule atomic percent (at. % Cs) = 2.09-1.29 at % in the core to 0.8-0.2 in the mantle), with local peaks (up to 2.05 at. % Cs). In the rim slight enrichment in Ba is again observed. The equilibrium feldspar pairs show the temperature in the range of 340-380^{o}C.

The Afs megacryst associated with 2nd type schlieren are surrounded by thin (5-20 μm in thickness) albite envelope and altogether are rimmed by micaceous layer. The internal zonation is underlined by rows of inclusions (Pl, Bt, Qtz) and Ba distribution. The Ba zonation is complicated and shows several steps: core 7.9-3.6 at. % Cs, inner mantle 3.2-3.8, outer mantle 5.7-4.2 at.% Cs, wide rim 2.55-0.9 at. % Cs. For the rim – envelope pair the equilibrium temperature fall in the range of 490-510^{o}C. The perthitic albites in the same megacrysts equilibrated in the temperature range 300-390^{o}C.

DISCUSSION & CONCLUSIONS

The Afs from the 1st type schlieren are characterised by the relatively low Cs content, relatively gradational changes in chemistry and one cooling episode, what implies no random changes in chemistry of the granitoid system and slow cooling.

The complicated zoning observed in the Afs attached to 2nd schlieren type and very high celsjan content can be a result of intensive changes in magma chemistry, caused i.e. by magma mingling/mixing (Hibbard 1981, Słaby, Galbarczyk-Gąsiorowska 2002, Gawęda 2007). The presence of plagioclase rows are thought to be interpreted as episodes of water content lowering. Dropping water content in the magma favours the plagioclase crystallization and reduces Ba incorporation to the feldspar structure. The high-Ba zones could result both from the mixing/mingling of mafic magma with the felsic granitoid one, and the higher activity of water, released from the explosion of xenoliths (compare Gawęda 2007b) and the partial melting of the metapelitic xenoliths. The equilibrium temperatures are adequate to the feldspar structure stabilisation and/or perthite exsolution. Two thermal episodes imprinted in Afs phenocrysts attached to 2nd type of schlieren suggest the formation and stabilisation of rapakivi-like envelope and Pl inclusions predates the perthite exsolution and final cooling.

The biotite orientation in 1st type schlieren can be interpreted as a result of sedimentation in flowing magma while the biotite orientation in 2nd type of schlieren is concordant with metamorphic foliation in nearby xenolithic complex and can be treated as the feature inherited after the former metapelitic xenoliths.

The monazite age of 2nd type schlieren (300 Ma) could suggest the equilibration of formerly metapelitic material with the granite. The obtained age is adequate to 314 Ma obtained by Poller et al. (2001), as well as within the limits of K-Ar and U - Th - common Pb ages obtained from the Western Tatra Mts. mylonites (Deditius 2004, Gawęda, Burda 2005). The 255 Ma monazite age is astonishing and can be attributed to the Permo-Triassic tectono-thermal event, noted in that part of Europe (so called Silky Road Arc *sensu* Natal`in & Şengör, 2005). In the Polish Carpathians similar ages were noted from the metamorphic cover of the Western Tatra Mts (258 Ma, Burda, Dzierżanowski 2005) and from the exotics from the Silesian Unit, Outer Carpathians (Michalik et. al. 2004). At that moment we can also start speculations about the potentially Triassic age of Kazalnica overthrust, however that needs further investigations.

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MINERALOGIA POLONICA – SPECIAL PAPERS
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Adam SZUSZKIEWICZ[1]

SECONDARY Ba-ENRICHED DOMAINS IN ALKALI FELDSPAR PHENOCRYSTS FROM THE MONZOGRANITES OF THE WESTERN PART OF THE STRZEGOM-SOBÓTKA MASSIF, SW POLAND.

Abstract: This article describes Ba-enriched domains of microcline phenocrysts showing the composition of barium microcline to hyalophane – phases which have not been reported from the Strzegom-Sobótka granites so far. They are spatially bonded to albitic rims of plagioclase inclusions and seem to have resulted from the same deuteric changes that caused perthite coarsening.
Keywords: hyalophane, Ba-feldspar, microcline phenocryst, Strzegom-Sobótka massif

INTRODUCTION

The investigations were carried out on samples from the monzogranites of the W part of the Strzegom-Sobótka Late Variscian granitic massif, located in the Fore-Sudetic Block (SW Poland). This part of the massif is built mainly of hornblende-biotite (hbl-bt) monzogranite with minor biotite (bt) monzogranite (Majerowicz 1972; Pin et al. 1989; Puziewicz 1990). The monzogranites crystallised at a depth of 3-5 km from water-undersaturated magma of crustal origin though the magma of the biotite variety contained less water and could be derived from a different source (Janeczek 1985; Pin et al. 1989; Puziewicz 1990). Domańska-Siuda (2007) demonstrated that the magmatic evolution of hbl-bt type was controlled by fractional crystallisation of plagioclase, biotite and amphibole with subordinate influence of mixing with small portions of mafic magmas.

Feldspars are essential constituents of the monzogranites. Earlier observations distinguished several generations of plagioclase, albite and K-feldspar - described as microcline (Mc) microperthite (Borkowska 1959; Kural, Morawski 1968; Kowalski 1967; Majerowicz 1972). The latter also forms several cm long subhedral to almost euhedral phenocrysts giving the rock its porphyritic structure with the groundmass built of quartz, zoned plagioclase, biotite, hornblende and accessory ilmenite, allanite, apatite, zircon. Features recording magmatic crystallisation, subsolidus evolution and hydrothermal alteration of the Mc phenocrysts have been identified and discussed (op. cit.).

This article reports the presence of phenocrysts' domains with a composition of Ba-microcline and hyalophane – phases that have not been reported from the Strzegom-Sobótka massif so far.

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METHODS

The investigations included observations in a Nikon E600 POL standard polarising microscope and in cathodoluminescence (CL) using Citl CCL 8200 “cold” cathode at the Institute of Geological Sciences, University of Wrocław. Graphite-coated thin sections were analysed with scanning electron microscopy at the Polish Geological Institute in Warsaw (LEO 1430), Institute of Geological Sciences, Jagiellonian University (HITACHI S-4700) and Inter-Institute Analytical Complex for Minerals and Synthetic Substances at Warsaw University (Cameca SX100). The latter was used for EPMA analyses in the WDS mode. Excitation voltage and beam current were 15 kV, 10 nA for measuring Si, Al, Ca, Na and K, 100 nA and 15 kV for Fe and Mn, 100 nA and 20 kV for Rb and Ba. The standards were: sanidine (Al, K), albite (Na), synthetic glass (Ba, Rb), hematite (Fe), rhodonite (Mn) and diopside (Si, Ca, Mg). The data were PAP corrected.

Tab. 1. Representative analyses of Ba-enriched domains and their host microcline (Mc) from Rogoźnica (SS86c) and Paszowice (SS53b). Number of analyses in brackets.

	SS86c				SS53b	
	Ba-Mc1(1)	Ba-Mc3(1)	Ba-Mc5(1)	Mc(3)	Ba-Mc(1)	Mc(4)
SiO_2	58.00	55.88	56.68	63.82	61.91	63.94
Al_2O_3	19.96	20.99	20.24	18.26	18.88	18.50
CaO	0.00	0.39	0.13	0.00	0.00	0.00
Fe_2O_3	0.00	0.00	0.00	0.00	0.00	0.00
MnO	0.00	0.00	0.00	0.00	0.00	0.00
BaO	8.43	11.32	9.50	1.30	2.80	0.26
Na_2O	0.68	1.16	1.18	0.44	0.26	0.33
K_2O	12.02	9.87	11.27	15.40	15.18	16.22
Total	**99.09**	**99.62**	**98.99**	**99.22**	**99.04**	**99.24**
Ab	6.6	11.4	11.1	4.0	2.4	3.0
An	0.0	2.1	0.7	0.0	0.0	0.0
Or	76.9	63.9	70.1	93.5	92.3	96.6
Cn	16.6	22.5	18.1	2.4	5.2	0.5

RESULTS AND DISCUSSION

The investigations were carried out on phenocrysts from Strzegom, Borów, Kostrza, Paszowice, Goczałków, Rogoźnica (hbl-bt monzogranite) as well as Morów, Morawa and Graniczna II (bt monzogranite). Microscopic observations confirm earlier descriptions (op. cit.). The Mc phenocrysts are up to 4 cm long, usually subhedral, white or grey with inclusions of plagioclase, epidote, quartz, chloritised biotite, allanite, rutile, zircon, apatite, monazite, xenotime and opaques. Mc is often Carlsbad- or Manebach-twinned but does not display a crosshatched twinning. Relict areas remain unexsolved though most of the Mc volume abounds in exsolution (film and string) or deuteric (vein and patch) perthites. Patch perthites and plagioclase inclusions are usually surrounded by non-perthitic Mc what suggests that Na migrated towards them from exsolution perthites. Zoning of Mc is conspicuous in CL and marked by the distribution of inclusions and perthites. Albitisation may lead to a complete substitution of the phenocrysts by chessboard albite. Subhedral to euhedral plagioclase inclusions are oligoclase whose cores may reach andesine composition. The outermost part forms an albitic rim, which may pass into patch perthites. CL of the inclusions is green-yellow, sometimes brown or dark blue while the albitic rims and deuteric perthites always display dark blue CL.

Chemical composition of Mc (Szuszkiewicz 2006) is typical of phenocrysts from granites. Exsolved parts show high Or content 92.5-97.2 mol %, with little admixture of Na (Ab:2.2-5.7 mol %) Ab content increases in the unexsolved regions, sometimes exceeding 20 mol %, what probably approximates the phenocrysts' original composition. Although Mc is a main Ba collector in the Strzegom monzogranites (Kowalski 1967), Ba content is generally low and only sporadically exceeds 2 mol % of celsian particle (Cn). Plagioclase inclusions analysed are oligoclase: $An_{10.2-30}Ab_{69-89.1}$. The sodic rims show a composition similar to the deuteric perthites: $Ab_{96.1-98.6}An_{0.9-1.7}$.

Examination of the BSE images of several phenocrysts revealed a presence of small (up to 20 μm) domains deviating from a typical Mc composition. They occur along the margins of albitic rims around plagioclase inclusions and are often associated with micropores. The contacts with a typical Mc are sharp, very rarely partly diffused. EMPA analyses of two examples show that they are markedly enriched in Ba. In SS86c sample from Rogoźnica (Fig. 1) and SS53b from Paszowice the domains display compositions of hyalophane ($Cn_{16.6-22.5}An_{0-2.1}Ab_{6.6-11.4}Or_{63.9-76.9}$) and Ba-microcline ($Cn_{5.2}Ab_{2.4}Or_{92.3}$), respectively (Tab. 1). The host phenocrysts are typical Mc: $Cn_{2.4}Ab_{4.0}Or_{93.5}$ and $Cn_{0.5}Ab_{3.0}Or_{96.6}$.

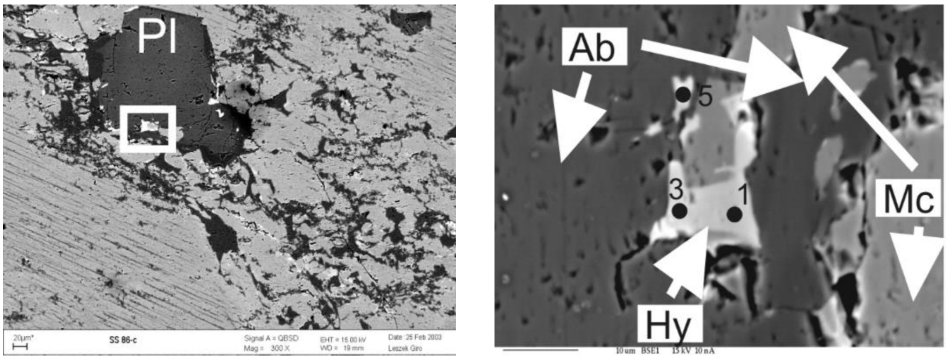

Fig. 1. **left**: Oligoclase (Pl) inclusion among deuteric perthites in SS86c microcline (Mc) phenocryst from Rogoźnica. Exsolution perthites in bottom left corner. Marked area is enlarged (and rotated) on the right image. **right**: Hyalophane (Hy) domain in contact with microcline and albitic rim (Ab) of plagioclase. Spots of EPMA analyses are marked.

Enrichment in Ba (up to 1% of Cn) was detected in hydrothermally altered Mc from Borów (Ciesielczuk, Janeczek 2004). Ba-enriched zones of K-feldspar were documented from resorption areas formed due to magma mixing (Gagnevin et al. 2005). However in the case discussed the occurrence of Ba-enrichment solely within deuterically reworked areas and its association with plagioclase albitic rims indicate that they were formed in a deuteric process (below 400°C; Lee et al. 1995). This is in agreement with observations that trace elements may become mobile during deuteric alteration of K-feldspar (Brown, Parsons 1994; Siebel et al. 2005). Association with micropores and generally sharp contacts with Mc could suggest dissolution-recrystallisation mechanism operating on a local scale.

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Adam SZUSZKIEWICZ[1], *Jan CHOJCAN*[2]

NATURE OF GREEN COLOUR OF MICROCLINE FROM THE STRZEGOM GRANITIC PEGMATITES (SW POLAND) – AN INSIGHT FROM ^{57}Fe MÖSSBAUER SPECTROSCOPY

Abstract: Two kinds of green microcline from the granitic pegmatites of the Strzegom-Sobótka massif were investigated by means of ^{57}Fe Mössbauer spectroscopy. One is represented by zones of feldspars associated with Fe-bearing ore minerals and the other by euhedral crystals from pegmatitic cavities. The results document a correlation between green colour of microcline and high $Fe^{2+}/\Sigma Fe_{tot}$ ratio of substitutional iron.
Keywords: amazonite, pegmatite, colour, Mössbauer spectroscopy, Strzegom-Sobótka

INTRODUCTION

The origin of the amazonite colour has caused much controversy among mineralogists (vide Petrov et al. 1993). Elements recently proposed to be either a direct source of the colour or in some way responsible for its origin include Fe, Pb, Rb, Tl, OH, F (Hofmeister, Rossman 1985; Vokhmentsev et al. 1989; Petrov et al. 1993). Petrov et al. (1993) proposed to confine the term *amazonite* to ordered microcline whose colour is brought about by a complex $[Pb\text{-}Pb]^{3+}$ centre.

Pegmatites of the western part of the Late Variscan Strzegom-Sobótka granitic massif (Fore-Sudetic Block, SW Poland) are an occurrence of green and bluish-green microcline best known in Poland. Its presence was reported already by Fiedler (1863) and Schwantke (1896). Although no systematic research on the origin of their colour has been conducted, several explanations have been proposed including admixtures of organic substances and compounds of Cu or Fe (*vide* Schwantke 1896; Waleńczak 1959; Kowalski 1967). Janeczek (1985) argued that dispersed Fe compounds give rise to green colour in microcline closely associated with pyrrhotite, Mn-fayalite, and goethite pseudomorphs after fayalite.

An EPR study of microcline (including a green variety) from the pegmatites of the Strzegom-Sobótka massif did not reveal the presence of the paramagnetic $[Pb\text{-}Pb]^{3+}$ centre though it documented radiation defects, substitutional Fe^{3+} centre and Fe-bearing micro- and nanoinclusions (Szuszkiewicz 2006). The ^{57}Fe Mössbauer spectroscopy investigation was meant to evaluate the role of Fe ions as a possible colour origin of green microcline from the pegmatites of the Strzegom-Sobótka massif.

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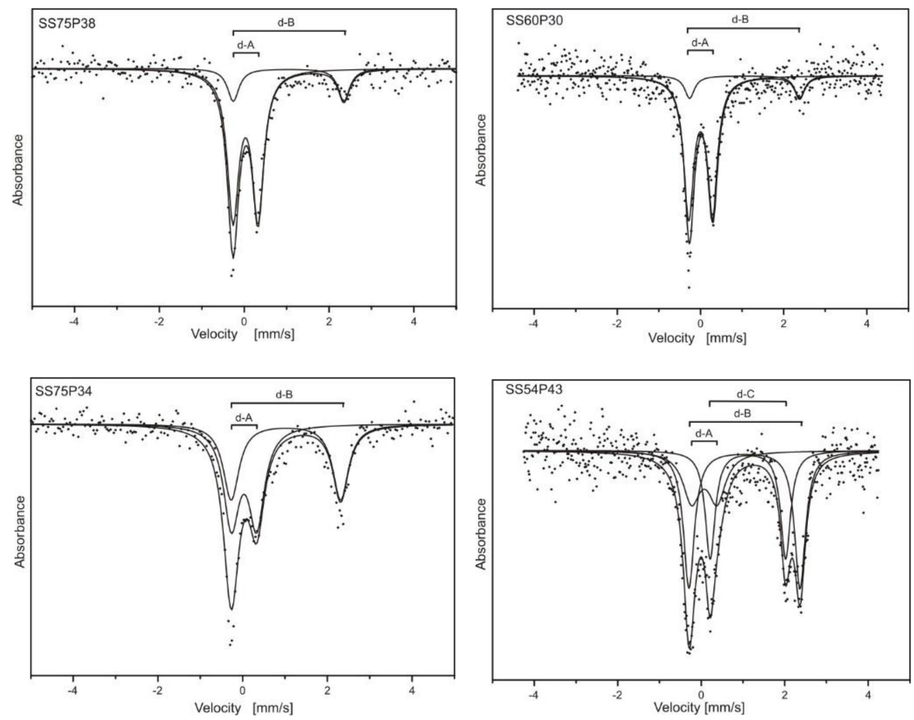
METHODS

Fragments of the feldspars were hand-picked under a binocular and powdered in an agate mortar. Attention was paid to avoid inclusions and weathered areas. Purity of the separates was checked by X-ray diffractometry. Chemical composition was determined using a Cameca SX100 electron microprobe (WDS mode) at the Inter-Institute Analytical Complex for Minerals and Synthetic Substances, Warsaw University. The standards used were: orthoclase (Al, K), albite (Na), barite (Ba), hematite (Fe), diopside (Ca, Mg), rhodonite (Mn) and wollastonite (Si). Excitation voltage and beam current were 15 kV, 10 nA for measuring Si, Al, Ca, Na and K, 15 kV and 100 nA for Mg, Fe, Mn and Ba. The data were PAP corrected.

^{57}Fe Mössbauer spectroscopy analyses were performed at the Institute of Experimental Physics, University of Wrocław. They were conveyed at room temperature in transmission geometry using a standard constant-acceleration POLON spectrometer. The γ-radiation source was ^{57}Co(Rh). Initial measurements were performed in the range of ±10 mm/s allowing detection of Fe compounds with ordered magnetic structure. More precise analyses were obtained for the range of ±4 mm/s. Experimental data were cumulated over 3 weeks. Isomeric shift was calculated relative to metallic Fe foil. Theoretical absorption curves with assumed Lorentzian shape were fitted to the data by the least-square method.

Fig. 1. ^{57}Fe Mössbauer spectra of some microclines from pegmatites of the Strzegom-Sobótka granitic massif.



RESULTS & DISCUSSION

Two cases of green colour of microcline from the pegmatites of the Strzegom-Sobótka massif were studied by means of Mössbauer spectroscopy. The SS75P34 and SS75P38 samples were obtained from a blocky zone of a nest pegmatite from the Morów deposit near Strzegom. SS75P34 comes from a 1-2 cm thick area of green microcline, developed in the vicinity of around 2 cm big pyrrhotite aggregate whereas SS75P38 represents typical white microcline, obtained about 4cm away from the pyrrhotite. Both samples show signs of strong hydrothermal alteration, are devoid of perthites and contain subhedral inclusions of albite around 100 μm big. SS75P34 is Na-enriched ($Or_{85.1}Ab_{14.9}$) comparing to a typical K-rich composition of $Or_{97.0}Ab_{3.0}$ in SS75P38 (Szuszkiewicz 2006). Greenish colour of some euhedral microcline crystals from miarolitic pegmatites was researched on SS54P43 and SS60P30 samples. The green-coloured SS54P43 comes from Paszowice, near Jawor, and is not associated with ore mineralisation. SS60P30 is a similar feldspar of white colour from Żółkiewka near Strzegom. Both are typical perthitic microcline with compositions of $Or_{97.5}Ab_{2.5}$ and $Or_{97.7}Ab_{2.3}$, respectively (op. cit.).

