XIII Meeting of the Petrology Group of the Mineralogical Society of Poland

Extended Abstracts

Leśna, Poland, 19-22 October 2006

Mineralogia Polonica-Special Papers – continuation of Polskie Towarzystwo Mineralogiczne – Prace Specjalne

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Editor of Volume 29: Jacek Puziewicz Technical Editor: Wojciech Bartz

ISSN 1896-2203

DTP - Beniamin Buszewski, tel. 0608 027 630

Druk i oprawa –Proofini Drukarnia Cyfrowa 54-239 Wrocław, ul. Wejherowska 28 tel.: 071 793 00 75, tel./fax: 071 793 00 76 e-mail: biuro@proofini.pl www.proofini.pl

XIII Meeting of the Petrology Group of the Mineralogical Society of Poland

organised by

Mineralogical Society of Poland

Institute of Geological Sciences, University of Wrocław

Institute of Geological Sciences, Jagiellonian University

Leśna, Poland, 19-22 October 2006

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The Meeting was organized thanks to financial support of the Ministery of Science and Higer Education and sponsorship of Łużyckie Kopalnie Bazaltu "Księginki" S.A.

Sesja została zorganizowana dzięki dotacji Ministerstwa Nauki i Szkolnictwa Wyższego oraz wsparciu Łużyckiej Kopalni Bazaltu "Księginki" S.A.

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MANTLE BENEATH SW POLAND AND SOME OCCURRENCES OF RELATED TERTIARY VOLCANISM

Dawid BIAŁEK¹, Anna SZYNKIEWICZ¹

UPPER MANTLE XENOLITHS FROM THE WESTERN PART OF THE DARIGANGA PLATEAU (SE MONGOLIA)

Abstract: Petrography, mineral chemistry and textures of mantle xenoliths from Dariganga Plateau have been studied to constrain the thermal state of the uppermost mantle beneath SE Mongolia. Used thermometers yields temperatures ranging from 850°C to 930°C. **Keywords:** Central Asia, mantle xenoliths, petrography, geothermometry.

INTRODUCTION

Mantle xenoliths in alkali basaltic lavas and cinder cones occur in several areas in central Asia. The Dariganga lava plateau is the largest Cenozoic lava field in Mongolia and arguably the largest one in central and eastern Asia. The alkaline volcanic field of SE Mongolia comprises more than 200 volcanic cones and a number of sub-horizon-tal lava flows.Volcanic eruptions in the Dariganga region took place from Miocene to Holocene to produce a lava plateau that covers an area of about 10,000 km² (Genshaft and Saltykovsky 1985). This lava plateau is located outside regions of intensive Cenozoic tectonic activity and is regarded as being linked to the formation of rift grabens in northern China (Khutorskoy and Yarmolyuk 1989). Numerous models have been proposed to explain the petrogenesis of these magmas, including a mantle plume or effect of collision between India and Asia during the Eocene.

The Cenozoic volcanic rocks of Dariganga plateau are represented solely by basalts strongly depleted in silica. The volcanics are primarily alkali-olivine basalts (mostly of the Na-K type). Ultramafic xenoliths entrained in the alkali basalts and basanites from SE Mongolia include refractory spinel-harzburgites and dunites accompanied by subordinate amount of spinel lherzolites.

SAMPLING AND METHODS OF INVESTIGATION

The mantle xenoliths for this study were collected from 5 cinder cones near the town of Dariganga, the most western part of the plateau. Electron microprobe examinations were carried out with a CAMECA SX100 instrument at the Inter-Institution Laboratory for Microanalysis of Minerals and Synthetic Substances (Faculty of Geology, Warsaw University). An acceleration voltage of 15 kV and a sample current of 20 nA were used.

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RESULTS AND CONCLUSIONS

The volcanic rock samples consist of fine-grained matrix with medium-sized (< 5 mm) phenocrysts of olivine and coarse-sized (up to 8 cm) phenocryst of clinopyroxene and feldspar. The xenoliths are rounded to discoidal in shape, and have maximum dimensions up to 35 cm. The boundary with the host lava is very sharp in hand specimen.