The Mössbauer spectra obtained (Fig. 1) display a high noise level and a relatively wide scatter of experimental data due to low Fe content in the samples. They consist of two asymmetric lines at about –0.25 (stronger) and 0.3 mm/s (weaker) and a broad band at about 2.2-2.3 mm/s. The latter is very weak in SS75P38 and virtually indiscernible in SS60P30. In SS54P43 it reveals a complex structure resulting from two closely spaced lines.

The spectra (Tab. 1) consist of two or, in case of SS54P43, three doublets with different isomeric shift (IS) and quadrupole splitting (QS). The doublet d-A is characterised by IS=0.13±0.03 to 0.18±0.04 mm/s and QS=0.57±0.05 to 0.61±0.06 mm/s. The values correspond to tetrahedrally coordinated Fe^{3+} in the K-feldspar structure (Annersten 1976; Bychkov et al. 1995). Lower QS values (~0.32-0.33 mm/s) obtained by Bychkov et al. (1995) for Fe^{3+} in a synthetic Fe analogue of K-feldspar are probably due to distorted cubic local symmetry in a feldspar with a significant substitution of Fe^{3+} for Al^{3+} (Annersten 1976). The doublets d-B and d-C show values of IS (~1.15 and 1.23 mm/s) and QS (~2.5-2.6 and ~1.8 mm/s) similar to those found for Fe^{2+} in plagioclases (Smith 1974; Dyar et al. 2002). The first was attributed to the octahedrally coordinated sites and the second to a position with higher than four-fold coordination.

Exact determination of the structural sites occupied by Fe^{3+} and Fe^{2+} is hindered by scarcity of comparative data and polymineral nature of the samples studied. For instance, Fe^{3+} may substitute for Al in microcline, perthitic albite or both. It could, however, be concluded that the d-A doublet corresponds to Fe^{3+} whereas d-B and d-C to Fe^{2+}. The spectra of green microcline (SS54P43 and SS75P34) display much more intense signal from Fe^{2+} than the spectra of their white counterparts (SS60P30 and SS75P38). The share of Fe^{2+} signals in the green microcline spectra is 75% and 50.5% for SS54P43 and SS75P34, respectively. In the white samples it is below 20% (Tab. 1). Thus the green colour of the microcline correlates with higher $Fe^{2+}/\Sigma Fe_{tot}$ ratio of substitutional iron. A research has been undertaken to reveal the exact mechanism, through which Fe^{2+} ion take part in the colour origin.

Tab. 1. ^{57}Fe Mössbauer parameters of microcline from the pegmatites of the Strzegom-Sobótka granitic massif.

Sample symbol/colour/total Fe as Fe_2O_3 content [wt %]	Doublet	I.S. [mm/s]	Q.S. [mm/s]	S [%]	Ion/coordination
SS60P30/cream-white	d-A	0.13(3)	0.57(5)	87.5	Fe^{3+}/IV
Fe_2O_3=0.09	d-B	1.17(15)	2.65(35)	12.5	Fe^{2+}/VI
SS54P43/greenish	d-A	0.18(4)	0.61(6)	25	Fe^{3+}/IV
Fe_2O_3=0.04	d-B	1.15(1)	2.66(2)	33.3	Fe^{2+}/VI
	d-C	1.23(1)	1.81(2)	41.7	Fe^{2+}/?
SS75P38/white	d-A	0.14(1)	0.58(2)	82.3	Fe^{3+}/IV
$Fe_2O_3 \leq 0.02$ (detection limit)	d-B	1.15(3)	2.62(5)	17.7	Fe^{2+}/VI
SS75P34/green	d-A	0.16(1)	0.59(2)	49.5	Fe^{3+}/IV
$Fe_2O_3 \leq 0.02$ (detection limit)	d-B	1.13(1)	2.54(2)	50.5	Fe^{2+}/VI

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MINERALOGIA POLONICA – SPECIAL PAPERS
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Joanna TRĄBSKA[1]

DETERMINATION OF BURNING TEMPERATUTE IN LOESS LINING OF AN IRON AGE BLOOMERY FURNACE

Abstract: Reconstruction of ancient bloomery processes, though many experimental and theoretical works of interdisciplinary teams were undertaken, still remain unsolved. This work is a part of a project that aims at reconstruction of them. The knowledge of temperature of burnt loess furnace lining and tuyere may become a significant help in determination of heat circulation. The method accepted here involved structural and phase changes of clay components of loess.
Keywords: ancient metallurgy, bloomery, burnt loess, experiment, clay minerals

INTRODUCTION

Clay minerals transform when heated their phase and microstructure; this phenomenon was applied in research of archaeological objects (comp. e.g. Cultrone et al. 2001). Determination of heat influence exerted at bloomery furnace lining and tuyere from Pokrzywnica, Świętokrzyskie Province, is a part of multidisciplinary project (Orzechowski et al. 2006) that aims at reconstruction of the Świętokrzyskie Mts. area iron production process. Attempts to establish a "clay thermometer" for the loess rock were undertaken.

MATERIAL AND METHODS

Lining of tuyere and a bloomery furnace were sampled (Fig. 10) and samples of raw loess from the furnace neighbourhood were burnt in the range from 200 to 700°C and in 900°C, with 100°C interval, in oxidising atmosphere. Observations were performed with: a) scanning microscope NovaNano SEM 200 Fei Company (analyses by B. Trybalska), b) Debye-Scherrer powder diffractometry, with Philips X'Pert apparatus at $Cu_{K\alpha}$ radiation and secondary curved graphite monochromator (analyses by A. Gaweł).

RESULTS

Features of raw loess and burnt raw loess.

Clay minerals of raw loess have subtle, platy and flake morphology (Fig. 1), After heating a sample up to 400°C, this structure is partially preserved but has more "stiff" appearance. Sinter-like, "cell" structures become to appear (Fig. 2). In 500°C there remain only a few clay plates; they possess stiff habit. Instead of plates, there appear irregular lumps and crusts (Fig. 3). For this temperature numerous researches signal apparent phase changes in clay materials (e.g. Szymański 1997). Single and tiny

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phases with calcium (calcium carbonates or iron-calcium silicates) are signalled by the EDS analysis. In 600^{o}C clay plates are almost utterly replaced by sinters of "cell" structure (Fig. 4, 5). Only a few plates with stiff habit remain. EDS analyses point at presence of very low amount of very fine crystalline iron and manganium alumosilicates. An image of a sample burnt in 900^{o}C points very apparently at complete lack of platy structures and reveals presence of "cell" structures (Fig. 6). It is interesting that powder diffraction analysis did not reveal any significant results: though 13 hrs loess burning in 900^{o}C was conducted, only increase in haematite concentration was noted. Calcite remains intact. Illite structure (Stoch 1974) is also left intact though its irreversible changes above 700^{o}C are signallised (Tab. 2).

Table 1. Raw and burnt raw loess.

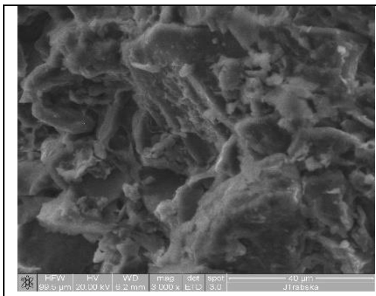

Fig. 1. Raw loess

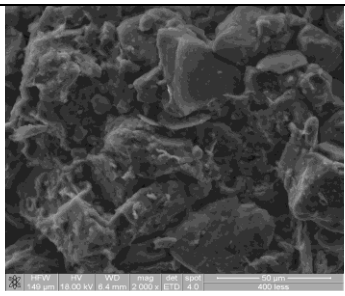

Fig. 2. Loess burnt in 400^{o}C

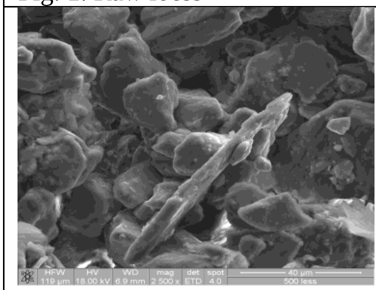

Fig. 3. Loess burnt in 500^{o}C

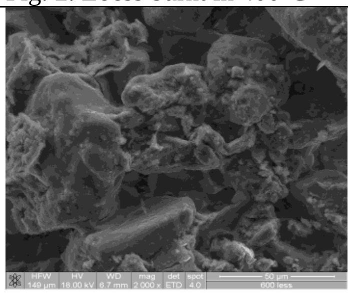

Fig. 4. Loess burnt in 600^{o}C

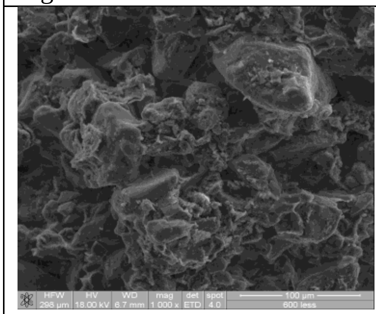

Fig. 5. Loess burnt in 600^{o}C

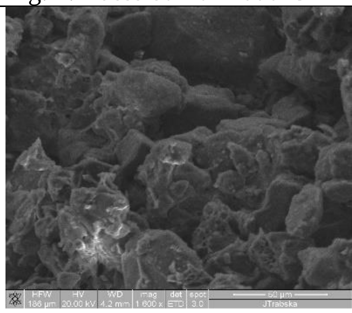

Fig. 6. Loess burnt in 900^{o}C

Table 2. Results of powder diffraction analyses of raw loess and loess burnt in 900°C.

Sample	Results
Burnt raw loess, 1 h	quartz (33-1161), plagioclase (9-466), K-feldspar (19-931), illite (26-911), calcite (5-586), haematite (33-664), amorphic phase
Burnt raw loess, 13 hrs	quartz (33-1161), plagioclase (9-466), K-feldspar (19-931), illite (26-911), calcite (5-586), haematite (33-664), mixed layer illite/smectite mineral, amorphic phase
Raw loess	quartz (33-1161), plagioclase (9-466), K-feldspar (19-931), calcite (5-586), smectite, haematite (at the identification limit of XRD metod), amorphic phase

Table 3. Burnt loess of the bloomery furnace lining and tuyere.

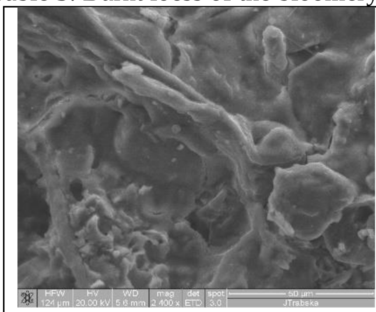

Fig. 7. Sample 1

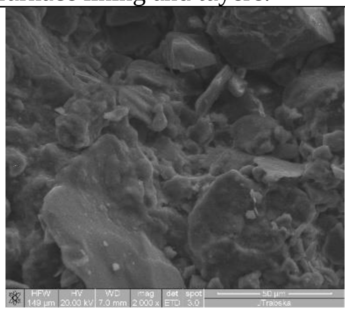

Fig. 8. Sample 2

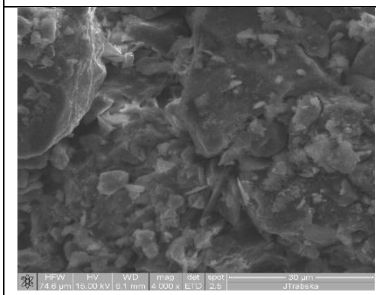

Fig. 9. Sample 6

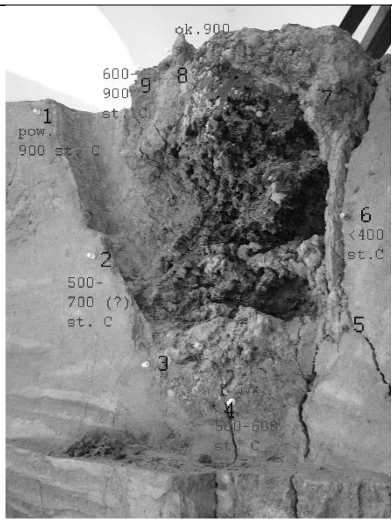

Fig. 10. Bloomery furnace: a section. Numbers 1-9 sign sampling areas. Interpretated temperatures are added. Phot. I. Suliga

Features of loess of blomery furnace and tuyere lining

Morphology of sample 1 (see Fig. 10) is characterised by crust-like structure (Fig. 7), no platy habits were found. Chemical composition (EDS) does not differ from the one of the raw loess and this statement is valid for the other samples. In the sample 2 a few plates are observed (Fig. 8) together with sinter-like phases with „cell" structure. In sample 6 platy minerals are present, but their structure is different than in raw loess (Fig. 9, comp. with Fig. 1), having stiffer habit.

CONCLUSIONS

Morphological features of the loess lining of a bloomery furnace and tuyere allow to interpret the following temperature ranges and heat influence: maximum at the uppermost tuyere part: higher or equal 900ºC, lowering to the range of 500 – 600ºC (possibly 700ºC) in the central part of the tuyere and the lowest, below 400ºC, at the central part of the furnace lining (Fig. 10). Results of other samples interpretation (4, 5, 8, 9) are quoted here for better understanding and can be found at Trąbska 2007 (not published). The interpreted temperatures contribute to reconstruction of heat flow in a bloomery furnace.

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MINERALOGIA POLONICA – SPECIAL PAPERS
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Joanna TRĄBSKA[1], Adam GAWEŁ[2]

CRYSTALLITE SIZE OF HAEMATITE: A PROMISING FACTOR IN PROVENANCE STUDIES

Abstract: Ferruginous raw materials are widespread in archaeological context, unluckily, their provenance is difficult to establish, especially when powdered material (pigment, leather processing remnants) is considered. Crystallite size measurement of haematite may cast some light on powders provenance. It may also appear a prompt in interpretation of geological processes.
Keywords: archaeometry, haematite, crystallite size

INTRODUCTION

Provenance studies of ferruginous raw material and artefacts have long been recognised as complex (Trąbska 2006). Especially provenance study of a powdered rock or a mineral seemed to be impossible. Another problem with the fine grained material concerns the difference between a natural ferruginous powder (e.g. a hardpan, soil iron oxides or Terra Rosa) and a powder introduced originally into an archaeological layer or onto a surface of an artefact. Haematite crystallite size, known in interpretation of geological processes (e.g. Durn et al. 2000) may appear a fingerprint.

MATERIAL AND METHODS

Natural haematite-bearing rocks of various origin and geological time and artefacts made of haematite and haematite-bearing rocks (Tab. 1) were investigated. The latter come from the Magdalenian site Dzierżysław 35 (Upper Silesia, Poland) (Ginter et al. 2002) and Klissoura site (Aurignacian material) in Greece, researched by Polish-Greek expedition directed by Prof. B. Ginter, Prof. J. K. Kozłowski and Dr. M. Oumoudelis. Samples were examined with X-Ray Powder Diffraction methods. The XRD patterns were obtained using $Cu_{K\alpha}$ radiation with the Philips APD X'Pert PW 3020 diffractometer with a secondary curved graphite monochromator. Haematite was identified according to the data in ICDD (International Centre for Diffraction Data) catalogue and computer programme XRAYAN. Concentration of haematite in each sample varied. No isomorphic substitutions in haematite structure were found. Crystallite size, perpendicular to lattice plane (104) (d = 2.70Å), was measured with the Scherrer method, based on a half-width of a 104 analytical peak.

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RESULTS

The results are listed in Tab. 1 (for more detailed data see at Trąbska, Gaweł in press). All substances are natural mixtures of haematite and other minerals.

Table 1. Crystallite size, geological setting and archaeological sites of the examined haematite.

Locality	Geological origin and setting	Age of a rock	Crystallite size
Kudowa (Lower Silesia)	Powdery, light cherry haematite in hydrothermal zone of Kudowa granitoide (Osika 1987:249)	Carboniferous	432 Å (av. of 3 samples)
Tatra Mts. (Małopolska Province)	Cherry red clay-haematite sedimentary slate (Bac-Moszaszwili et al. 1990: 83)	Lower Triassic	625 Å (av. of 2 samples)
Chęciny (Świętokrzyskie Province)	Sedimentary or residual haematite silt (Hakenberg 1971)	Lower Triassic	410 Å[3] (av. of 3 samples)
Baranów (Świętokrzyskie Province)	Sedimentary or residual haematite clay (Filonowicz 1980)	Lower Triassic	390 Å (av. of 2 samples)
Kopulak quarry (Świętokrzyskie Province)	Sedimentary or residual haematite clay (Filonowicz 1980)	Lower Triassic	380 Å (av. of 3 samples)
Jaźwica quarry (Świętokrzyskie Province)	Terra Rosa (Hakenberg 1971)	From Upper Devonian to Eocene	630 Å
Chęciny (Świętokrzyskie Province)	Sedimentary or residual haematite clay (Hakenberg 1971)	Upper Triassic	70 Å[3]
Polichno (Świętokrzyskie Province)	Sedimentary or residual haematite clay (Hakenberg 1971)	Upper Triassic	76 Å[3]
Klissoura (Greece)	Terra rosa	Recent	100 Å[3]
Klissoura (Greece)	Silicified, hard, haematite-bearing rock	Unknown	1230 Å
Tvrdkov (Moravia-Silesia, Czech)	Metamorphic, hard, quartz-haematite-magnetite ore	Precambrian (Biely et al. 1966)	5420 Å
Soviansko (Slovakia)	Coarse crystallite haematite of hydrothermal origin (150–300° C), a vein fragment (Ozdin et al. 2006)	Tertiary	> 6000 Å
Krivyj Rig (Ukraina)	Metamorphic haematite-quartz formation (Smirnow 1986: 499-501)	Precambrian	2050 Å
Dzierżysław-35 site	Red brown or dark violet, hard or soft. Slaty texture. An artefact	Unknown	383 Å (av. of 6 samples)

	probably worked out intentionally.		
Klissoura site	Dark cherry powder on a surface of a small pebble	Unknown	1100 Å

[3] This result may posess an error due to a very low peak intensity.

DISCUSSION AND CONCLUSION

Powdered (intentionally or naturally) haematite obviously preserves its crystallite size and in some archaeological contexts allows to discern a human originated material from a natural one. A pebble from the Klissoura site, covered with cherry red powder is an example: the powder resembled very much a local Terra Rosa. However, crystallite size of the latter equals 100 Å, and the one of the artefact: 1100 Å. Cherry red powdered haematite must have been of utterly different origin, probably intentionally powdered silicified haematite rock from Klissoura or another haematite of magmatic, metamorphic or vein origin (Tab. 1) mineral was introduced. Detailed examination of local, haematite-bearing rocks seems to be reasonable.

A correlation between crystallite size and geological age of haematite was noted, e.g. for Terra Rosa: contemporary rock is characterised by a very low crystallite size haematite (Klissoura), compared with older Terra Rosa of at least Eocene age (Jaźwica quarry). A difference between the Lower and Upper Triassic haematite may have appeared due to detritic orogin of the Lower Triassic haematite. A genetic factor is also decisive: sedimentary, residual, vein and metamorphic haematites differ apparently (Tab. 1; compare e.g. samples from Kopulak quarry, Krivyj Rig and Soviansko).

For several artefacts from Dzierzysław-35 site we tried to establish some rule. Obviously, a sample 1370 is different from others with its 3690 Å (Trąbska, Gaweł in press) and its origin must vary (actually, macroscopic observation suggest a Lahn Dill type). The differences suggest a multi-source origin of the raw material, in some cases a genetic type of a sourcing outcrop may be pointed at.

Discrepancies in haematite crystallite size in samples from the same outcrop may result from: a) natural diversity of the mineral structure, b) low concentration of haematite, c) backgroung fitting in results processing. Whereas the latter factor can be, more or less, eliminated, the two firts remain beyond our control. Nevertheless, we are convinced that futher data, both from natural environment and ferruginous artefact would allow to collect a number of statistically significant data.

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MINERALOGIA POLONICA – SPECIAL PAPERS
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THE SPIŠ-GEMER POST-OROGENIC S-TYPE GRANITES, WESTERN CARPATHIANS: TOURMALINES AND Nb-Ta-W MINERALS AS TRACERS OF MAGMATIC EVOLUTION

Abstract: The Spiš-Gemer granites (Gemeric Unit, eastern Slovakia) represent a Permian-Triassic tin-bearing post-orogenic S-type suite with tourmalines (schorl to foitite) and accessory Nb-Ta-W oxide minerals (ferrocolumbite to manganocolumbite, Nb,Ta-rich rutile, Ti-rich ixiolite, Nb,Ta-rich ferberite and qitianlingite?). The compositional variations of the tourmaline and the Nb-Ta-W phases are sensitive indicators of the magmatic fractionation degree. The highest Fe/Mg and F/OH ratios in tourmalines and Mn/Fe and Ta/Nb ratios in Nb-Ta-W minerals are typical of the most fractionated, greisenized and Li-mica + topaz-bearing alkali-feldspar granites. On the contrary, younger metamorphic tourmaline shows Mg-rich compositions.
Keywords: tourmalines, Nb-Ta-W oxide minerals, granites, Gemeric Unit, Western Carpathians, Slovakia

INTRODUCTION

The Spiš-Gemer granites (SGG) represent a post-orogenic (post-Hercynian) S-type suite intruded into Lower Paleozoic metapelites and metavolcanic rocks of the Gemeric Unit, the Central Western Carpathians. Recent U-Pb zircon dating indicates Permian to Triassic age of the SGG (Poller et al. 2002). The most common rocks are biotite to two-mica leucogranites, locally granite porphyries. The most evolved members are represented by greisenized granites and topaz + Li-mica-bearing leucogranites (Dlhá Dolina, Hnilec, Betliar). The SGG show peraluminous character with high Na, K, Rb, Cs, B, locally also P, Li, Ga, Sn, Nb, Ta, W and U contents and low Mg, Ca, Sr, Ba, Zr and REE contents. Zircon, fluorapatite, monazite-(Ce), xenotime-(Y), garnet (almandine-spessartine s.s.) and tourmaline (schorl-dravite-foitite s.s.) belong to the characteristic accessory minerals of the SGG. Moreover, the most fractionated members contain also rare-element magmatic to post-magmatic mineralization with cassiterite, topaz and Nb-Ta-W oxide minerals.

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ANALYTICAL METHODS

Chemical compositions of tourmalines and Nb-Ta-W minerals were studied by a CAMECA SX100 electron microprobe in the wave-length mode at the Geological Survey of the Slovak Republic, Bratislava. Operating conditions were set at 15 kV and 20 nA with a beam diameter of 1-3 μm. Natural and synthetic standards were used. The data were reduced by the PAP corrections.

TOURMALINES

Minerals of the tourmaline group form widespread anhedral to subhedral disseminated crystals in granites, fan-shaped aggregates mainly in aplitic veins or larger irregular masses in greisens. The tourmaline is developed also in adjacent metamorphic rocks of the SGG exocontact aureole, where massive tourmalinites occur in some places (Zlatá Idka). Published results indicated schorl-dravite s.s. composition of the SGG tourmalines (Faryad, Jakabská 1996). Based on our electron-microprobe study, the magmatic tourmalines of the SGG belong to schorl, rarely foitite with large compositional variations: $^{Y}Fe/^{Y}(Fe+Mg)$ = 0.7 to 1 and X-vac./(X-vac.+Na) = 0.0 to 0.7 (Fig. 1). Older primary magmatic schorl shows lower X-vacancies and higher Na contents [(X-vac./(X-vac.+Na) = 0.1-0.3], whereas younger, probably early post-magmatic schorl to foitite displays a relatively large vacancy in the X-site (Broska et al. 1998, 1999), up to 0.68 apfu. Moreover, the youngest metamorphic tourmaline in the SGG reveals mainly dravitic composition with $^{Y}Fe/^{Y}(Fe+Mg)$ = 0.1 to 0.6. Ti and Ca contents in the magmatic tourmalines are generally low to moderate (up to 0.1 apfu). $^{Y}Fe/^{Y}(Fe+Mg)$ ratio in the tourmalines increases with the degree of magmatic fractionaction. The ratio attains 0.75–0.97 in relatively less-fractionated granites not containing of the rare-element, Li-Nb-Ta-Sn-W mineralization (Poproč, Zlatá Idka, Hummel, Betliar, Podsúľová), whereas $^{Y}Fe/^{Y}(Fe+Mg)$ = 0.92-1.00 in the most fractionated granite members with the rare-element mineralization (Dlhá Dolina, Hnilec). Similarly, the F content or the $^{W}F/^{W}(F+OH)$ ratio generally increase with the magmatic fractionation of the SGG tourmalines. The $^{W}F/^{W}(F+OH)$ is equal 0.3 to 0.6 in the less fractionated granite members, whereas the ratio attains 0.5 to 0.9 in the most fractionated Li-mica and topaz-bearing granites with presence of the Nb-Ta-W minerals.

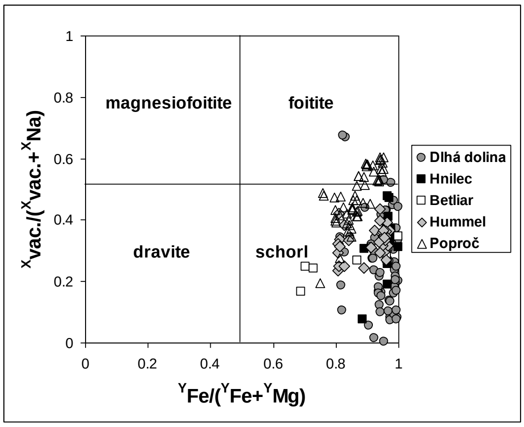

Fig. 1. Composition of magmatic tourmalines from SGG.

Nb-Ta-W MINERALS

Nb-Ta-W phases form disseminated accessory mineralization only in the most fractionated members of the SGG, in alkali-feldspar leucogranites with muscovite or Li-mica (polylithionite-protolithionite s.s.), topaz, cassiterite etc. (Dlhá Dolina, Hnilec, Betliar, Poproč). Ferrocolumbite to manganocolumbite, Nb,Ta-rich rutile, titanian ixiolite, Nb,Ta-rich ferberite and qitianlingite? were detected. Ferrocolumbite to manganocolumbite shows large Mn/Fe but resctricted Ta/Nb compositional variations: Mn/(Mn+Fe) = 0.05 to 0.90, Ta/(Ta+Nb) = 0.01 to 0.45 (Fig. 2). Elevated W and Ti contents are characteristic for the ferrocolumbite-ferrotantalite of the SGG (max. 14 wt.% WO_3 and 7 wt.% TiO_2). Generally, increasing of Ta and W from center to rim of the columbite crystals was detected. The highest Ta and Mn contents in the columbite occur mainly in the most fractionated rare-element SGG (Dlhá Dolina) in comparison to the less fractionated Hnilec and Poproč granites. Nb,Ta-rutile (ilmenorutile to strüverite) contains max. 5 wt.% WO_3, 15 wt.% Nb_2O_5 and 27 wt.% Ta_2O_5; Mn/(Mn+Ta) = 0.00 to 0.18 and Ta/(Ta+Nb) = 0.06 to 0.76. The highest W, Nb and Ta concentrations are in the most fractionated granites of the SGG again. W-rich ixiolite and the Nb,Ta-rich ferberite are the most widespread W-bearing minerals. In addition, a rare phase with stoichiometry close to qitianlingite $(Fe,Mn)_2(Nb,Ta)_2WO_{10}$ was identified in intergrowths with ferberite or W-rich ixiolite (Dlhá Dolina, Hnilec and Poproč granites). Qitianlingite (?) contains 32 to 39 wt.% WO_3, Mn/(Mn+Fe) = 0.26-0.39 and Ta/(Ta+Nb) = 0.05 to 0.35.

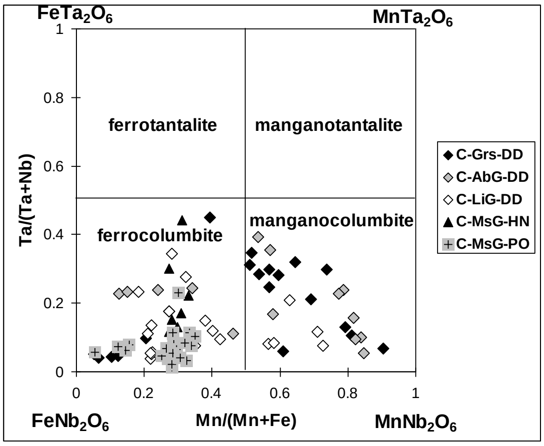

Fig. 2. Composition of columbite-tantalite (C) from the SGG. Parental rocks: greisens (Grs), albite granites (AbG), Li-mica granites (LiG), muscovite granites (MsG). Locations: Dlhá Dolina (DD), Hnilec (HN), Poproč (PO).

CONCLUSIONS

The compositional variations of accessory tourmalines and Nb-Ta-W minerals in the highly fractionated granite suites are usefull tracers of magmatic evolution in their parental rocks, especially of a magmatic fractionation degree and a magmatic versus subsolidus evolution. The case study from the Spiš-Gemer granites, the Western Carpathians, reveals a positive correlation of Fe/Mg and F/OH ratios in tourmalines, and Mn/Fe and Ta/Nb ratios in the Nb-Ta-W phases (especially columbite and Nb,Ta-rich rutile) with a fractionation degree of the parental granites. On the contrary, younger metamorphic tourmaline shows Mg-rich compositions.

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MINERALOGIA POLONICA – SPECIAL PAPERS
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LIMESTONE AS THE PROBABLE PROTOLITH OF THE MASSIVE QUARTZ-BODY AT JĘDRZYCHOWICE (WESTERNMOST SUDETES, SW POLAND)

Abstract: Structures similar to trochites occur in massive quartz-body in Jędrzychowice. Bioclastic limestone is concluded to be a protolith of this rock. A size (50-70 m thick and 150 m long) of silicified rock-body indicates a large, rarely-noted scale of silicification.
Keywords: silicified trochites, silicified limestone, large-scale silicification

INTRODUCTION

Two large massive quartz bodies, noted on the 1:25000 geological map of Frydrychowicz, Frydrychowicz (1957), occur close to Jędrzychowice village (Fig. 1). Today, the Jędrzychowice quartz-body forms a positive morphological, typically denudational form in the generally flat area. These quartz-bodies have been described by Śliwa (1967) as fragments of a giant quartz-

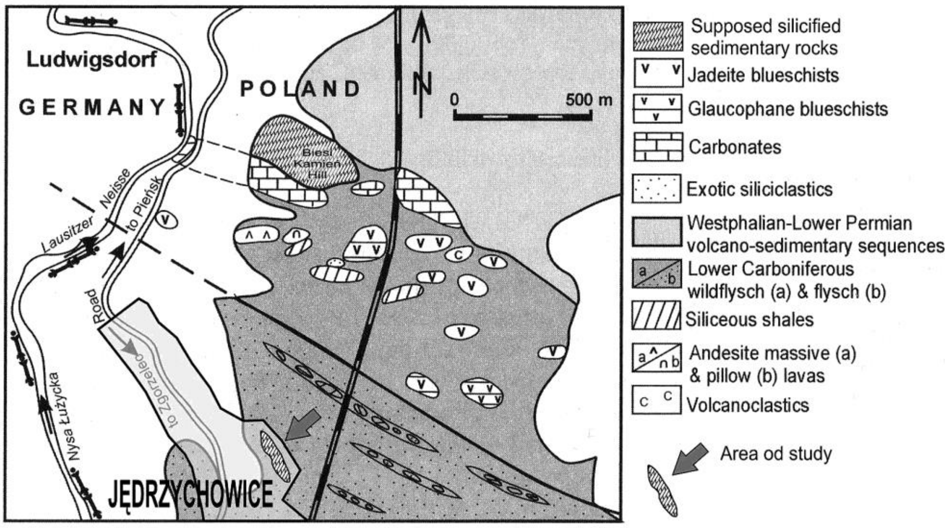

Fig. 1. Geological sketch-map of the Jędrzychowice area (Wajsprych, Achramowicz, 2003).

vein. Recently, Wajsprych & Achramowicz (2003, 2004) have interpreted one of these fragments, the Biesi Kamień quartz-body, that derived its present-day characteristics as a metasomatic rock originated from the total silicification of the

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sedimentary, probably evaporite-dominated protolith series. Its structural features, like protected outlines of primary minerals and structures (gypsum, dolomite, halite, oolites, etc.) and mineralogic features, especially the common presence of length-slow chalcedony, are the main arguments for this interpretation.

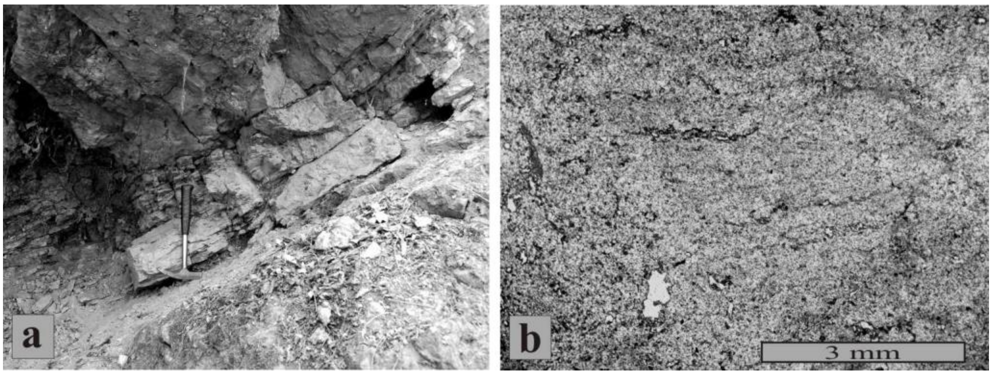

Fig. 2. Probable bedding (a) and microlamination (b).

Another massive quartz-body occurs in the central part of Jędrzychowice village, about 1100 m to the south of that of the Biesi Kamień one (Fig. 1). There is no observation which could confirm a spatial connection between both bodies. The structural, lithological and petrographical features strongly suggest them as rather different protolith series. Also the geological contexts of these bodies are different. The Biesi Kamień fragment is associated with lithologically variable Jędrzychowice unit, comprising ?Cambrian dolomites, middle Famennian cherts (Wajsprych et al. 2006), blueschists (Wajsprych, Achramowicz 2003; Achramowicz, Wajsprych 2004), flysch and mudflow/olistostrome-type deposits, etc. The rocks adjacent to the Jędrzychowice body consist of Lower Carboniferous flysch clastics (Wajsprych, Achramowicz 2003). The relation of the silicified rock to this flysch series is unclear because of lack of exposures in this area. The regular, monoclinal SW-directed, relatively steep dip of the flysch series in contrast to the north-directed, much flatter dip of planar structures that are assumed to represent former bedding planes within the silicified body, suggests an unconformable contact between both rock units.

DESCRIPTION

The silicified rocks at Jędrzychowice form an elongated hill with some exposures on its slopes and in a small abandoned quarry. Characteristic and common features are planar structures assumed to represent primary bedding (Fig. 2a). In some places, fine parallel lamination is well visible. Under the microscope, very fine, irregular lamination (Fig. 2b), associated with structures resembling micronodular lamination, is rather common. Approximately rectangular voids (Fig. 3a & 3b) occur relatively often. We interpret them as trochites cut along (Fig. 3a) or obliquely (Fig. 3b) to their axes, where the trochites themselves were completely dissolved before the silicification, by analogy to silicified crynoidal limestone from the Donbass Basin (Fig. 3d, 3e & 3f). Some of them are similar to complete sections of trochites.

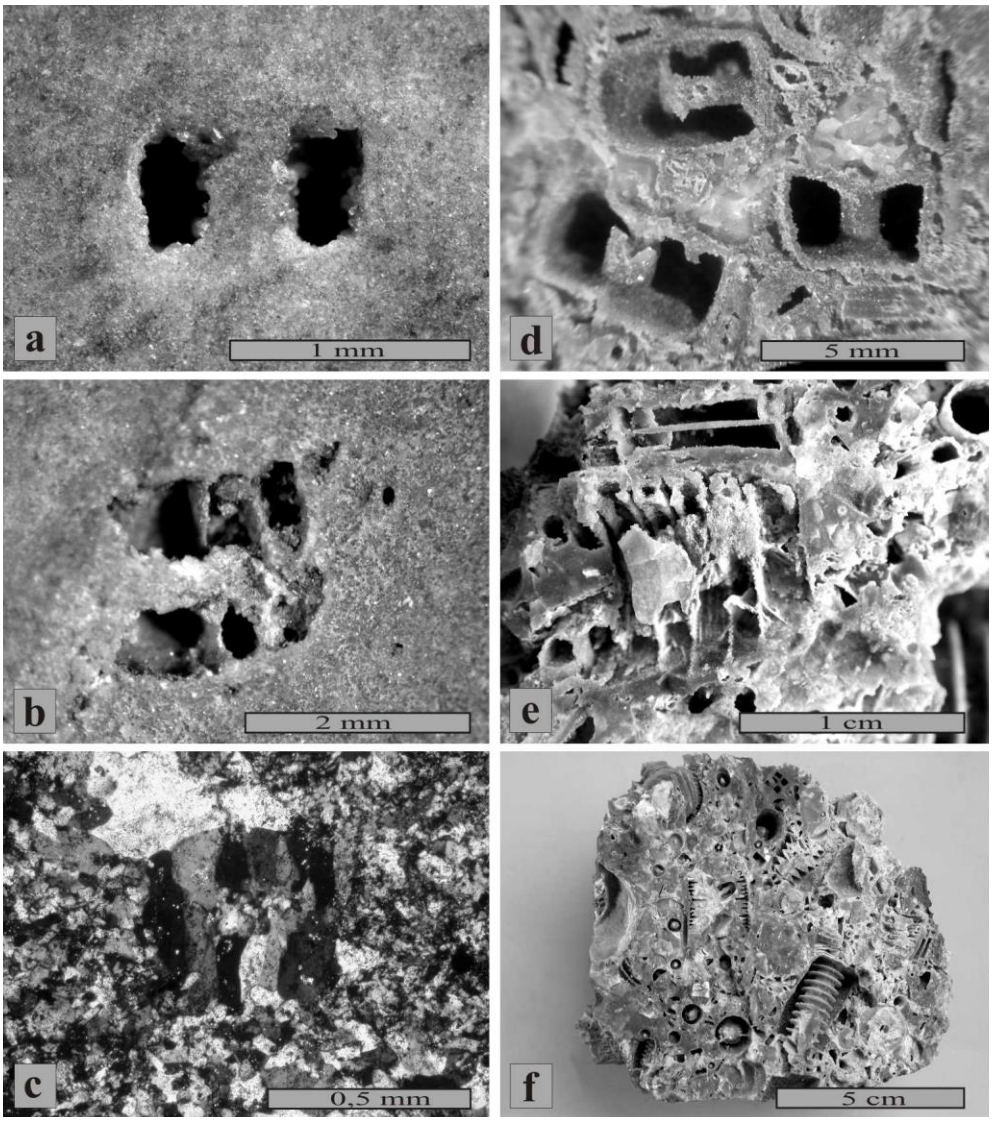

Fig. 3. Microstructures within the Jędrzychowice silicified rock (a, b, c) and their possible equivalents in the sample of silicified Carboniferous crynoidal limestone (d, e, f), From the Donabass Basin, Ukraina.