Fig. 1. (a) Photomicrograph of representative pyroxenite from the Dariganga xenoliths, showing coarse-grained texture; (b) BSE image of ameboidal spinel from the spinel peridotite.

The xenoliths were classified using nomenclature and subdivisions based on mineralogical criteria as well as textural properties (Mercier and Nicolas 1975; Zipfel and Wörner 1992). Most of the xenoliths are typically medium- to coarse-grained rocks (Fig. 1 a) with protogranular or mosaic equigranular texture and are similar to those commonly observed in worldwide spinel-peridotite (Mercier and Nicolas 1975).

Olivine grains are up to 1 cm, have straight mutual grain boundaries. Olivine is $Fo_{822.90.1}$ and contain minor MnO (0.14-0.23 wt %) and NiO (0.13-0.40 wt %). The range of MgO, as well as NiO and MnO, is similar to those of olivine from mantle-derived peridotite xenoliths worldwide. Within 10-30 µm from the grain boundaries in contact with clinopyroxene, olivines show a marked increase or decrease in magnesium and increase in calcium.



All orthopyroxene within Dariganga plateau xenoliths is broadly classified as enstatite (Fig. 2). The Mg# vary from 0.84 to 0.91, which are similar to or slightly, but constantly, higher than those of coexisting olivines, implying that Fe-Mg distribution between the two phase reflects complete chemical equilibrium. Both TiO₂ and Al₂O₃ de-

Fig. 2. Wollastonite-enstatite-ferrosilite (Wo-En-Fs) endmember plot of pyroxene analyses, classified according to the scheme of Morimoto et al. (1988).

crease from 0.130 to 0.057 wt % and from 4.32 to 3.02 wt %, respectively with increasing the Mg# of orthopyroxene. The Cr_2O_3 (0.287-0.410 wt %) concentration is well correlated with Mg#.

Clinopyroxene in Dariganga plateau manle xenolits consist predominantly of diopside (Fig. 2.). The Mg# vary from 0.900 to 0.930 and display a well-defined correlation with those of olivines. As with orthopyroxene, clinopyroxene shows a positive correlation of Cr_2O_3 (0.47 to 1.30 wt %), and negative correlations of TiO_2 (0.1 to 0.5 wt %) and Al_2O_3 (3.5 to 6.5 wt %) with Mg#. Na₂O is in the range of 0.5-1.6 wt %.

Spinel grains are up tp 0.5 cm, and often are interstitial (Fig. 1 b). The low TiO_2 concentrations in the spinels of the xenoliths attest to the residual nature of spinels. The Mg# of spinels range from 0.636 to 0.783, which are lower than any silicate minerals. All spinel are chromiferous with Cr-number [=Cr/(Cr+Al)] ranging from ~0.15 to ~0.4. Spinels display the requisite negative relationship between Mg-number and Cr-number, identical to that defined for abyssal peridotites. The rims of spinel show slightly higher Mg# in contact with orthopyroxene than contact with olivine.

The NiO and MnO of olivine in the Dariganga xenoliths mostly plot within the upper mantle array of Takahasi (1986). Plots of the Cr/(Cr+Al) ratio of spinel against Fo of coexisting olivine are within the upper mantle array of Arai (1994).

Geothermometers based on two-pyroxene (Wells 1977; Brey et al. 1990), Ca-inorthopyroxene, (Brey and Köhler 1990), as well as with the empirical thermometer of Witt-Eickschen & Seck (1991), based on Cr-Al exchange between orthopyroxene and spinel yields temperatures ranging from 850°C to 930°C.

The *T* estimates for the most western part of the Dariganga plateau xenoliths are lower than those reported for spinel peridotite from central Mongolia (Press et al. 1986) and overlap with the *T* values reported for spinel peridotites from northern China by Fan and Hooper (1989). Temperatures of 900°C to 1100°C are common in similar suites of upper mantle xenoliths and do not appear to define anomalously high thermal regimes.

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METASOMATISM OF THE EAST SERBIAN SHALLOW MANTLE: CONSTRAINTS FROM STUDY OF MANTLE XENOLITHS AND HOST ALKALINE ROCKS

Abstract: The refertilization in the East Serbian lithospheric mantle is interpreted by study of three different textural associations found in xenoliths as well as by geochemical modelling of the host alkaline rocks. The study implies that there is an agreement in mineral composition, at least qualitatively, between the observed secondary assemblages in the studied xenoliths with inferred metasomatic phases in the source of host magmas. A two-phase model is proposed involving (1) percolation of CO_2 and H_2O -rich mafic alkaline melts and precipitation of primary metasomatic assemblages containing phlogopite and amphibole(?), and (2) the uplift of hot asthenospheric mantle, temperature rise and breakdown of previously formed hydrous metasomatic phases.

Keywords: Refertilization, phlogopite, basanite, lithosphere, asthenosphere.

INTRODUCTION

Mafic alkaline metasomatism is usually caused by infiltration of small amounts of alkaline melts genetically related to the host alkaline magmas (e.g. Dawson 2002). A detailed understanding of the effects of this metasomatism is usually difficult to achieve because the primary metasomatic textural relationships may often be destroyed during magma ascent and because there is frequently an overlap in geochemical effects with those produced by carbonatitic melts (e.g. Rivalenti et al. 2004). Therefore, any additional information provided by study of the presumed metasomatic associations found in mantle xenoliths is essential. The study of host alkaline rocks can be also significant, for instance, if can be proved that metasomatic assemblages, similar to those found in xenoliths, could have played a substantial role in the petrogenesis of host rocks.

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In this study we suggest that the metasomatic associations found in East Serbian mantle xenoliths have mineralogical characteristics similar to the possible source of basanites, which is inferred from inversion quantitative trace element modeling.

GENERAL CHARACTERSTICS OF XENOLITHS AND HOST BASANITES

Peridotite xenoliths from the Paleogene East Serbian basanites are mostly harzburgites and clinopyroxene-poor lherzolites with characteristics that are much more depleted than typical non-cratonic peridotites, orogenic ultramafic massifs and average abyssal peridotite (e.g. silicate Mg#s = 90-92; Cr# in spinel up to 0.7, Al₂O₃ in opx – 1-2 wt %). This highly depleted mantle is very similar in composition to a supra-subduction zone oceanic mantle lithosphere which was probably accreted to the European continent during Mesozoic collision (Cvetković et al. 2004a, 2006, in pres).

The host basanites are olivine (Fo76-86) ±clinopyroxene (Mg# 75-85) phyric with groundmass consisted of clinopyroxene (Mg#>70), nepheline, plagioclase feldspar (An~60) and Ti-bearing magnetite (TiO₂~15 wt %). They have high Mg# (~70) and high concentrations of incompatible elements (Ni mostly > 200 ppm and Cr > 450 ppm) and show low Sr and high Nd initial isotope ratios (0.7030-0.7036) and that indicates that they represent fairly uncontaminated magmas (Cvetković et al. 2004b).

METASOMATIC ASSOCIATIONS IN XENOLITHS

The refertilization in the East Serbian lithospheric mantle is inferred from the presence of three different textural associations found in the xenolith suite: (i) Fe-rich dunite xenoliths and clinopyroxene megacrysts, (ii) fertile xenoliths with metasomatic spongy-rimmed Ti-Al-rich clinopyroxene, and (iii) tiny discrete metasomatic assemblages in veinlets and pockets in the highly depleted xenoliths. A detailed study of the textural assemblages and composition of present minerals will be published elsewhere.