CONCLUDING REMARKS

Our observations suggest that the Jędrzychowice quartz-body originated from a limestone protolith. All data presented here come from one of the exposures (the quarry), but the lithological and structural homogeneity of the entire body suggests that it presents a lithologically uniform protolith. If so, the Jędrzychowice body might be interpreted as a metasomatite of a biodetrital limestone series. Field observations indicate a thickness of some tens (50-70) of meters. The silicification of carbonates and sulphates is a well known phenomenon (e.g., Folk, Pittman 1971, Milliken 1979, Ulmer-Scholle et al. 1993), but most of the works concern the silicification of small parts of evaporites or carbonates. In contrast, the Jędrzychowice rocks are due to large-scale supposed to be a silica-metasomatite of a combined evaporite and limestone series, of some tens (50-70 m; Jędrzychowice rock-body) to some hundred (150-200 m; Biesi Kamień rock-body) meters thick. Such volumes of totally silicified rocks are very rare.

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THE OCCURRENCE OF Zr-BEARING PHASES IN THE SYENITE ROCKS FROM THE POLISH WESTERN CARPATHIANS

Abstract: In nepheline syenite from Polish Western Carpathians Zr-bearing phases: pyroxene, amphibole, titanite, zircon and garnet were found. They show high concentrations of Ti and Zr. The high activities of alkalis and silica are the important factors leading to the formation of these minerals. Relations between Zr-enriched phases suggest that the elevated concentration of Zr occurs in strongly peralkaline residual melts under reduced conditions, near QFM buffer.
Keywords: Zr-bearing phases, nepheline syenite, Polish Western Carpathians.

INTRODUCTION

Zr is expected to have a higher solubility in peralkaline melt than in metaluminous or peraluminous ones. Marr et al. (1998) showed that the solubility of Zr-bearing phases reached a maximum of 4 and 3.5 wt. % ZrO_2, respectively, in H_2O-saturated, peralkaline, aluminosilicate melts with 57 to 60 wt. % of silica. In most glasses, Zr is 6-coordinated by O; the ZrO_6 units can co-exist with ZrO_7 or ZrO_8 units in anhydrous and highly polymerized compositions but these two last units are destabilized by the introduction of water with the main topology of Zr preservation (Farges et al. 2000). This structural environment around Zr occurs only in some highly differentiated peralkaline rocks such as the nepheline syenites and peralkaline granites. The structure of the phases crystallizing from peralkaline melts is also important. Because the inosilicate structures crystallizing from peralkaline melts provide 6-coordinated environment similar to that occupied by Zr in the silicate melt these factors favors an increase in the crystal-melt partition coefficient of Zr for Na- and Fe^{2+} rich clinopyroxenes and amphiboles (Farges et al. 1994). The increase of the Fe^{3+}/Fe_{total} ratio in late-stage melts favors the crystallization of Fe^{3+} rich clinopyroxenes, which are an unlikely host for Zr because Fe^{3+} in M1 sites adjacent to Zr would result in an excess of bond valence at O1 atoms around Zr. So, the incorporation of Zr in clinopyroxene structure is connected to the fO_2 value; Zr-rich aegirines crystallize under reduced conditions near QFM buffer (Duggan 1988). Similar factors can help to explain the observed presence of both $^{[6]}$Zr and $^{[6]}$Ti in Zr-rich minerals as kimzeyite garnets or titanite.

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MATERIALS AND METHODS

In compliance with the above presented information samples for Zr-phases investigation were collected from nepheline syenite rocks occurring in the teschenite-picrite association of Cretaceous age of the Polish Western Carpathian. In this magmatic province the nepheline syenite occurs as small, irregular bodies in the upper parts of the teschenite sills resulting from a fractional crystallization of a parental mafic magma (sample from Puńców sill). The individual magmatic bodies were also sampled (bore hole Dębowiec 43, 44). Major-element data for Zr-bearing phases were obtained using a Cameca SX 100 in the Inter-Institutional Laboratory of Microanalysis at the Faculty of Geology, Warsaw University.

RESULTS AND DISCUSSION

In both types of samples mentioned above, the following Zr-bearing phases were detected: zircon, zirconium-bearing amphibole, pyroxene, titanite, and garnet.

The Zr-amphibole was detected only in syenite veins cross-cutting the lower chilled margins of the Puńców sill. In teschenite rocks of this sill the amphiboles range in composition from kaersutite through ferrokaersutite to hastingsite. This trend is termed the primary miascitic magmatic trend (Mitchell 1990) and is a cause of decreasing Mg/Fe ratio, at constant Si/Al and Ca content. In nepheline syenite veins the evolution of amphibole composition from calcic to sodic-calcic ones follows the increasing substitutions of Ca + Al^{IV} ↔ Na + Si; the sodic amphiboles were not detected in these rocks (Fig. 1). In syenite veins amphibole compositional trend from ferrokaersutite through to katophorite and taramite is observed, for two last varieties an important amount of zirconium were established (up to 6.0 wt. % ZrO_2, Table 1, an. 10-11). For comparison in the teschenites and nepheline syenites from Scotland only up to 1.2 wt. % ZrO_2 was detected (Preston et al. 2000). Analyses of relationships among cations occurring in these amphiboles shows that Zr entries into their structure by following substitution: 0.5 (Zr^{4+}+ Ti^{4+}) + Na_B = Ca_B + 0.5 (Mg, Fe, Mn)$^{2+}$.

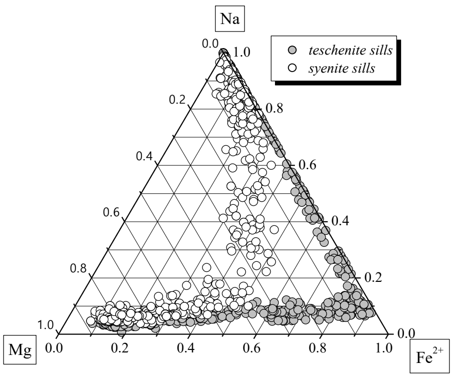

Fig. 1. Plots of clinoamphibole compositions of syenite rocks from Polish Western Carpathians in the Na-Ca-Na diagram.

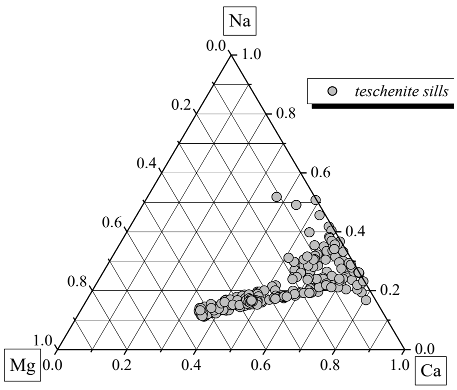

Fig. 2. Plots of clinopyroxene compositions of syenite rocks from Polish Western Carpathians in the Na-Fe^{2+}-Na diagram.

Table 1. Representative results of electron-microprobe analyses of Zr-bearing phases occurring in syenite rocks from Polish Western Carpathians.

	Zircon		*Titanite*		*Pyroxene*		*Amphibole*		*Garnets*	
	1	2	4	5	7	8	10	11	12	13
Nb_2O_5	0.00	0.00	4.42	0.49					0.07	
Ta_2O_5			0.35	0.23					0.28	
SiO_2	32.11	32.50	28.14	29.24	51.31	50.98	37.02	36.87	31.74	31.99
TiO_2	0.07	0.09	24.41	24.24	1.73	0.81	0.42	0.24	1.93	4.95
ZrO_2	**60.91**	**55.52**	**10.28**	**14.46**	**3.37**	**4.10**	**2.90**	**5.00**	**1.30**	**4.68**
HfO_2	0.35	0.56	0.29	0.39						
ThO_2	0.46	0.21	0.18	0.08						
UO_2	0.00	0.00	0.07	0.08						
Al_2O_3	0.20	1.50	1.13	1.67	0.49	0.37	9.08	8.68	19.06	1.02
V_2O_3			0.00	0.00	0.18	0.13				0.10
Cr_2O_3					0.02	0.00	0.00	0.03		0.12
Fe_2O_3			2.73	1.49	20.46	22.98			2.81	22.21
Y_2O_3	0.77	3.04	0.12	0.03						
La_2O_3	0.77	0.59	0.38	0.15						
Ce_2O_3	1.53	1.34	0.37	0.44						
Nd_2O_3	0.38	0.65								
Gd_2O_3	0.15	0.30								
Dy_2O_3	0.14	0.11								
Ho_2O_3	0.02	0.14								
Er_2O_3	0.17	0.25								
Tm_2O_3	0.03	0.01								
Yb_2O_3	0.18	0.35								
MgO					1.00	0.19	0.18	0.03		1.16
CaO	0.21	0.41	25.45	25.37	3.70	2.41	7.92	7.09	34.05	32.78
MnO			0.00	0.02	0.91	0.54	1.96	2.46	0.23	0.03
FeO	0.24	0.31			5.68	5.47	31.52	29.51		
Na_2O			0.28	0.00	11.16	11.78	3.79	4.06	0.82	0.21
K_2O					0.00	0.00	1.74	1.71		
F			0.14	0.21			0.30	0.30	1.98	
Total	98.69	97.88	98.72	98.60	100.02	99.76	96.84	95.96	94.25	99.25

As opposed to amphibole group, pyroxene minerals occurring in both types of samples show the full evolution toward the Na-end-member (aegirine). In the Mg-Fe^{2+}-Na diagram (Fig. 2) pyroxenes from syenite veins show full Fe^{2+} enrichment; their evolution trend is continuous from diopside through hedenbergite to aegirine. In individual syenite sills pyroxene show limited Fe^{2+} enrichment only with Mg-hedenbergite compositions. Such pyroxene evolution is controlled mainly by the fO_2 conditions. Pyroxene / amphibole trends with persistent magnesian character indicate relatively high fO_2 conditions (between NNO and HM buffers) during the evolution towards sodic-calcic and sodic varieties than those with full Fe^{2+} enrichment (QFM buffer) (Dyulgerov, Platevoet 2006).

In syenite veins occurring in teschenite sill both aegirine-augite and Ti-aegirine contains the same amount of Zr, up to 1.7 wt. % of ZrO_2. The Ti content change considerably, growing to 4.0 wt. %. (Table 1, an. 7-8) in aegirine. The antipathetic (Ti-aegirine) and sympathetic (aegirine-augite) relations between Zr and Ti in presented pyroxenes were established. Zr and Ti enters to pyroxene structure as a Fe^{2+}-*NAT* molecule [$Na(Ti, Zr)_{0.5}Fe^{2+}{}_{0.5}Si_2O_6$] but under different conditions. In strongly peralkaline melts capability to dissolve Zr increases and that element is retaining in residual melts up to full Zr saturation to zircon precipitate after Ti-aegirine (Table 1, an. 1-2).

In syenite sills the zirconium distribution is more complicated; aegirine-augite crystals contain up to 1.2 wt. % of ZrO_2 and its concentration decrease to 0.6 wt. % in aegirine with high amount of TiO_2, up to 7.0 wt. %. The relations between Zr and Ti are similar as described above for syenite veins. The very high concentrations of Zr were detected only in irregular areas of Ti-aegirine crystals which were the product of aegirine-augite replacement (Table 1, an. 7-8). The differences in Zr distribution seems to be linked to fO_2 value; Ca-Na and Na-pyroxenes shows higher Zr content in reduced conditions (near QFM buffer).

Zr-bearing titanite (Table 1, an. 4-5) crystals occur only in syenite veins where the concentration of ZrO_2 reached the upper limit for titanite (15 wt. %). Incorporation of Zr into titanite structure takes place by substitution: $Ti^{4+} + Al^{3+} \leftrightarrow Zr^{4+} + Fe^{3+}$ (Seifert et al. 2003).

Within metasomatically altered syenite veins from Puńców sill secondary F-bearing hydrogarnets and Ti-garnets were identified with amount of Zr up to 5 wt. % (Table 1, an. 12-13).

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MINERALOGIA POLONICA – SPECIAL PAPERS
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ZONED PYROXENES FROM GRODZIEC BASANITE (LEGNICA-ZŁOTORYJA-JAWOR REGION, LOWER SILESIA, SW POLAND)

Abstract: Mega- and phenocrysts of olivines and pyroxenes are present in the Grodziec basanite (Legnica-Jawor-Złotoryja region). The fine-grained groundmass consists of olivines, pyroxenes, nepheline and analcite. The pyroxene phenocrysts are represented by two different mineralogical types, the cores of which vary in Mg# number, amounts of Fe, Ti, Al, Na, and Cr. The cores are xenocrysts of different origin. Only pyroxenes forming rims are comagmatic.
Keywords: basanite, pyroxene phenocrysts, core, rim, zoning

INTRODUCTION

Most of the known occurrences of Cenozoic volcanic rocks from the area of Lower Silesia, generally called "basalts", are situated in the Fore-Sudetic Block, and in the western part of the Sudetes Mts. These volcanics constitute the eastern part of the *Central European Volcanic Province* (CEVP), nearly 700 km long. The studied basanite was sampled at Grodziec (Legnica-Jawor-Złotoryja region), a locality situated already in the Sudetic Block, SW of the Sudetic Marginal Fault. The K-Ar age of this rock was found to be 32.16 ± 1.37 Ma (Badura et al. 2006).

METHODS OF INVESTIGATION

Microscopic observations of thin sections were carried out in transmitted light using JENAPOL microscope. Chemical composition of mineral phases was defined by means of scanning electron microscopy SEM (JEOL 5410), equipped with an energy dispersive spectrometer EDS Voyager 3100 (NORAN), and of scanning electron microscopy accompanied by energy dispersive spectrometry HITACHI S-4700 field emission microscope with Thermo NORAN vantage analytical system. According to the "standardless" procedure of calculation the data were normalised to atomic percentage.

PETROGRAPHY AND GEOCHEMISTRY

The basanite studied has dark-grey, nearly black colour, and is massive and very fine-grained. Microscopic observations indicate that the structure is fine-grained, porphyric, and seriate.

Olivine and pyroxene megacrysts occur in the studied sample. Their size ranges from 3.3 to 4 mm, and these megacrysts probably represent nodules of ultramafic

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rocks (peridotites, pyroxenites, dunites). Anhedral olivine megacrysts are represented mainly by Mg-rich (Fo 90-89) chrysolite. Euhedral and subhedral olivine phenocrysts (0.7-1.3 mm in size) are depleted in MgO and enriched in FeO. These phenocrysts reveal chrysolite (Fo 79-76) composition. These mega- and phenocrysts of olivines are altered to a variable degree; they are surrounded by red iddingsite rim. Nickel and chromium are commonly present in olivine mega- and phenocrysts.

Anhedral pyroxene megacrysts (1.5-4.0 mm in size) show fractural surfaces, fine-grained, colourless mineral with high Mg# 89-88. In the outer part of these megacrysts, red rims of iddingsite occur. Euhedral and subhedral pyroxene phenocrysts are very common in the studied rocks. These phenocrysts vary in size from 0.2 to 1.3 mm. They are represented by two types, and show an oscillatory and sectoral zoning patterns. Very rare sieve texture (inclusion of alkali glass and opaque minerals) is observed in central parts of pyroxene phenocrysts.

In fine-grained (max. 0.07 mm in size) groundmass of the studied basanite, clinopyroxenes and opaque minerals (iron oxides, ilmenite) are mainly observed. The titanium-aluminium diopside crystals (according to Morimoto et al.'s, 1988 nomenclature) display variable content of TiO_2 (4-5 wt. %). Small crystals of olivine (0.07-0.04 mm in size) occur in the groundmass. They are represented by hyalosiderite (Fo70-67), iddingsitized to a variable degree. In the groundmass of the examined basanite, there also occur small crystals of nepheline and analcite.

In the geochemical TAS (Le Maitre et al., 1989) classification, the basaltoid studied plots in the field of basanites/tephrites. Since the content of normative olivine in the rock exceeds 10 %, it can be classified as a basanite. This result corresponds to Thompson's (1984) and Winchester and Floyd's (1977) classification, because on the CIPW normative projection and in the Nb/Y - Zr/TiO_2 diagram this rock plots in the fields representing basanites.

SiO_2 content in the basanite from Grodziec is relatively low (43 wt. %). The rock contains high amounts of MgO and Fe_2O_{3total} (12.0 wt. % each). TiO_2 concentration of 2.7 wt. % characterises it as a high-titanium basaltoid. The total of alkalies is 3.8 % wt. and Na_2O overweights K_2O (ratio of Na_2O/K_2O = 2.3).

The rock has LREE-enriched REE patterns, similar to those of many ocean island basalts (OIB) (Wilson 1993) and alkaline volcanic rocks derived from continental settings. It is high in LREE and low in HREE, showing high $(La/Yb)_N$ values (27.5). As follows from the Nb/Y vs. Zr/Nb diagram (Harangi 2001), the examined basanite is characterized by a low degree of melting of the source, which for this rock is slightly more than 0.5 %. Moreover, it was produced by melting at the greatest depth of a garnet-bearing source.

The basanite has Ni (375 ppm) and Cr (466 ppm) contents high enough for this rock to represent near-primary mantle melts (Wilson 1993). The Mg-number equals to 67.

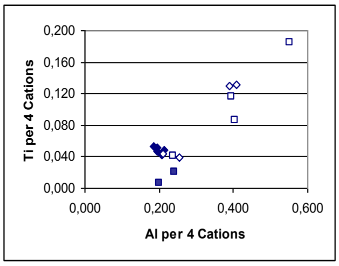
CHARACTERISTICS OF TWO PYROXENE PHENOCRYSTS TYPES

All analysed pyroxenes are clinopyroxenes and have a QUAD composition, according to the pyroxene classification of Morimoto et al. (1988).

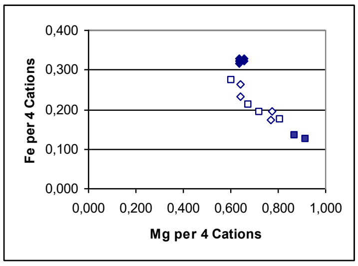
Two types of pyroxene phenocrysts (A and B), differing by chemical composition of cores, were distinguished.

Cores of the type A phenocrysts consist of cataclastic, colourless pyroxene, showing a medium birefringence. This pyroxene has the composition of aluminian augite and diopside, Mg# =89-87, *sensu* Morimoto (1988). It contains an admixture of Al atoms ranging from 0.24-0.20 apfu. and those of Cr and Na being 0.08-0.03 apfu. and 0.15-0.08 apfu., respectively. Low content of Ti (0.01-0.004 apfu.) is significant. The core zones are surrounded by zoned rims, in which the inner zones, formed of colourless pyroxene, evolve into a violet-brownish one in the outer rim. Towards phenocryst margins, the changes in composition become apparent. The Mg (0.60 apfu.) and Cr (0.008-0.006 apfu.) contents decrease in rims, whereas the amounts of Fe (0.27-0.23 apfu.) and Ti (0.13-0.10 apfu.) increase, compared to the core. The violet-brownish pyroxene from the outer rim corresponds to the titanian aluminian diopside *sensu* Morimoto (1988), with Mg# = 76-71.

In cores of the type B phenocrysts, a green pyroxene showing pleochroism from pale yellowish-green to pale green and low birefringence, occurs. It is ferrian aluminian diopside or subsilitic diopside *sensu* Morimoto (1988), of Mg# = 66-67. The admixture of Ti atoms ranges from 0.08-0.05 apfu. and that of Al is from 0.21-0.19 apfu. The contents of Cr (0.006-0.001 apfu.) and Na (0.08-0.05 apfu.) are lower compared to the core of A type. The rim is composed of colourless and violet-brownish pyroxenes. It is richer in Al (up to 0.34 apfu.) and Ti (up to 0.13 apfu.), and poorer in FeO (up to 0.25 apfu.), Cr (up to 0.003 apfu) and Na (0.06-0.04 apfu.). In outer rims of these phenocrysts Mg# is 76-71. The variation in chemical composition of the two types of pyroxene phenocrysts (their cores and outer rims) is illustrated in Fig. 1.



A



B

Fig.1. Variations in composition of the two clinopyroxene types
(squares - clinopyroxene of the type A, filled squares – pyroxenes from the core, empty squares – pyroxene from the rim; rhombs – clinopyroxene of the type B; filled rhombs – pyroxenes from the core, empty rhombs – pyroxene from the rim).