Chemical compositional patterns of metasomatic clinopyroxene in the refertilized lithologies indicate that the inferred metasomatic melts are genetically related to the host basanites. The Fe-rich xenoliths (i) are inferred to have formed from direct crystal-lisation of the alkaline magmas in the lithosphere, whereas the fertile xenoliths (ii) and discrete metasomatic assemblages (iii) formed by melt-peridotite reactions. Textural relationships and compositional variations in the discrete metasomatic assemblages indicate the presence of metasomatic clinopyroxene, xenomorphic spinel and altered glass, but substantial amounts of olivine, apatite, ilmenite, carbonate and feldspar are often present. Relicts of a high-TiO₂ (~11 wt %) phlogopite were found in one harzburgite xenolith (Cvetković et al. 2004a).

INVERSION SOURCE MODELING FOR HOST BASANITES

We have used the following two-fold approach: (a) performing inversion modeling based on the whole-rock trace element data of basanites adopting the method of Cebria, Lopez-Ruiz (1996) for constraining the source composition and bulk partition coeffi-

cients of incompatible elements during the partial melting, and (b) inferring possible mineralogical characteristics of the source and comparing them to the observed mineralogy of metasomatic associations found in xenoliths (see above).

The modeled source is enriched in highly and moderately incompatible elements (e.g. average estimates between ~35-40x chondrite for U-Th-Nb-Ta to around 2x chondrite for HREE). The results of the modeling imply that the primary magmas of Sokobanja basanites were not derived by melting of a homogeneous asthenospheric source, provided that it is MORB-like (Salters, Stracke 2004). Even extremely small degrees of partial melting (<<1 %) are not capable of producing the observed enrichment in most incompatible elements. Partial melting of deep mantle sources can be excluded as there is no geological evidence that mantle plume could have been related to the petrogenesis of East Serbian Paleogene alkaline rocks (Cvetković et al. 2004b).

To infer possible source mineralogy of the host basanites we compared D_0 values of the basanitic mantle source obtained by inversion modeling with the D_0 values of mantle lithologies differing in their mineral composition and using mineral-melt partition coefficients from literature (Fig. 1).

The unmetasomatized MORB-like mantle has much lower D_0 values for Th, U, Nb, Ta, Sr, P, Zr and Hf than the source calculated by the inversion modeling. Consequently, if a metasomatic assemblage was present in the source of Sokobanja basanites, which is indeed our hypothesis, it must be an association which can substantially increase



Th U Nb Ta La Ce Sr Nd P₂O₅Zr HfSm Eu Gd Tb Dy Y Ho Er YbLu

Fig. 1. A comparison between $D_{\rm mineral/melt}$ values for the source of basanite primary melts obtained by inverse modeling (full line) with $D_{\rm mineral/melt}$ values for unmetasomatized and variously metasomatized mantle.

 D_0 for the mentioned elements without affecting bulk partition coefficients for REEs. Amphibole-bearing metasomatized mantle (with or without phlogopite) is characterized by very high ^{REE} D_0 but the D_0 values for Nb, Ta, Sr and P are still too low. The presence of phlogopite alone is also unable to account for high D_0 for Nb, Ta, Sr and P (Fig. 1). The best fit with D_0 of the calculated basanitic source was produced using

anhydrous metasomatized mantle with small additions of metasomatic clinopyroxene and carbonate (\sim 5 %) and with traces of ilmenite (\sim 1 %) and apatite (\sim 0.05 %), i.e. the minerals which were found in metasomatic associations in the studied xenoliths.

CONCLUSIONS

Our data imply that there is an agreement in mineral composition, at least qualitatively, between the observed secondary assemblages in the studied xenoliths with inferred metasomatic phases in the source of host magmas. It is suggested that the metasomatic assemblages in the studied xenoliths may represent counterparts of similar metasomatic regions situated deeper in the lithosphere. A two-phase model of metasomatic processes can be proposed. The first phase involves percolation of CO_2 and H_2O -rich mafic alkaline melts and precipitation of primary metasomatic assemblages containing phlogopite and amphibole (?). The second phase is related to the uplift of hot asthenospheric mantle and this could have occurred at the very onset of the host basanitic magmatism. The increased heat flow and temperature rise produced breakdown of previously formed phlogopite and amphibole leaving behind anhydrous metasomatic associations, which are texturally and compositionally similar to the assemblages found in the ESLM xenoliths. Finally, these metasomatic portions were melted along with surrounding mantle and produced primary basanite magmas.