Rims of the two types of the phenocrysts studied are composed of colourless and then of violet-brownish pyroxene, showing similar chemical composition and optical properties in both types.

CONCLUSIONS

The cores of type A pyroxene phenocrysts (Mg# 89-87) are mantle xenocrysts and originated from cataclased and disrupted ultramafic nodules (pyroxenites, peridotites) derived from the upper mantle.

The green cores xenocrysts occurring in type B pyroxene phenocrysts (green Fe-Na cpx, Mg# 67-66) can be a product of relatively evolved melts, which have been mixed or migling into their present host magma (Dobosi 1989) of mantle origin with low degree of melting.

Two last zones forming the rims of phenocrystals, which occur in both clinopyroxene phenocrysts types, are comagmatic. The composition of phenocrysts in the outer rims (violet-brownish) corresponds to that of clinopyroxenes in the groundmass. In the rims, sector zoning is occasionally present, being probably the result of several kinetic mechanisms, i.e. rapid growth rate, charge-coupled substitutions, or diffusion limitations of Si tetrahedral on the different crystal faces in melt-crystal boundary (Schwandt, McKay 2006). The enrichment of the rim of pyroxene phenocrystals in Ti and Al is a result of polybaric crystallization during the magma ascent (Spišiak, Hovorka 1997).

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MINERALOGIA POLONICA – SPECIAL PAPERS
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MINERALOGICAL COMPOSITION OF THE MARTIAN SURFACE ON THE BASIS OF INFRARED SPECTROSCOPY

Abstract: Infrared spectroscopy is applicable as a method of structural analysis to research the composition of rocks and minerals. We use two Martian infrared spectra from TES (Thermal Emission Spectrometer) instrument aboard the Mars Global Surveyor spacecraft with atmospheric contributions removed by the Radiative Transfer Algorithm method. The first spectrum is of a pure basalt surface which represents the Martian terrain -Cimmeria Terra and second an average dusty surface. We modeled these spectra by matching the infrared spectra of minerals from mineralogical library (in the wavenumber range 1700-200 cm^{-1}) using the Deconvolution Algorithm without contributions of the atmosphere.
Keywords: Mars, basalt, weathered basalt, Deconvolution Algorithm, Radiative Transfer Algorithm, infrared spectroscopy, emissivity

INTRODUCTION

Mars is one of the most intensively studied planets in the solar system other than Earth. Space probes observing Mars are sending back a huge amount of data every day. They give us information about the probable mineral composition of Mars surface and atmosphere (Christensen 2000; Bandfield 2003; Smith 2000a,b; Pearl 2001).

The infrared radiation (5 – 50 μm or respectively in wavenumber 1700 – 200 cm^{-1}) is the best one to determine the mineral composition because the surface emits the radiation in this range of wavenumbers. Therefore we can obtain characteristic spectral features for different components of surface and atmosphere in this connection. The most important phenomena are absorption and emission by surface components as well as by atmosphere gases.

The major component of the Martian atmosphere is the carbon dioxide 95.3%, the other components are nitrogen -2.7%, argon -1.6% and trace admixtures as water vapour, carbon oxide, water ices, and dust. The largest seasonal and diurnal variation of abundance is observed for dust. During the changes of season there appear dust storms. Then the transparency of the atmosphere decreases (Smith 2000b; Martin 1993). The knowledge of the variations of abundance of dust and the atmospheric gases helps to eliminate their influence on the infrared spectra of radiance emitted by the surface.

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On the basis of TES measurements we find out Mars' geological dichotomy, determining that the northern hemisphere and some terrains on the southern hemisphere like Hellas [45 S; 70 E] or Daedalia Planum [18,4 S; 231,9 E] consist of lowlands and supposed remains of an ocean (Head, Hesinger 1999) composed of andesite or weathered basalt, whereas the southern hemisphere displays the features of alkali basalts (Mittlefehldt 2000). This is confirmed by measurements of Viking 1 and 2 and Pathfinder, and Rovers: Spirit and Opportunity. Thanks to those measurements have been estimated the basic elements of Mars' surface composition (Richard, Morris 2000; Bell, Mc Sween 2000; Bridges, Crisp 2001). Unfortunately, the full confirmation of these measurements was not possible, as in the present study we used the data from small part of Mars surface only, thus not reflecting the global petrologic structure of the whole planet. The research that was carried was devoted only to spectra from Cimmeria Terra. [37,8 S; 189,4 E] (Christensen 2000) (Fig. 2) and the average dusty surface (Bandfield 2003) (Fig. 4).

METHODS

First of all we would like to retrieve surface emissivity spectrum without contributions caused by atmospheric components. We present two methods that are used to separate the spectral features of atmospheric gases and surface. One of them (Deconvolution Algorithm) relies on fitting the linear combination of spectral features of each mineral and of atmospheric components to the measured spectrum simultaneously. This method uses the spectral mineral library to find the appropriate mixture of minerals.

The second algorithm uses the radiative transfer through the atmosphere (Radiative Transfer Algorithm). The radiances are calculated equation with assumptions regarding the amounts of dust, aerosols, water vapour. Then we can compare the calculated values with the measured ones to find successively the spectral shapes, first for atmospheric dust, then for water-ice aerosols and then, finally, for surface emissivity by least square fitting. Additionally we can assume the size of dust and water ice crystals and seek the best fit (Christensen 2000; Smith 2000a; Wolff 2003).

RESULTS

We modeled spectra by matching the infrared spectra of minerals. We added spectra of particular minerals from the mineralogical infrared library with size range 700-1000 μm for pure basalt and powder size for weathered basalt to receive spectrum similar to Martian spectrum from TES. We used the Deconvolution Algorithm method. The Martian atmospheric spectra used for comparison were removed by Radiative Transfer Algorithm.

Basalt spectrum is modeled with Decan basalt and weathered basalt spectrum is modeled with weathered basalt from the Krzeniów, Sudetes.

The Decan basalt contains labradorite 65%, augite 28%, forsterite 4% and hornblende 3% (Fig. 2). For the purpose of modeling augite was replaced by bronzite to smooth out the spectrum between 900 –1100 cm^{-1}. Then the fitting to Mars' spectrum is better. Bronzite is very common meteorite's component (Fig. 1).

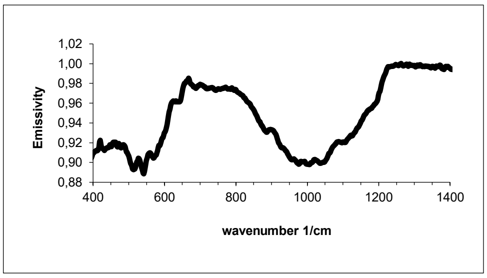

Fig.1 Basalt spectrum modeled with Decan basalt spectrum using the Deconvolution Algorithm.

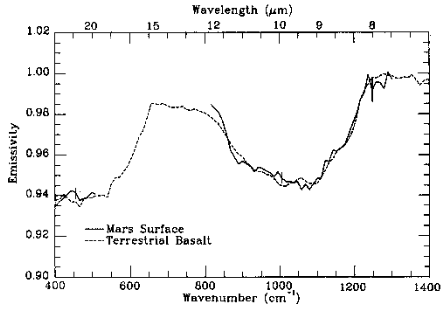

Fig.2 Comparison of the spectra of Cimmeria Terra and Decan basalt with atmosphere separated by the Radiative Transfer Algorithm (Christensen 2000).

The Martian surface is regarded as dusty when the albedo >0.18. Dust can be found on the surface and can be suspended in the atmosphere with particle sizes < 70 μm. We claim that a dust has in its composition weathered basalt.

The composition of a weathered basalt (waste) from Krzeniów contains 90-100% of smectite, 5-10% of kaolinite, magnetite and goethite. For the purpose of modeling we set up the composition: 90% of smectite, 7% of kaolinite and 3% of magnetite (Fig. 3). We believe that water existed on Mars in the past and Mars' atmospheric pressure in some places allows water to remain in a liquid state, so clay minerals can appear on Martian surface.

This waste the best match to the dusty surface of Mars, but makes a problem with fitting minimum at 800-900 cm-1. This minimum is shifted toward shorter waves with components available from the used library.

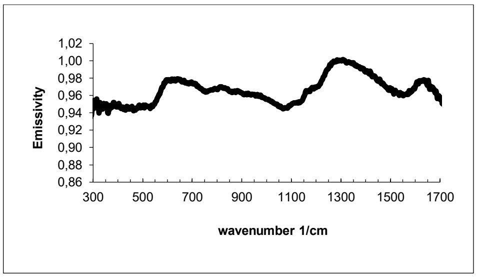

Fig.3 Weathered basalt spectrum modeled with the weathered basalt from the Krzeniów, Sudetes using the Deconvolution Algorithm.

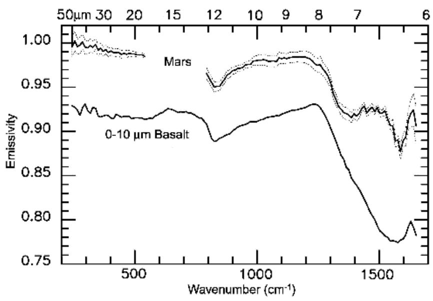

Fig.4 Comparison of the spectra of Mars surface dust and fine basalt with atmosphere separated by the Radiative Transfer Algorithm (Bandfield 2003)

SUMMARY

The spectrum of Cimmeria Terra surface (Fig. 2) best matched by the spectrum of the Decan basalt where augite was replaced by bronzite. It is surface without dust (Fig. 1). A dusty Mars' surface is compared to a spectrum of weathered basalt from Krzeniów Sudeten (Fig. 3) but the fitting agrees roughly with the Mars' spectrum (Fig. 4).

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MINERALOGIA POLONICA – SPECIAL PAPERS
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PATINA ON THE BEDROCKS OF THE GIZA, ABU ROWASZ REGION, EGIPT

Abstract: The hill of Abu Rowash is situated on the edge of the Western Desert at the southern end of the Nile Delta about fifteen kilometers North West from Cairo. At present it is the area of a national park. In its central part there is located a cone-shaped pit of roughly 30 meters in diameter and about 15 meters deep. Both the size and the shape of the object indicate its impact origin.

The samples of calcareous rocks taken from the central part of the crater and from the base have been examined both in the University of Science and Technology in Cracow and the Jagiellonian University laboratories. The results of the tests confirm the hypothesis about the craters being formed as a result of an impact by some extraterrestrial matter.

Analyzed rock samples were classified as an organogenic micrite-sparite limestone. Some shells from the inner walls of the crater reflect traces of a shock wave. Part of the fossilized shell at the epicentral side of the crater has dark inclusions visible to the naked eye. The border zone of the thin section has an amorphous layer. The rocks surrounding the crater have numerous fractures in the less metamorphosed layers. The SEM-EDS analysis affirmed that the transparent coating is carbon (C) which is separated from the limestone by a thin layer of sulfates. A more detailed analysis of the sulfates between the calcite-dolomite rock and the layer of carbon revealed the presence of the iron.

Patina present on the rock was probably formed in high temperature conditions. Such conditions could be a result of the impact of meteorite that contained metallic elements and high amounts of graphite.
Keywords: Egypt, Giza, meteorite crater, mineralogical research

INTRODUCTION

Ancient Egypt is well known to everyone, especially widespread is the knowledge concerning the period of the union of Upper and Lower Egypt, rapid advance in engineering and architecture and creation of the pyramids, right to the fall of the Egyptian civilization. The period of great interest to us is the time when the pyramids in Giza. Abu Rowash and Dahshur were built and that time is called by the scientists the Old Kingdom and involves the years 2686 to 2125 BC (Lipińska 2003). It is unknown whether the fall of this great civilization was caused by incompetent rulers from the last dynasty or some other event.

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In the history of Egypt the First Intermediate Period, 2125 to 2055 BC (Lipińska 2003) (an official date), is full of mysteries. We do not know how long it lasted, neither do we know how many kings ruled during that time. Those questions give rise to stormy arguments among the researchers even nowadays. Never again has the Middle Kingdom reached the civilizational apex that the Old Kingdom enjoyed. As a result, all new discoveries concerning the pyramids and their surrounding may lead to solving the mysteries from the past. This is why geological and mineral-petrographic research was focused on the Giza plateau.

The Giza plateau and the objects it hosts are also full of secrets. Their discovery and further research require many years spent learning the merits beforehand. To conduct on-site research, you need to obtain passes and permits - this can also take several years, and might be foiled by circumstances beyond anyone's control. Due to those factors, finding the answers to several questions that have been rankling the researchers for a long time is sometimes impossible, as the local government has introduced drastic measures and regulations in order to protect the ancient monuments. Despite that, our research is still being carried out. Below you can find its results.

FIELD OBSERVATIONS

While examining limestone outcropping beds that are exposed on the Giza plateau (Fig. 1) we have noticed unusual, often unidirectional traces of eolian erosion. In several cases, they were covered with a thin glassy and transparent layer. It seemed that determining the origin of those traces should not be difficult, since this region is dominated by north winds.

They were also present in ancient times, as seen in images with hieroglyphs, in which sailboats with set sails are always southbound, while their sails are lowered when travelling in the opposite direction, using Nile's current (Lipińska, Koziński 1977). This suggests that the aforementioned eolian erosions should have been orientated accordingly.

An initial examination of the plateau proved that the traces have different directions in various locations. In the northern part of the plateau they are orientated to north-west, and in the western part - to the west. Furthermore, by the northern side of Khafre's pyramid the traces indicate a western direction of the wind, along the wall.

Similar traces have been found by the south side of the first subsidiary pyramid of the Great Pyramid. They also pointed westwards. Additional examination proved that similarly oriented traces were present on a larger area and formed a radial pattern. In several locations there were two overlapping erosion traces. Such a place was found about 200 metres to the north-west of Khafre's pyramid (Fig. 2).

Fig. 1. The Giza plateau from the south-west perspective.

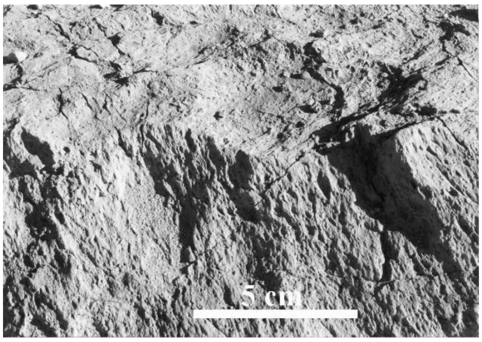

Fig. 2. Overlapping erosion traces on Giza limestone.

It has also been established that the layer covering almost all monadnock formations rising from the sand, including fragments of megalithic buildings, is thin, smooth and glassy. Against the prevalent notion that it is desert glazing or patina, samples have been taken and examined in laboratories.

Further field observations showed that such erosion traces with a transparent glazing were present in limestone outcropping beds in the north-west part of plateau, as well as at the base of Khafre's pyramid, near its north-east corner and by its first subsidiary pyramid, near its southern wall. Such traces have not been found on the opposite sides of these monuments or on the rocks present in the southern part of the plateau.

The examination area was extended beyond the Giza plateau, following the north-west direction indicated by channel traces found on rocks. It has been established that after about 500 metres in that direction, the plateau ends abruptly with a steep precipice about a kilometre long and 2 to 8 meters high. There the plateau is separated from modern living quarters by a quarry. The area beyond that is covered with sand and gravel. There are no natural limestone outcropping beds present earlier in Giza. While coming back to the plateau, it has been observed that the glazing found on the rocks is thicker and more pronounced. This location also yielded samples for laboratory research.

Further observations showed that single natural lime blocks, present a few metres to the north of the asphalt road near Khafra's pyramid also displayed traces of a strong and directional erosion (Fig. 3).

These observations served as the basis for a larger expedition into that area. It took place in December 2006, and was led by prof. Maciej Pawlikowski and financed by H.M. Rector of AGH University of Science and Technology in Krakow, Poland.

One of the goals of the expedition was to investigate the plateau on the western bank of Nile - the area between Abu Rowash and Giza.

The observations in Abu Rowash allowed to affirm the existence of erosion traces similar to those found in Giza. However, their direction was different from the one observed in Giza - the traces in Abu Rowash go from the west to the east.

All the acquired data concerning the direction of erosion traces found on limestone outcropping beds near Giza and Abu Rowash pointed to a central location situated between Giza and Abu Rowash.

Fig. 3. A limestone block near Khafra's pyramid with visible unidirectional erosion.

Fig. 4. The varied terrain morphology resulting from tectonic distortions. The photo was taken facing the pyramid in Abu Rowash.

This place was of particular scientific interest during the expedition. Field investigation conducted by us in that region helped to identify a massive distorted geological structure of the area. We have found numerous foldings, faults and uplifts called local diapirs. The area morphology displays also two circular forms, partially deformed by strong erosion. They can be found on both sides of the asphalt road leading to Alexandria (Fig. 4). Contrary to the surrounding areas, the area in question is distorted to a large extent, while neighbouring locations have a much more "calmer" structure based on plates.

Samples have been taken from the edges of both circular forms which are supposedly meteorite craters.

RESULTS OF MINERALOGICAL EXAMINATION

The results presented here are mostly preliminary. They contain data from the limestone coating found on the Giza plateau - the location where directional erosion was observed.

The research included microscopic observations of the glazing area and the areas directly below the glazing. A Nikon 120 polarizing microscope and a scanning FEJ Quanta FEG microscope with an EDS analysis adapter were used in the laboratory examination.

The results obtained with the polarizing microscope show that the glazing present on the rocks varies in thickness and contains mainly opaque minerals - ferrous and manganese oxides and hydroxides (Fig. 5). However, the glazing on the convex areas of the limestone has other characteristics. It is structurally amorphous and transparent (Fig. 6).

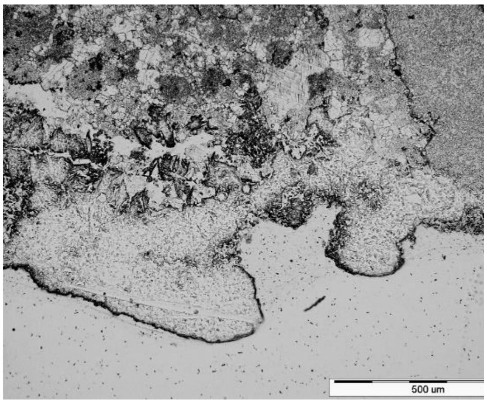

Fig. 5. A cross-section of an erosion trace (rift) from a rock taken from the Giza plateau. A dark layer of Fe-Mn compounds visible in the hollow. Polarizing microscope, partially II polaroids, magnification x 80.

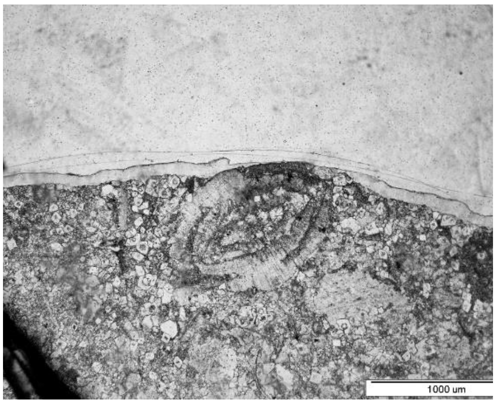

Fig. 6. A thick layer enriched with coal, found on an eroded limestone in Giza. Polarizing microscope, partially X polaroids, magnification x 80.

At first, it was assumed that this layer is a kind of a glaze and a sample of the material was prepared for XRD analysis. Despite many attempts at interpretation of the X-ray research results, establishing the mineral content of the aforementioned glossy layer on the limestone turned out to be impossible. Next, scanning research was conducted, which allowed to state that the analysed glossy layer covering the limestone contained mostly carbon.

Microscopic observation of surface areas and regions right below the patina allowed to suggest that the coating of the rocks contains a lot of carbon in several locations (Fig. 6, Fig. 7, Fig. 8).

Research also shows that some of limestone presents dolomite characteristics. By conducting scanning research combined with EDS method, metallic granules have been found under the corroded surface of the rocks, which also sometimes contained metallic intrusions (Fig. 9, Fig. 10, Fig. 11, Fig. 12).

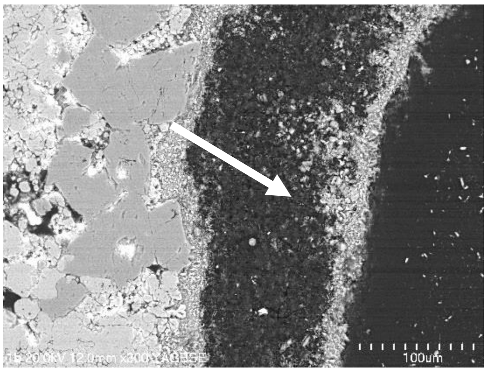

Fig. 7. The microscopic view - SEM of the the surface coal layer coating the eroded limestone in Giza.

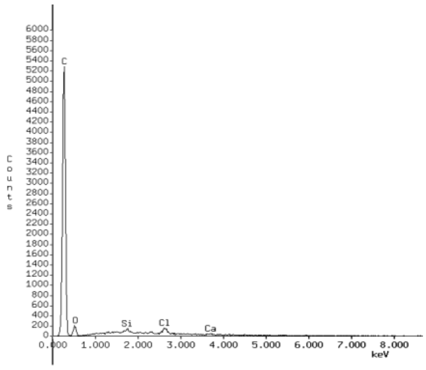

Fig. 8. The EDS spectrum of the coal-enriched layer (Fig. 7).

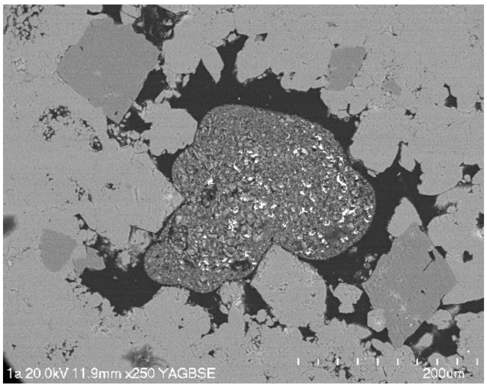

Fig. 9. The microscopic view of metallic granules present under the corroded surface of Giza limestone. The granules are enriched with nickel - the bright dots (Fig. 10).

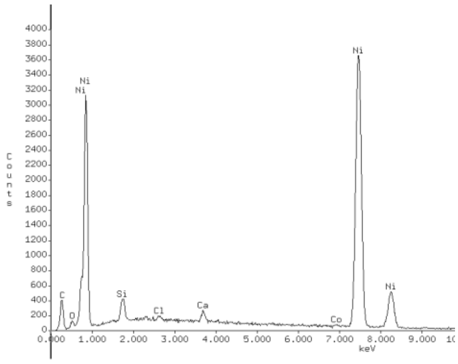

Fig. 10. The EDS spectrum of the metallic shard shown in Fig. 9.

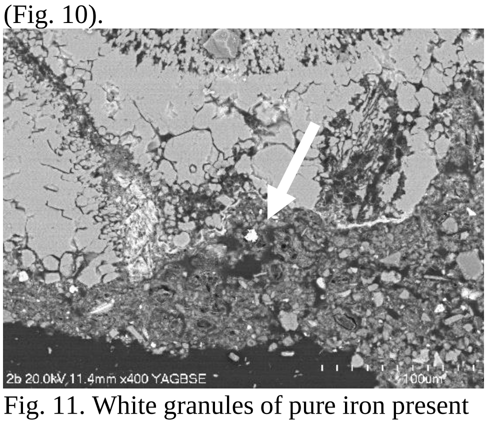

Fig. 11. White granules of pure iron present right beneath the corroded surface of Giza limestone.

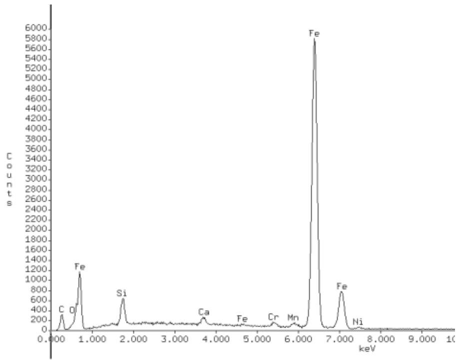

Fig. 12. The EDS spectrum of pure iron found beneath the corroded surface of Giza limestone (Fig. 11).

Continued research of characteristically corroded surface regions of rocks and the areas right below them using a scanning microscope allowed to recognize many metallic intrusions in the limestone. They vary in size - 5 to 200 microns.

The aforementioned intrusions have different shapes. Some of them are enriched with nickel (Fig. 9, Fig. 10) or even contain inclusions of pure metal, e.g. iron (Fig. 11., Fig. 12).

CONCLUSIONS

After conducting initial research it was established that the layer that covers the surface and some of the megaliths in Giza is made of carbon (C). This type of aeration of carbonate rocks has not been described yet in the literature on the processes of aeration of sedimentary rocks (Purdy, Clark 1987). This layer might have been created as a result of meteorites crash. The meteorites crash is dated back to historic period after the construction of pyramids.

Both the field research between Giza and Abu Rowash, and the preliminary laboratory research of the corroded limestone from that area, especially concerning the intrusions present in them, would suggest that a meteorite fell in that area. Its impact sent a very powerful shock wave that damaged rock outcropping beds and megaliths in a very characteristic way. Similar traces on the limestone were documented by a French expedition, however in their case the layer on the limestone consisted of silica (Meteorite 2005). The results of this impact can be found in surface rock layers in that region in the form of metallic intrusion containing nickel and iron, among others.

In the light of this hypothesis the glossy carbon layer also constitutes an interesting issue. At this stage of research it is impossible to define the date of the possible meteorite crash – whether it fell in the pre-dynasty or dynasty times. Observations of the morphology of rocks, which were used as construction materials of pyramids (the remains of the preserved primal rock covers), may suggest that the possible meteorite crash occurred when the pyramids were already there.

The confirmation of such a hypothesis requires a prolonged investigation on site, as well as an in-depth laboratory research of more rock samples. The rocks out of which the pyramids were built should be investigated and that requires obtaining a special permission.

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Photos: Franc Zalewski

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MINERALOGIA POLONICA – SPECIAL PAPERS
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PRIMARY AND SECONDARY ACCESSORY MINERALS IN THE STRZEBLÓW GRANITE (FORE SUDETIC BLOCK)

Abstract: Accessory minerals occuring in strongly albitized Strzeblów granite (subjected also to episyenitization, kaolinization and arenitization) were studied. Generally the content of accessory minerals is low. Apatite, xenotime, monazite and cheralite represent phosphate minerals. Rutile containing Nb, ilmenite, mossite containing W and Sc, zircon rich in U, Th and Hf, thortveitite with high Y content were noted. Form of occurrence and chemical composition suggest that most of the accessory minerals were formed during hydrothermal processes.
Keywords: granite, albitization, accessory minerals, mossite, thortveitite

INTRODUCTION

The Variscian granitoid Strzegom-Sobótka massif is situated in the Fore Sudetic block. Four types of granitic rocks occur there: biotite monzogranite, biotite granodiorite, hornblende-biotite granite and two-mica monzogranite. Different granite types originate from melts formed from various sources (Pin et al. 1989, Puziewicz 1990).

Hydrothermally alterated biotite monzogranite from Strzeblów (near Sobótka) was investigated. The rocks from Strzeblów quarry, called "white granite", consists mainly of albite, K-feldspar, quartz and two micas. According to Majerowicz (1960), transformation of this rock was related to metasomatic action of postintrusive hydrothermal solution. The granite from Strzeblów was subjected to albitization, episyenitization, kaolinization, and arenitization (formation of grus). The study is based mostly on samples strongly albitized.

METHODS OF INVESTIGATIONS

Sixteen samples were collected in the Strzeblów quarry. Optical microscopy, SEM-EDS (field emission HITACHI 4700 microscope with NORAN Vantage analytical system) and X-ray diffraction (Philips X`Pert APD diffractometer) were used.

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RESULTS

The studied rocks are characterized by relatively low amount of accessory minerals.

Phosphates (Tab. 1) are a dominant group of the accessory minerals in the studied rocks. Apatite and xenotime (Fig. 1) are relatively common. Two varieties of apatite are present – with very low REE content and with high REE and Th content. The highest noted content of Th in apatite is above 10 wt%. The content of Gd in xenotime can exceed 7 wt% (Tab. 1). Bigger individual crystals of monazite are scarce. Dominant form of monazite is an impregnation od biotite flakes (Fig. 2). Monazite in biotite is characterized by relatively high content of Ce, Nd, Th, U (Tab. 1). In several grains low content of Pb can be noted. Irregular grain of cheralite (Fig. 1) was identified inside xenotime.

Silicate minerals (Tab. 2) such as zircon and thortveitite are occasionally present in altered granite. Zircon usually exhibit an admixtures of UO_2 (to 1.5 wt %), ThO_2 (to 3.3 wt %) and HfO_2 (to 4.6 wt %). Thortveitite (Fig. 3) occurs as euhedral crystals. Beside Si and Sc it contains relatively high amount of Y_2O_3 (up to ca 15 wt%).

Oxides (Tab. 2) are relatively common. Fe-Ti oxides are represented mostly by ilmenite usually with high content of MnO (up to 15 wt%). Rutile is characterized by significant content of Nb_2O_5 (up to 8.7 wt%). Nb-Fe oxides occur as important group of accessory minerals. Their composition corresponds to mossite (Fig. 4). Nb-Ta-Fe-Mn oxide contains usually WO_3 (ca 3 wt%) and Sc_2O_3 (ca 0.5 wt%).

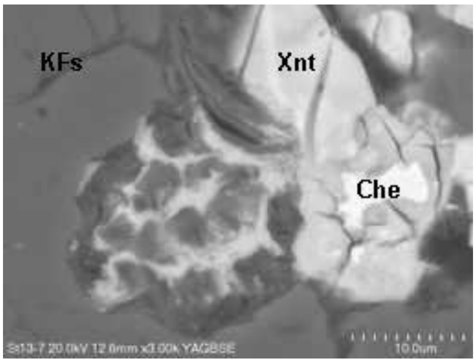

Fig. 1. Cheralite in xenotime.

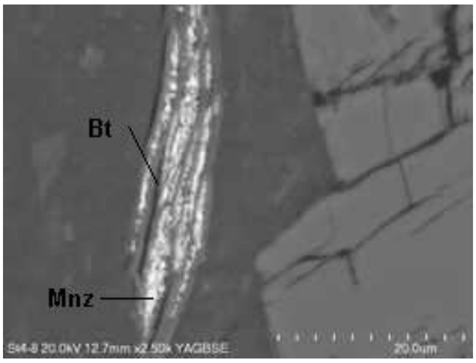

Fig. 2. Monazite and biotite in albite.

Table 1. Chemical composition of phosphate minerals from the Strzeblów granite (selected examples).

Component	Apatite	Monazite	Xenotime	Cheralite
SiO_2	6.02	4.33	1.43	6.14
Al_2O_3	2.04	3.14	2.31	2.78
CaO	18.66	4.97	bdl	7.06
Na_2O	bdl	0.92	bdl	1.09
P_2O_5	63.68	50.66	26.81	34.69
UO_2	bdl	5.84	1.54	1.94
ThO_2	bdl	6.62	bdl	23.84
Y_2O_3	bdl	bdl	42.20	bdl
La_2O_3	1.86	bdl	bdl	11.44
Ce_2O_3	bdl	7.74	bdl	bdl
Nd_2O_3	3.19	7.23	bdl	11.02
Sm_2O_3	bdl	3.02	3.12	bdl
Gd_2O_3	2.49	bdl	4.13	bdl
Dy_2O_3	2.05	5.53	7.91	bdl
Ho_2O_3	bdl	bdl	6.88	bdl
Er_2O_3	bdl	bdl	3.67	bdl
Total	**99.99**	**100**	**100**	**100**

bdl - below detection limit

Table 2. Chemical composition of oxides and silicate minerals from Strzeblów rocks (selected examples).

Components	Thortveitite	Zircon	Ti-Fe oxide	Nb-Ta-Fe-Mn oxide	Rutile
SiO_2	43.23	30.16	3.01	6.76	1.79
TiO_2	bdl	bdl	56.46	1.45	94.10
Al_2O_3	0.34	0.37	1.70	0.48	1.03
FeO	2.69	bdl	29.28	14.34	1.01
MnO	bdl	bdl	8.72	4.09	bdl
CaO	0.59	bdl	bdl	bdl	bdl
Sc_2O_3	37.63	bdl	bdl	0.51	bdl
Na_2O	bdl	bdl	0.42	bdl	bdl
P_2O_5	0.67	bdl	bdl	bdl	bdl
Nb_2O_5	bdl	bdl	bdl	63.48	2.07
Ta_2O_5	bdl	bdl	bdl	6.20	bdl
WO_3	bdl	bdl	bdl	2.65	bdl
ZrO_2	bdl	64.98	bdl	bdl	bdl
HfO_2	bdl	2.72	bdl	bdl	bdl
UO_2	bdl	0.56	bdl	bdl	bdl
ThO_2	bdl	1.20	bdl	bdl	bdl
Y_2O_3	14.84	bdl	bdl	bdl	bdl
Total	**100**	**99.99**	**99.59**	**99.96**	**100**

bdl - below detection limit

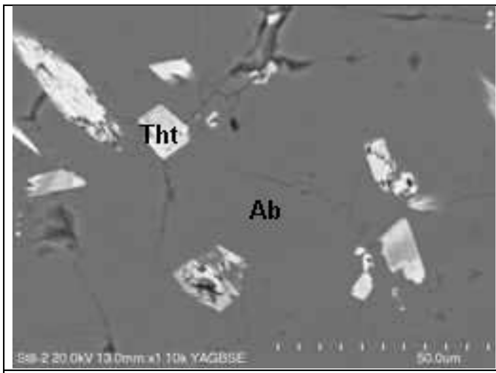

Fig. 3. Thortveitite in albite.

Fig. 4. Mossite in quartz.

CONCLUSIONS

Assemblage of accessory minerals in the Strzeblów granite is strongly influenced by hydrothermal alterations (presence of Nb-Ta-Fe-Mn oxide, thortveitite, chemical composition of the accessory minerals). Also form of occurrence of accessory minerals is related to their secondary origin (e.g. monazite impregnating biotite).

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FIELD TRIPS

MINERALOGIA POLONICA – SPECIAL PAPERS
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Jan ŚRODOŃ[1]

HISTORY OF THE PODHALE FLYSCH BASIN REVEALED BY K-Ar AND AFT DATING AND XRD STUDY OF CLAY MINERALS

The shale and sandstone rocks, outcropping today in Podhale, fill a Tertiary sedimentary basin developed on the basement, composed of the Hercynian crystalline rocks and their Mesozoic carbonate cover, which itself is outcropping in the Tatra (Fig. 1). The Podhale basin is a remnant of a much larger Tertiary basin, which once covered entire Inner Carpathians, but was latter broken into parts and preserved in tectonic depressions, but removed by erosion from the elevated blocks, including the Tatra block (Fig. 2).

The Podhale basin continues towards the west into the Orava basin. Their northern border with Pieniny is tectonic and the contact with the Tatra is erosional (Fig. 1). In the east the basin continues into Magura Spisska area and it is separated from the Levoca basin by a major Rużbachy fault, which is a continuation of the Tatra fault (Fig. 2). The preserved column of the Tertiary basin fill reaches 3 km in the axial western part of the basin and decreases to less than 1 km in the east, close to the Rużbachy fault. Locally, next to the fault, the Mesozoic basement is outcropping at the surface (Fig. 2). The flysch strata are lying almost flat over most of the basin, steeper only close to its northern and southern border. The tectonic deformations are minimal, compared to the underlying Mesozoic basement and to the contemporary Tertiary flysch basins of the Outer Carpathians, situated further to the north (Fig. 1). The present-day elevation of the basin surface increases gradually from ca. 600 m asl in the west to the maximum of 1100m close to the Rużbachy fault. Also topography becomes slightly more rugged towards the east and the local differences in elevation increase from 200 to 600 m.

Such tranquil geology and topography offers no apparent clues to the surprising history of this basin, which was revealed recently by combined X-ray diffraction (XRD) study of clay mineralogy, radiometric K-Ar dating (Środoń et al. 2006) and apatite fission track (AFT) dating (Anczkiewicz et al. 2005).

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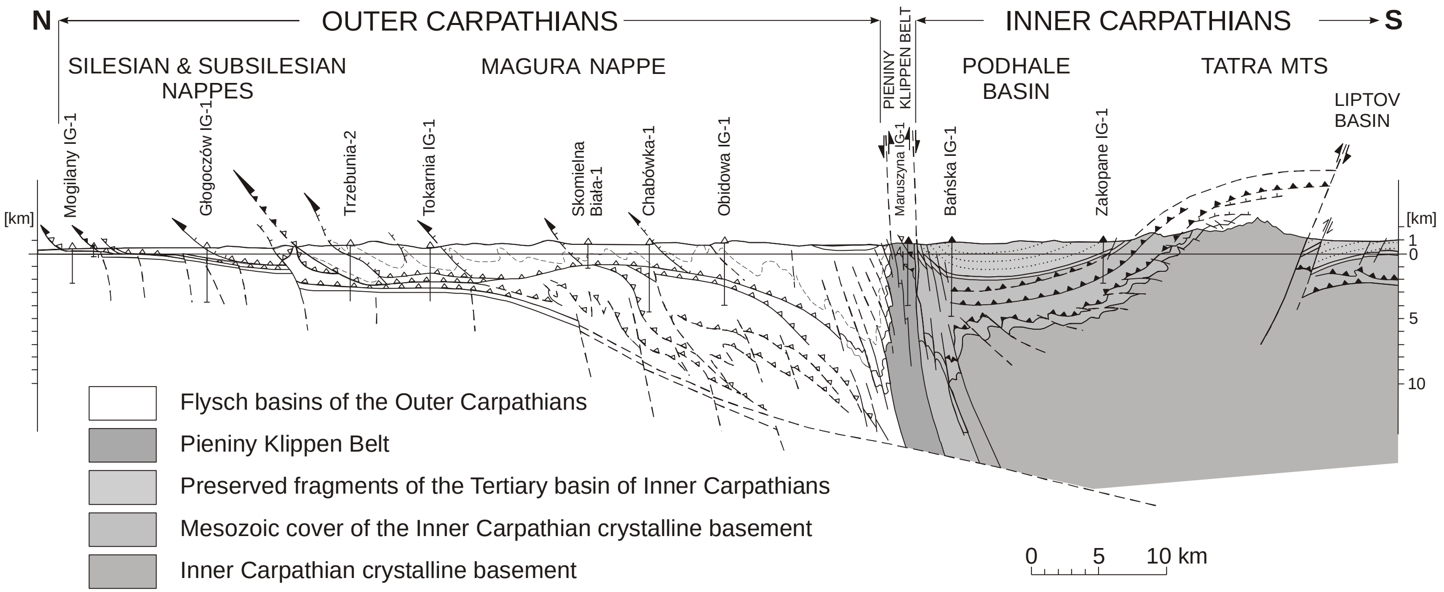

Fig. 1. Cross-section of the Carpathians along Kraków-Zakopane transect (after K. Birkenmayer), illustrating the geotectonic position of the Podhale basin.