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APPLICATION OF Lu-Hf ISOTOPES AND TRACE ELEMENTS TO PROBLEMS OF MANTLE PETROGENESIS: AN EXAMPLE FROM THE FRENCH MASSIF CENTRAL

Abstract: The lithospheric mantle beneath the Massif Central (France) is formed of two distinct terranes. The mantle beneath the northern part is older, thicker and more refractory than the mantle beneath the southern region. Lu-Hf isotope systematics have been applied to clinopyroxenes from mantle peridotite xenoliths from both terranes. Those from the northern terrane extremely high Lu/Hf ratios and ultra-radiogenic Hf isotope ratios, indicating long-term depletion. Xeno-liths from the southern terrane have much higher Hf abundances and their Hf isotope ratios are much less radiogenic, indicating overprinting by silicate-melt metasomatism. **Keywords:** mantle, xenolith, France, Lu-Hf isotopes.

INTRODUCTION

Sub-continental lithospheric mantle (SCLM) is isolated from the convecting mantle and hence may preserve chemical and isotopic heterogeneity over billions of years. Although the SCLM is volumetrically insignificant comprising only ~2.5 % of Earth's mantle, it is an important geochemical reservoir. Direct melting of SCLM or delamination and recycling of SCLM into the convecting mantle is widely invoked to account for the chemical and isotopic signatures of some continental and oceanic basalts. Therefore, studies of the SCLM yield direct information concerning crust-mantle differentiation, mantle metasomatic processes and the mineralogical, geochemical and isotopic composition of sub-continental mantle roots that may be an important source for some types of volcanism.

The assembly of the European continent preserves a record of plate tectonics since the Precambrian. Cratonic regions in northern Europe experienced successive crustal additions through formation and accretion of crustal terranes and underlying SCLM at their southern margins during the Cadomian/Caledonian (~440 Ma), Variscan (~360 Ma) and Alpine (~35 Ma) orogenies. Beneath the Variscan belt of central Europe, the SCLM reaches depths of 100-120 km. However, regions of young extensional tectonism and Cenozoic intraplate volcanism (e.g. French Massif Central, Pannonian Basin) have notably thinner lithosphere (~60 km) underlain by "finger-like" zones of hot, upwelling upper mantle identified by seismic tomography. Cenozoic intraplate magmas in these areas have traversed various Phanerozoic terranes and sampled their sub-continental mantle roots.

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In general, the European SCLM sampled by intraplate volcanism is dominated by spinel lherzolites with a range of Mg#s, Al₂O₃ and TiO₂ contents, variably enriched in incompatible and fluid-mobile trace elements such as light rare earth elements (LREE) and large ion lithophile elements (LILE) (Downes 2001). Its evolution requires variable degrees of melt extraction followed by a complex history of cryptic and/or modal metasomatism. Little trace element evidence for the initial melt extraction event(s) in SCLM xenoliths from Europe is still preserved, and Rb-Sr (LILE) and Sm-Nd (REE) isotopic systems were almost entirely reset during episodes of metasomatic enrichment (Downes 2001).