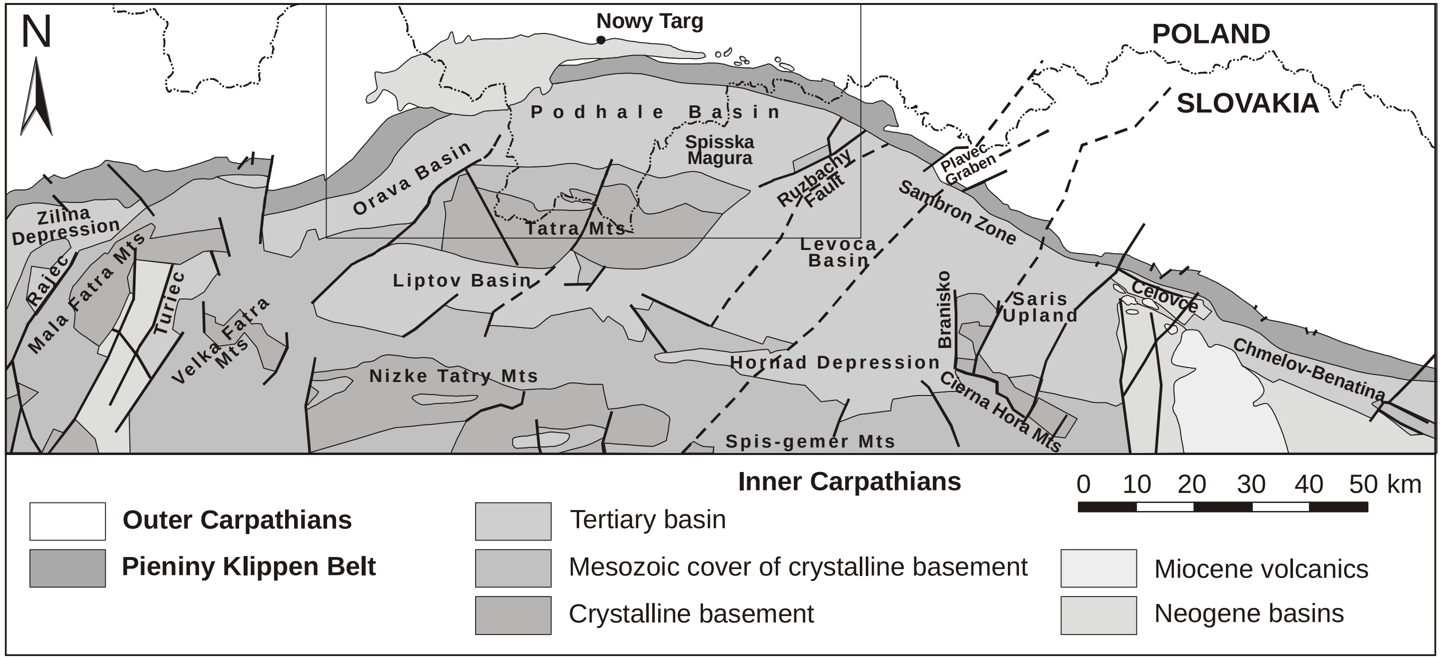

Fig. 2. Part of the geological map of the Western Carpathians (compiled by A. Łaptaś) with the study area marked by the rectangle.

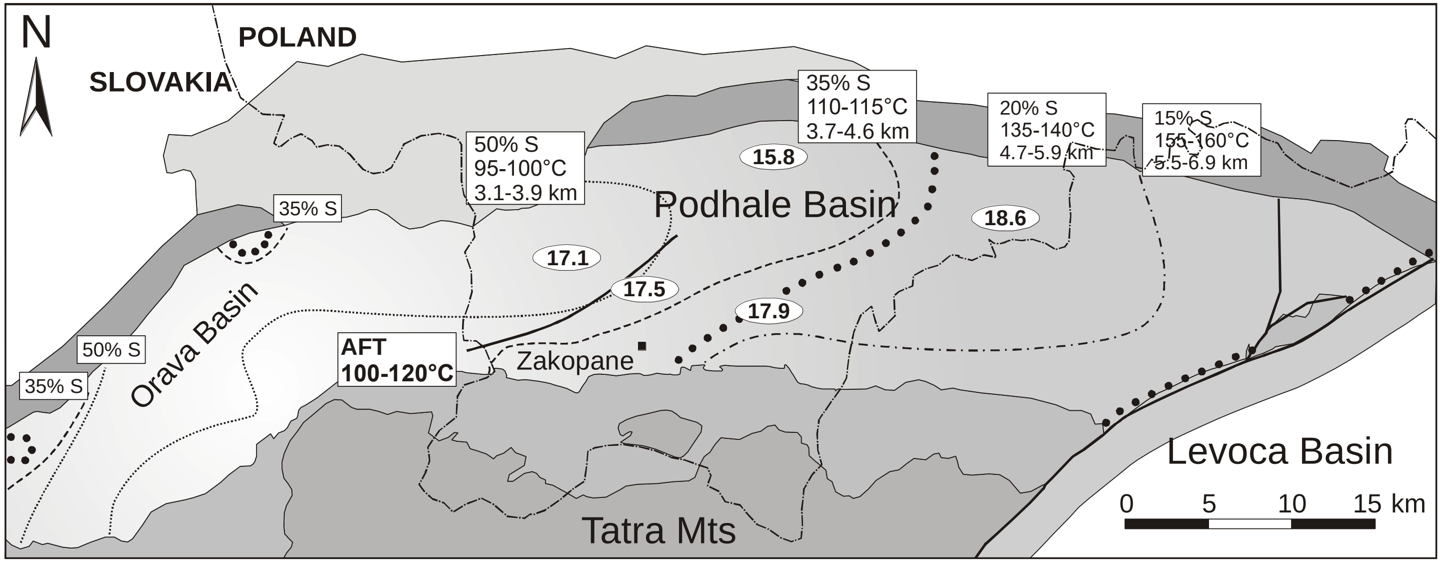

Fig. 3. Thermal history indicators for the Podhale-Orava basin. The maximum burial temperatures and the thickness of eroded cover were calculated for %S isolines, established from the XRD data, which were collected for the surface samples. Dotted lines mark the limit of kaolinite, which disappears due to diagenesis in the eastern part of the basin and reappears in the Levoca basin. The pink line separates AFT dates totally reset (east) from incompletely reset (west). K-Ar dates from bentonites in the ellipses. Modified from Srodon et al. 2006.

Each of these techniques provides a specific type of information on the basin history. Clay mineralogy of sediments deposited in a basin is evolving during burial in response to increasing temperatures. XRD allows for quantification of this evolution and to evaluate the maximum paleotemperatures, in particular by measuring the ratio of smectite to illite layers (%S) in mixed-layer illite-smectite minerals separated from shales. K-Ar dating of illite-smectite separated from bentonites, i.e. from altered volcanic ash layers free of detrital contamination, provides the age of the smectite illitization process (age of locking potassium in the illite crystalline structure), which approximates the age of the maximum paleotemperatures (Środoń et al. 2002). AFT dating is based on counting defects (tracks) in the crystalline structure of detrital apatite produced by fission of uranium nuclei, both spontaneous and induced in a nuclear reactor. Such tracks undergo thermal annealing (resetting) at 100-120°C, thus AFT technique provides two types of information: 1) whether the rocks were buried in the basin to >100-120°C (detrital vs. reset AFT ages), and if yes 2) when they passed the 100-120°C isotherm on the way back to the surface i.e. during uplift and erosion.

XRD studies of shales were performed over entire surface of the basin and in five boreholes. K-Ar dating was completed for three grain-size fractions of five bentonite samples collected at the surface. AFT dating was made for apatites separated from sandstone samples, which were collected both at the surface and from the Bukowina Tatrzańska borehole. The results of these measurements are presented in synthetic form in Fig. 3.

The measured %S values indicate that the rocks outcropping today at the surface experienced in their burial history very different maximum paleotemperatures: from <100°C in the west to >160°C in the east. This temperature gradient across the basin surface is confirmed by the disappearance of kaolinite in the east and by the AFT dates, which are totally reset in the east and only partially reset in the west. Grain density measurements for the Chochołów and the Bukowina borehole samples confirmed that these profiles were buried to very different depths and that they can be superimposed into one continuous diagenetic profile (Fig. 4). The paleothermal gradient measured from %S data is the boreholes ranges from 20 to 25°C/km, which is identical to the measured present-day gradient. Based on these values, the thickness of rocks removed by erosion from the surface of the basin can be evaluated as ranging from <3 km in the west to >7 km in the east. The basin uplift started after the maximum paleotemperatures evaluated by K-Ar measurements were reached (16-19 Ma), as confirmed by younger reset AFT dates (6-12 Ma). Using the K-Ar values, the uplift rates can be estimated as ranging from 200m/Ma in the west to 360m/Ma in the east. A similar value of 420 m/Ma was obtained independently from the AFT dates measured in the Bukowina profile. The nature of contact of %S isolines with the basement outcropping in the Tatra indicates that the Tatra block surface was strongly inclined towards the east during the flysch sedimentation.

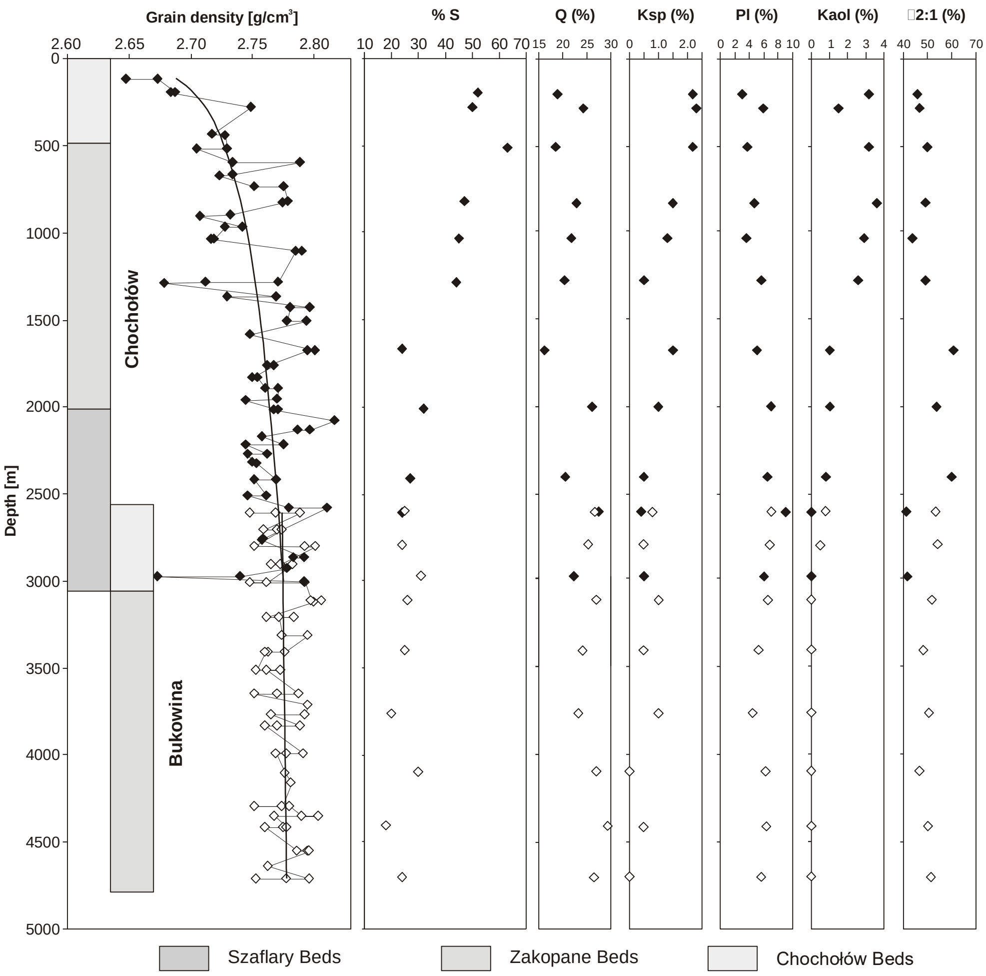

Fig. 4. Superposition of the Chochołów and Bukowina wells into one continuous diagenetic profile of the Podhale Basin based on the grain density data (from Srodon et al. 2006). The weight % of the sum of the dioctahedral 2:1 phyllosilicates (□2:1) and the most prominent diagenetic trends are presented %S – percent smectite in illite-smectite, Q – quartz, Ksp – K-feldspar, Pl –plagioclase, Kaol – kaolinite.

Using these data the Podhale basin history can be reconstructed as follows:

1) The basin developed due to uneven subsidence of the tectonic block comprising present day Podhale and Tatra area: the rate of subsidence and sedimentation was highest in the east.
2) The subsidence and sedimentation continued much longer than previously evaluated from the preserved sedimentary record: a thick layer of Lower Miocene sediments was deposited until 16-19 Ma. Only the Tatra block started to rise earlier.
3) The Podhale basin uplift was also very uneven: much faster in the east than in the west. The consequences are: a) much higher grade of diagenesis of the surface rocks, and b) more elevated and rugged topography in the eastern part of the basin.

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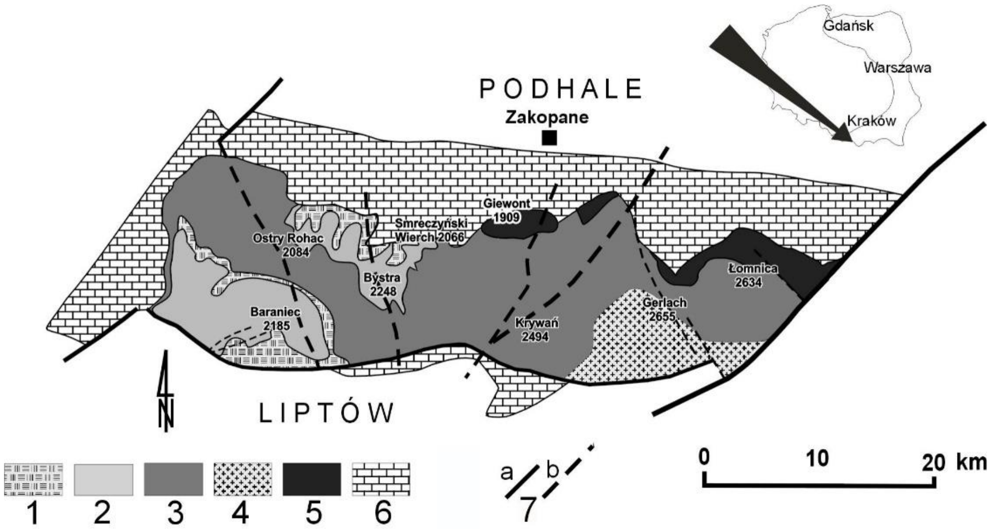
THE CRYSTALLINE BASEMENT ROCKS OF THE HIGH TATRA MTS., POLAND

GEOLOGICAL SETTING

The Tatra Mts. are the northernmost part of the Tatric Unit which belongs to the Central Western Carpathians. The crystalline basement of the Tatra Mts. comprises a polygenetic granitoid intrusion and a metamorphic envelope overlain by Mesozoic and Cenozoic sedimentary complexes.



Simplified geological map of the Tatra Mountains (compilation after Kohut, Janak 1994; Bac-Moszaszwili 1996; Gawęda et al. 2005).
Symbol explanations: 1 – metamorphic cover (Lower Unit), 2 - metamorphic cover (Upper Unit), 3 – Common Tatra type granite, 4 – High Tatra type granite, 5 – Goryczkowa type granite, 6 – sedimentary cover, 7 – main faults: a – identified, b – assumpted.

The metamorphic envelope, cropping out mainly in the westernmost part of the massif is composed of two superimposed units (Upper and Lower Unit) that differ in petrographical and chemical character, P-T conditions of metamorphism and tectonic deformation (Kohut, Janak 1994; Gawęda et al. 1998; Gawęda, Burda 2004). In the Lower Unit mica schists predominate while gneisses and amphibolites

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form subordinate intercalations. The metamorphic conditions were estimated for T = 550-600°C and P = 5-8 kbar (Kozłowski, Gawęda 1999). Upper Unit is composed of migmatitic rocks: gneisses and amphibolites, graphite quartzites and subordinate intercalations of mica schist (Burda, Gawęda 1997, 1999; Gawęda et al. 2000). Peak of metamorphism in this Unit took part in the upper amphibolite facies conditions (T = 690-780°C, P = 7.5-10 kbar, Burda, Gawęda 1999; Gawęda, Burda 2005) which caused the migmatitic character of most of these rocks. Excluding amphibolites (originally tholeiitic basalts, Gawęda et al. 2000), the rest of the metamorphic rocks have a sedimentary protolith (Jaroszewski 1967; Burchart 1970; Gawęda et al. 2000). Locally the eclogitic remnants, most probably tectonically emplaced, are present among predominantly metapelitic lithologies (Janak et al. 1996). Age of the migmatization was recently stated by zircon U-Pb dating for relatively short time range of 358-367 Ma (Burda 2006 a,b).

The crystalline basement of the Tatra Mts. is dominated by polygenic granitoid intrusions consisting of a few petrographical varieties, which reflect the following magmatic events (Kohut, Janak 1994; Poller et al. 2000): (1) intrusion of the Older Tatra granite (now present as orthogneisses- dated at ca.405 Ma); (2) formation of the Younger Tatra granite (common Tatra type) and Goryczkowa type granite - subduction-related granites-granodiorites, which intruded the metamorphic complex around 350-360 Ma; (3) formation of leucogranites of the same age (360 Ma), resulting from partial melting of the metamorphic complex during thrusting and metamorphic inversion (Burda, this volume); (4) intrusions of quartz diorites (ca.341 Ma) found as small dykes and sills cutting the metamorphic rocks (Poller et al. 2000; Gawęda et al. 2005); (5) formation of porphyritic granodiorite and equigranular biotite monzo- to syenogranites ca.314 Ma (Poller et al. 2000).

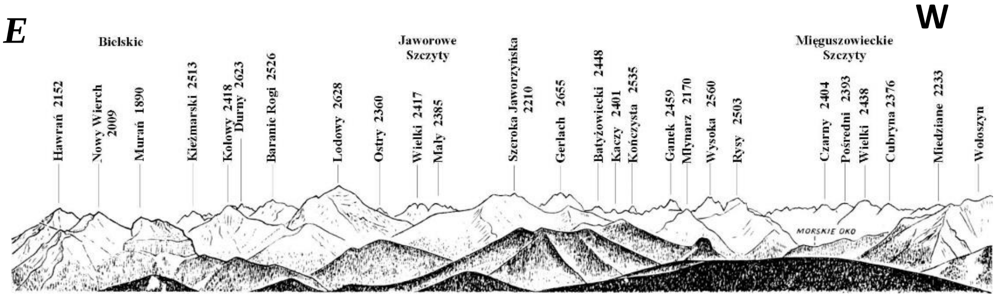
During the Triassic, Jurassic and Early Cretaceous, the crystalline core of Tatra Mountains were covered by sediments. Nappe-thrusting and folding processes took place during the Late Cretaceous. In the Paleogene, the Tatra massif was buried again and covered by carbonate deposits and a post-orogenic flysch sequence. The uplift of the Tatra massif and appearance of the mountain range in morphology took place in the Late Miocene (Jurewicz 2007).

FIELD TRIP

Itinerary: Bukowina Tatrzańska, Polana Głodówka, Wodogrzmoty Mickiewicza, Morskie Oko, Wielki Piarg, Czarny Staw pod Rysami

STOP 1
Polana Głodówka – short photo-stop

We begin the trip from Głodówka, where we can observe one of the most fabulous panoramas of the Tatra Mountains. Above the erosion depression in Zakopane layers (Eocene-Oligocene), there are ridges built of rocks of the Križna nappe series spreading from Osobita in the west to the Bielskie Tatra in the east. The Bielskie Tatra summits are the highest elevations among the Križna nappe series. There is a group of mountains towards the south, called Sołtysie Kopy, built of Jurassic deposits (the Križna nappe). Slightly to the east, light dolomite rocks can be spotted among the forests on the summit of Gęsia Szyja and Rusinowa Polana, with Eocene conglomerates stuck among the Križna nappe series lying just in front of us. Further in the back, there are massifs of Wołoszyn and Koszysta, further to the east the highest summits in the Tatra Mountains appear with a dominating massif of Lodowy Szczyt (2627 m a.s.l.) and Gerlach (2654 m a.s.l.) to the right in the back, above Biała Woda Valley. Łomnica (2632 m a.s.l.) can be seen on the left. All those summits are built of granitoid crystalline basement of the Tatra Mts. In front of them, there are naked slopes and the ridge of Szeroka Jaworzyńska massif built of autochthonous sedimentary rocks and closer to the north of Križna nappe rocks.