Lu-HF ISOTOPE SYSTEMATICS

The advent of plasma source mass-spectrometry now allows the routine measurement of Hf isotopes in geological materials. Lu-Hf isotopes have recently been shown to hold great potential in dating mantle melt extraction events. Therefore, we have applied the Lu-Hf isotope system to clinopyroxenes from subcontinental lithospheric mantle xenoliths from the French Massif Central (FMC). Lenoir et al. (2000) and Downes et al. (2003) have shown that mantle xenoliths and their constituent clinopyroxenes from the southern FMC have major and trace element systematics and Sr-Nd isotopic compositions comparable to depleted MORB-source mantle. In contrast, clinopyroxenes from northern FMC mantle are marked by low Al₂O₂, Na₂O, and high Mg and Cr numbers compared to the more fertile major element compositions of the southern FMC xenoliths (Zangana et al. 1997; Downes et al. 2003). High ratios of trace elements with different incompatibility (e.g. Lu/Hf) and high ¹⁴³Nd/¹⁴⁴Nd ratios (up to 0.5173) further suggest significant (time-integrated) depletion of the northern FMC sub-continental mantle roots (Downes et al. 2003). However, high ratios of elements like U, La and Sr to moderately incompatible elements such as Yb require the mantle from both areas of the FMC to have undergone metasomatic overprinting of fluid-mobile and/or all the most incompatible elements. Both Lenoir et al. (2000) and Downes et al. (2003) proposed that the Variscan orogeny welded pre-Variscan lithosphere (sampled by the northern volcanoes) together with a juvenile (or reactivated) lithosphere now found beneath the southern FMC.

Our new Hf isotope results confirm the existence of different lithospheric domains beneath the northern and southern FMC. Clinopyroxenes from xenoliths in the northern FMC have rather low Lu concentrations and very low Hf concentrations (Lu < 0.14 ppm; Hf < 0.07 ppm). They have extremely high Lu/Hf ratios and ultra-radiogenic Hf isotope ratios ($\Sigma_{\rm Hf}$ = +40 to +2600). These data reflect ~15-25 % partial melting. Model ages and ¹⁷⁶Hf/¹⁷⁷Hf-¹⁷⁶Lu/¹⁷⁷Hf systematics indicate that melting occurred in Variscan times (360Ma). The very low Zr and Hf abundances in the clinopyroxenes were unaffected by Neogene hydrous/carbonatitic metasomatism that overprinted LILE and light REE abundances and caused decoupling of Lu/Hf-Sm/Nd ratios and Nd-Hf isotopes (the same xenoliths have values of $\Sigma_{\rm Nd}$ from +2.1 to +91.2). Thus, Lu-Hf isotope systematics of the clinopyroxenes from the northern FMC provide evidence for the incorporation of refractory mantle, likely a subduction zone mantle wedge into the SCLM beneath Europe. The decoupling of Nd and Hf isotopes results from later metasomatic enrichment, which

overprinted fluid-mobile trace elements such as U, Sr and light REE (including Nd). This highlights the robustness of the Lu-Hf isotope system to some metasomatic agents and its ability to preserve mantle melting signatures over long time-scales.

Clinopyroxenes from southern FMC lherzolites are generally marked by overall incompatible trace element enrichment including high Zr and Hf abundances. They have significantly higher Lu and Hf concentrations than those from the northern FMC (Lu = 0.12 to 0.36 ppm; Hf = 0.51 to 2.90 ppm). ¹⁷⁶Lu/¹⁷⁷Hf ratios (0.01087 to 0.05029) and $\Sigma_{\rm Hf}$ (+5.4 to 41.5) are similar to estimates for MORB mantle although a number of samples have ¹⁷⁶Lu/¹⁷⁷Hf ratios that are comparable to or lower than estimates for primitive mantle. Lu-Hf and Sm-Nd isotope systematics of these clinopyroxenes do not lie on the 360 Ma Lu-Hf reference "isochron" defined by the samples occurring in the northern parts of the FMC. Generally, Σ Nd and Σ Hf of these samples are within ±10 epsilon units of the "mantle array" with $\Sigma_{\rm Nd}$ values between +0.8 and +16.0 and Σ Hf = +9.9 to +28.2. However, one harzburgite from Ray Pic has strongly decoupled Nd-Hf isotope systematics with relatively unradiogenic Nd ($\Sigma_{\rm Nd}$ = +5.4) at high $\Sigma_{\rm Hf}$ = +41.5. Hf isotope ratios for the southern FMC are less radiogenic than for northern FMC mantle and have been overprinted by metasomatism derived from small degree silicate partial melts.

We conclude that mantle peridotites from different parts of the FMC record differing styles of enrichment. The different styles of metasomatism relate to pre-existing variations in the thickness of the continental lithosphere, which controlled the extent to which upwelling mantle could ascend and melt. In the northern FMC, a thicker and more refractory lithospheric lid (\geq 80 km) allowed only incipient degrees of melting, resulting in fluid/carbonatitic metasomatism of the lithospheric mantle. The thinner lithospheric lid of the southern FMC (\leq 70 km) allowed larger degrees of melting and resulted in silicate-melt-dominated metasomatism, and also focused the location of the volcanic fields of the FMC above this region.

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UPPER MANTLE EVOLUTION DURING THE VARISCAN OROGENY: A XENOLITH PERSPECTIVE FROM PUY BEAUNIT (FRENCH MASSIF CENTRAL)

Abstract: The Cainozoic Puy Beaunit (French Massif Central) carries both mantle-derived ultramafic xenoliths and magmatic ultramafic-mafic (sometimes layered) rocks that constitute the Beaunit layered complex, emplaced at the crust-mantle boundary, during the late Permian. This complex would belong to the large Late-Variscan calc-alkaline province of Western Europe. Its geochemical (LIL and Pb enrichment, Nb-Ta negative anomalies) and isotopic (intermediate between DM and EM1 reservoirs) signature can be related to a pre-Variscan metasomatic event (subduction).

Keywords: Puy Beaunit, French Massif Central, ultramafic xenolith, calc-alkaline magmatism, Variscan orogen, upper mantle.

INTRODUCTION

The Puy Beaunit is a famous Cainozoic volcano from the Chaîne des Puys (French Massif Central). It is known in the geological literature for the exceptional diversity and abundance of xenoliths that comprise both crustal and mantle varieties (i.e. Brousse and Rudel 1964). Recent studies on mafic and ultramafic xenoliths have shown that they can be classified into two groups (Féménias et al. 2001; 2003): 1) spinel-bearing upper mantle xenoliths (lherzolites, harzburgites and dunites) and 2) lower crustal mafic and ultramafic magmatic xenoliths derived from a deep-seated layered intrusion – the Beaunit Layered Complex (BLC). The latter show a wide range of mineralogical composition: peridotites, websterites, plagioclase- and garnet- bearing pyroxenites, garnet- and amphibole-bearing gabbronorites and composite mafic/ultramafic xenoliths (Féménias et al. 2005). A single mm-sized zircon has been found in a layered xenolith and dated at 257+/- 6 Ma (Late Permian) by SIMS (Féménias et al. 2003). The genetic relationship between these two groups, newly inferred by Sr and Nd isotopic compositions, highlights and strongly constrains the evolution of the lower crust and shallow upper mantle during the Variscan orogeny.

The xenoliths record the complex geological history (deformation, melting episodes and magmatic differentiation) millions of years before the Cainozoic volcanic activity of Puy Beaunit.

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UPPER MANTLE-LOWER CRUST GENETIC LINK

Sr and Nd isotopic compositions (Fig. 1) have been measured on 35 samples (9 mantle peridotites and 26 ultramafic/mafic magmatic samples) and recalculated at 257 Ma. The initial isotopic compositions, $(\Sigma Nd)_i$ and $({}^{87}Sr/{}^{86}Sr)_i$ values, for the mantle peridotites are in the range +5.3 to -3.8 and 0.7032 to 0.7062 respectively. These values are closely similar to those reported for present-day mantle xenoliths (i.e. Batan Island) and volcanics (i.e. Fidji islands) from island arcs (Vidal et al. 1989). The dispersion of values observed for the Beaunit mantle xenoliths argue for a heterogeneous upper mantle source that has been variously enriched by a crustal component, most probably during an early-Variscan subduction (Féménias et al. 2003). The ultramafic and mafic magmatic xenoliths have similar isotopic composition: $(\Sigma Nd)_i$ is in the range +6.4 to -5.8 and +4.6 to -4.9 respectively and (${}^{87}Sr/{}^{86}Sr)_i$, ratios are comprised between 0.7027-0.7041 and 0.7035-0.7062 respectively.