Tatra' panorama from Polana Głodówka (Nyka 1981).

Travelling further south, we can observe covers of glacial sediments of older glaciation on the slopes of Wierch Poroniec and approaching Łysa Polana we cross frontal moraine ridges (approx. 920 m a.s.l.), which mark the maximum range of the Białka glacier during the last glaciation. Łysa Skałka, built of Triassic dolomites of the Križna nappe series, topped with schist-sandstone rocks, rises above Łysa Polana. After passing Łysa Skałka we enter a vast plain reaching Waksmundzki Potok. It contains coarse fine detritic deposits in the bed, which are probably the filling of a glacial lake formed after melting of the glacier tongue. Passing Polana Palenica we cross a fluvioglacial cone of Waksmundzki Potok, which was formed in the recession stage, when the Waksmundzki glacier built frontal moraines reaching approximately up to 1180 m. A kettle lake appears below in Białka Valley.

The road climbs up the slope of Wołoszyn, where lateral moraines cover sedimentary rocks of Križna nappe and autochthonous sedimentary cover, and than granitoides. Along the slopes of Wołoszyn we reach Wodogrzmoty Mickiewicza.

STOP 2
Wodogrzmoty Mickiewicza - short photo-stop

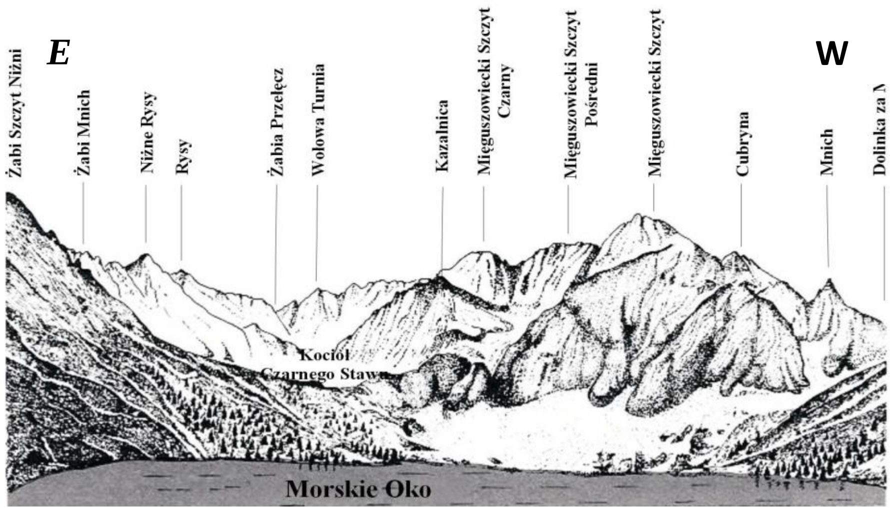
Wodogrzmoty Mickiewicza are a waterfalls on Roztoka Potok, cutting, through a deep gorge, granitoids forming a threshold of Roztoka Valleys, hanging above Biała Woda Valley. From the bridge, there is a good view on the middle one of the three waterfalls. They were named after Adam Mickiewicz in 1890, the year when his ashes were brought back to Poland.

Common Tatra type granites appear on the slope of Roztocka Czuba. Exposed rock series of the Szeroka Jaworzyńska massif can be seen on the opposite side of Biała Woda Valley. The summit of Szeroka Jaworzyńska is built of granitoids covering sedimentary rocks of the autochthonous series. It is a tectonic cap, being a fragment of the overthrust block of Szeroka Jaworzyńska. Crystaline rocks of Zamki and Horwacki Upłaz, which are visible towards the north, is another tectonic cap. Steep limestone rock slopes below Zamki are built of limestones and dolomites of the Triassic autochthonous series. Two kilometres further, we reach „Wanta" forester's lodge. Magnificent view of the southern end of the U-shaped Biała Woda Valley spreads from the curve. We leave Biała Woda Valley near "Wanta" and climb up the mountain through the hanging valley of Rybi Potok to Włosienica Glade. We leave the forest entering Szałasiska glade and follow the naked part of the Opalony Wierch slope. The road cuts a wide couloir, called Gendarmerie Couloir, which is famous for avalanches, which fall on the road frequently. Following moraine deposits of the Rybi Potok glacier, we reach the wall of a recession moraine closing Morskie Oko (1393 m a.s.l.). There is a mountain shelter built on the moraine in 1908. Over there you can enjoy a splendid panorama of the highest Polish summits in the Tatra Mountains, which overtop the lake by almost a kilometre.

STOP 3
Morskie Oko - glacialy-modified granite landscape

Climatic changes in Pleistocene caused glaciation in the Tatra Mountains There are numerous traces of devastating activity of glaciers: cirques, glacial valleys, abrasion hollows, moutons, scraps and scratches. Such forms built by a glacier like ground, ablation, lateral medial and frontal moraines occurring in the Tatra Mountains are mostly the results of the last glaciation. It covered 50% of the High Tatra Mountains and approximately 21% of the West Tatra (Klimaszewski 1988). The largest glacier was 14 km long and occupied Białka Valley. The glacier was formed by several glaciers coming from the following valleys Pięć Stawów Polskich, Rybi Potok, Waksmundzki, Żabie Stawy Białczańskie and Białej Wody. Its maximum thickness was 300 m and its total area was approximately 58 km^2.

The Rybi Potok glacier began with two vast firn fields filling the cirques of Czarny Staw and Dolina za Mnichem. The tongues moving out from the cirques deepened the valley of Morskie Oko. The lake covers the area of approximately 345 400 m^2 and its dimensions are 862 x 566 m. The water level is at 1395 m a.s.l., and its depth reaches 50.8 m.



Tatra' panorama from Morskie Oko lake (Bac-Moszaszwili 1996).

In the 19th and the 20th century, the surrounding area was the subject of a legal dispute concerning the ownership between Poland and Hungary, a part of Austria in that time. The owner of the neighbouring land, on the Hungarian side – the duke Christian Hohenlohe, usurped the right to annex the western slopes of Żabi and the vicinity of Morskie Oko. Hungarians based their demand on inaccurate documents and even fake maps, while Poles supported their rights by indisputable historical and legal proofs. However, the dispute was lasting for dozens of years and finally ended with the final judgement of the international tribunal in Graz, which confirmed the Polish rights to the disputed territory in 1902.

There is a rock threshold above the water level on the southern side of Morskie Oko, which separates the cirque of Czarny Staw pod Rysami. Following a tourist trail along the west shore of Morskie Oko, we can reach the 200 m high rock threshold. On the way, we can stop at Wielki Piarg and observe rocks building granitoide massif of the High Tatra Mountains. Description of rocks occurring there is below.

STOP 4
Wielki Piarg

Variscan granitoid types

The crystalline basement of the High Tatra Mts. is dominated by polygenic granitoid intrusions consisting of a few petrographical varieties:

1. The two mica granodiorite-granite (called common Tatra type) is the more abundant type in the Western Tatra Mts., forming tongue-shape intrusion. It is peraluminous in composition (ASI = 0.98 – 1.35), with SiO_2 ranging from 67.1 to 73.4 %wt. and prevalence of Na_2O over K_2O. It belongs to calc-alkaline – high-K calc-alkaline suites (Kohut & Janak, 1994), with the VAG–type tectonic setting (Poller et al.,2000). The age of emplacement was in the range of 357 – 363 Ma (Poller et al., 2000). High I_{Sr}^{360} values (I_{Sr}>0.708), together with accessory minerals parageneses and zircon crystals characteristics suggest the S-type origin of that type of granite. The common Tatra type granite is interpreted as a crustal partial melt, formed during ocean closure and collision of Armorica and Gondwana plates at the beginnning of the Variscan accretion (Poller et al. 2000).

Two mica granodiorite (common Tatra granite). High Tatra Mts.

2. Fine-grained leucogranites, with oriented fabric occur as small intrusions, from some tens of cm to 150 m in thickness among the metamorphic envelope rocks of the Western Tatra Mts.. They are located in the shear zone dividing the LSU and USU and inside the USU migmatitic rocks. Leucogranites are in general haplogranitic in composition, peraluminous (ASI = 1.01 – 1.45, SiO_2 = 69-78 % wt.)

with $K_2O > Na_2O$ and high Rb/Sr ratios (0.9 – 4.5). They are typical products of muscovite dehydration melting during syncollisional tectonic regime (Gawęda 2001). The difference in source rock chemistry is the most likely cause of the Sr isotopic heterogeneity, while δ^{18}_{SMOW} cover the range 12.2 – 14.1 ‰, typical of crustal melts. Zircon U-Pb dating point out the age of 361 Ma (Burda 2007). The recent U-Pb monazite and zircon dating of migmatites from the Western Tatra Mts. point out the same time period 360-365 Ma as the peak of metamorphism and migmatisation (Burda 2006 a, b).

4. Goryczkowa type granite with a porphyritic fabric and pinkish K-feldspar up to 2 cm in length. The mineral assemblage mainly consists of perthitic K-feldspar, plagioclase (25-28% An), quartz, muscovite and biotite. Accessory phases comprise apatite, zircon and monazite. Porphyritic granites are peraluminous (A/CNK = 1.6) with silica content around 73 wt.%, characterized by $K_2O > Na_2O$ and high Rb/Sr ratio = 2.5. The chondrite-normalized REE diagram show LREE enrichment expressed as $(Ce/Yb)_N > 5$ and negative Eu anomaly (Eu/Eu* = 0.71). Normative corundum is about 3.8%. Porphyritic granites show low Zr and Y content (31 ppm and 6.3 ppm respectively). Pearce et al. (1984) diagrams suggest the VAG–type tectonic setting. The LA-MC-ICP-MS U-Pb zircon data indicate an Upper Devonian/Lower Carboniferous age of the Goryczkowa type granite at around 356 Ma (Burda, Klötzli 2007).

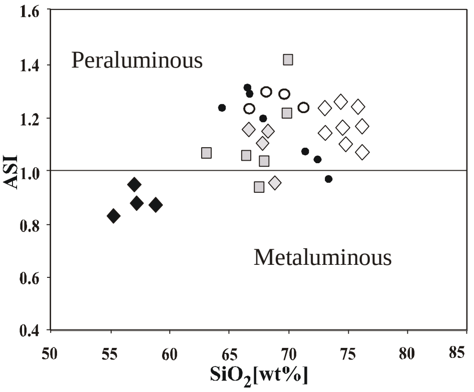
The contact zone of leucogranite (left) with biotite monzogranite (right). Wielki Piarg, High Tatra Mts.

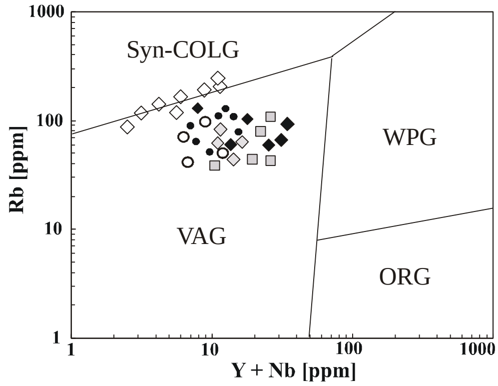
Porphyritic granite. Morskie Oko, High Tatra Mts.

5. Quartz-diorites occur both in the Western Tatra Mts. – as sills in the metamorphic cover - and as enclaves in High Tatra granites. There are predominantly metaluminous (ASI = 0.684–0.970), with SiO_2 content in the range of 53-61 wt.% and low Rb/Sr ratios (0.064-0.108). They are characterised by high total REE (256-394 ppm), wide range of REE fractionation (Ce_N/Yb_N = 6.32-22.04), low I_{Sr} values (0.70399-0.70414), ε_{Nd}^{340} of 0.7-1.9 (Poller et al 2001), δ^{18}_{SMOW} of 8.3-8.58 (Gawęda et al. 2005). The contradictory (crustal + mantle-derived) mineral populations together with geochemical patterns were interpreted in terms of mingling of mantle-derived, not fractionated and crustal-derived, anatectic magmas. The intrusion of hybrid magma was dated for 341 Ma (Poller et al. 2001).

Two main granite varieties define the so called High Tatra type granite. There are:

6. Grey, equigranular **biotite monzogranites** are the most popular rock-type in the High Tatra Mts. Biotite monzogranites are metaluminous, with silica content in the range of 70.9 - 75.6 wt.%. K_2O/Na_2O ratio changed from 1.66 to 0.34, influencing Rb/Sr ratio (0.11-0.36) and Ba content (258-1163 ppm). Calculated I_{Sr}^{314} is in the range of 0.705 – 0.707 (Gawęda, 2007a) suggesting the I-type or mixed I/S origin of monzogranite. The U-Pb zircon dating gave 314 Ma (Poller et al. 2001).





• 1 ◇ 2 ○ 3 ◆ 4 ◇ 5 □ 6

The Tatra granitoids plotted on the Shand's diagram. ASI – aluminium saturation index, 1 – two mica granodiorites; 2 – leucogranites; 3 – Goryczkowa type granite; 4 – quartz diorites; 5 – monzogranites; 6 – porphyritic granites

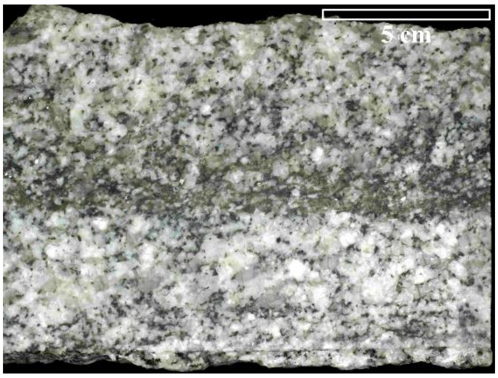
Discrimination plot of the Tatra granitoids (after Pearce): VAG – volcanic arc granites, Syn-COLG – syn-collisional granites, WPG – within plate granites, ORG – ocean ridge granites

7. Porphyritic granites presence in the High Tatra Mts. is restricted to areas rich in enclaves and xenoliths. The most pronounced feature of these granites is the presence of large (from about 1 cm to 6 cm in length) porphyrocrysts of pinkish or white-yellowish alkali feldspars. Porphyritic granites are weakly peraluminous to metaluminous, with silica content ranging from 62.9 to 70 wt.%, characterized by K_2O/ Na_2O = 0.53-1.32 and Rb/Sr ratio in the range of 0.15-0.29, coupled with enhanced Ba concentration (918-2422 ppm). Calculated I_{Sr}^{314} is in the range of 0.707 – 0.708. There is no isotope age for porphyritic granite, however, field and petrographic observations suggest that it can be slightly younger than biotite monzogranite (Gawęda 2007a).

Both the monzogranite and porphyritic granite were possibly influenced by the mantle-derived source mixed with crustal one, as it is suggested by the Sr-Nd isotopic data (Poller et al. 2001) and the presence of both hybrid MME (Gawęda 2007b) and mantle-derived mesoladogite (Gawęda, 2006). They show features of mixing and mingling during magma flow (Gawęda 2007a), what is also supported by the complex paleomagnetic properties (Grabowski, Gawęda 1999).

Magmatic schlieren formation and K-felsdpar megacrysts

Two types of schlieren were found in the High Tatra Granite. Both of them are present in the medium-grained biotite monzogranite. Schlieren are the discontinuous streaks, up to 1-5 cm in thickness and 20-70 cm in the lenght. In most cases, these two types of schlieren are associated with K-feldspar megacrysts.



Block of granite with 1st type schlieren from the slopes nearby the Morskie Oko.

2nd type schlieren with feldspar-quartz-mica pegmatite. Wielki Piarg.

2nd type schlieren associated with the K-feldspar phenocrysts from Lower Mięguszowiecki Kocioł.

Schlieren of 1st type are characterised by biotite flakes arranged according to schlieren plane. Their orientation differs within the schlieren from parallel in the axial part to more chaotic. In the 1st type schlieren two diffrent trends of temperatures for darker and lighter parts of the enclave were calculated. The zircons geothermometer by Watson & Harrison (1983) gave temperatures: 777°C (the darker part) and 695°C (the lighter part). Similar situation is observed with monazite geothermometer (Montel 1993), where temperature for the more mafic part is 714°C and 624°C for the felsic part. Ilm-Mt exsolutions were used to calculate the temperature of primary ulvöspinel decomposition according to Spencer & Lindsley (1981) and point out the interval 780 – 804°C.

Schlieren of 2nd type reveal oriented fabric, underlined by biotite flakes and feldspar-quartz aggregates elongation. The orientation is similar to the arrangement of foliation in xenoliths. Main mineral components are micas, plagioclase and quartz, accessories are represented by ilmenite, monazite, zircon and epidote. There are two types of monazite crystals present in this type of schlieren: 1st type shows two-fold internal structure: core and margin, differing in chemical composition, with LREE/Th_{wt} ratios 8.8 in margins to 10.7 in cores. The second type of monazites have complicated internal zonation with LREE/Th_{wt} ratios varying from 7.8 to 15.5 and the mean value for the whole sample 10.8. In some cases monazite crystals contain the inclusions of zircon, apatite, thorite and huttonite. Titanium-in-biotite geothermometer (Henry et al. 2005) were used for temperatures calculations which cover the range 648-690°C. Temperature calculations based on zircons and monazites have shown similar ranges: T_{mz}=580-660°C and T_{zr}=630-675°C.

The temperatures of perthite exsolution were calculated by using the software program SOLVCALC 2.0 with model Nekvasil & Burnham (1987).

In the first type of schlieren, the temperatures of perthite exsolution fall in the range from 338ºC to 358ºC. Distribution of barium content (1st type schlieren) is relatively low and homogeneous. Local higher Ba content is generally related to the occurrence of plagioclase inclusion and albite perthites. The alkali feldspars are undeformed. The lighter part of schlieren has a clear positive Eu anomally, while the darker part of the schlieren has weak negative Eu anomally. The surrounding granite show weak positive Eu anomally. In this type of schlieren the temperature of perthite exsolution changes in the range from 460ºC to 550ºC.

In 2nd type of schlieren barium content in K-feldspars is relatively high, achieving in some places the value of 8% at Cs. Ba content is extremly heterogeneous with numerous differences in the Ba content, related to the presence of albite perthites and structural deformations. Alkali feldspars experience continuous deformations in the marginal part- we suggest that the perthite exsolution was syn-deformational. Dark part of the schlieren has strong negative Eu anomally. The border between the darker and the lighter part of the schlieren has very clear negative Eu anomally.

In conclusion we suggest that the 1st type of schlieren could be formed by mineral sorting during magma flow. 2nd type of schlieren are supposed to be resisters after partial melting of the original metapelitic xenoliths.

The monazite U-Th-common Pb dating revealed the equilibration of reworked xenoliths (2nd type) with the granite (300 Ma), while in the magmatic layers (1st type) the episode dated at 255 Ma is clear, most probably connected to the Permo-Triassic event.

STOP 5
Czarny Staw pod Rysami

Czarny Staw is one of the alpine glacial lakes - as the relicts of the last Ice Age, which ended up some 10 to 8 thousand years ago.

Tectonic striae.
Wielki Piarg, High Tatra Mts.

Glacial striae.
Czarny Staw pod Rysami, High Tatra Mts.

The granitoid massif of the High Tatra is crossed by numerous dislocations. On the base of their geometry they are subdivided into two groups: low-angle faults with dips < 45° and steeply dipping shear zones with dips >45° (Jurewicz 2007). The first group is linked to the Alpine overthrusting. They are characterised by planar and smooth surface coated by quartz, epidote and chlorite. On mineralised surface the tectonic striatations occur. The second one (>45°) show poligenetic development (from Variscan to Alpine). During the uplift of the Tatra Block (25-10 Ma) the pseudotachylyte formation took place (Jurewicz 2007).

Today the more steep dislocations zones are the main transfer routes of weathered debris which form an extensive talus cones at the footslope of the rock's walls.

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