Fig. 1. Sr-Nd isotopic diagram for mantle and magmatic ultramaficmafic xenoliths from Puy Beaunit (BLC = Beaunit Layered complex). The compositional fields of mantle, mafic and metasedimentary xenoliths from the French Massif Central are from Downes et al. (1990). Compositional fields of lavas and mantle xenoliths from Fiji and Batan Islands are from Vidal et al. (1989).

The isotopic compositions of the mantle rocks and of the magmatic rocks are largely overlapping (Fig. 1). This shows that the sampled upper mantle beneath Beaunit is most probably the source of the parental magma of the Beaunit Layered Complex. The marked difference in isotopic compositions between the Beaunit magmatic xenoliths and the metasedimentary lower crustal xenoliths of the French Massif Central (Downes et al. 1990) precludes significant amount of crustal contamination during differentiation process in the lowermost crust. This is also confirmed by the general absence of correlations between isotopic compositions and concentrations of major and trace elements that are typically enriched in the crust (Al, K, Rb, U...).

IMPLICATIONS ON BLC MAGMATIC EVENT

The ultramafic magmatic xenoliths have strong calc-alkaline characters (enrichment in LILE, depletion in Nb, Ta, Zr and Hf; (Féménias et al. 2003). The mafic magmatic samples are typically sub-alkaline but it is quite difficult to distinguish calc-alkaline and tholeiitic trends in mafic cumulate rocks. Nevertheless, the various lithologies and the mineral compositions are comparable to what is observed in the roots of calc-alkaline island arcs (Berger et al. 2005a).

The BLC emplaced at the crust–mantle boundary (~1GPa; 750-800°C); its intrusion age (257±6 Ma) suggests that it belongs to the large Permian within-plate mafic (high-Mg) calc-alkaline magmatic event recognized in W Europe, i.e. Saar-Nahe volcanics in SW Germany (Schmidberger and Hegner 1999). This magmatism appears to be spatially controlled by post-Variscan transcurrent basin tectonics in an intracontinental setting (Féménias et al. 2003). The largely overlapping isotopic compositions of the mantle xenoliths and the magmatic ultramafic-mafic xenoliths point to a common source with geochemical features intermediate between the depleted mantle (DM) and the enriched mantle (EM1). The enrichment process of the shallow mantle is classically interpreted as resulting from a metasomatic event related to subduction (Hofmann 1997).

IMPLICATIONS FOR MANTLE EVOLUTION

Mantle xenoliths range from fertile spinel lherzolites to refractory dunites. Fertile peridotites have registered a modal (amphibole-bearing) and cryptic (EM1 isotopic signature; LILE and Pb enrichment, negative Nb and Ta anomalies in the spidergrams) metasomatic event that took place before the Permian melting episode. Depletion processes in the mantle series of rocks (lherzolites to dunites) are related to two melt extraction episodes. The first melting and metasomatic event is thus attributed to a fluid/liquid derived from a pre-Variscan subduction. It is sub-contemporaneous with the texture acquisition and deformation of the uppermost mantle (lithospheric delamination). The second melting event produced high-Mg basalts that gave rise to the BLC (Féménias et al. 2004).

VARISCAN MOHO DURING OROGENIC PROCESSES

The Beaunit lower crust and mantle xenoliths record a pre-Cainozoic history characterised by two major episodes: 1) a subduction-related process that induced the first melting stage, a metasomatic enrichment (cryptic and modal) including the isotopic modification of the classical mantle signature and the deformation of mantle rocks (texture acquisition during lithospheric delamination) and 2) a later Permian event related to basin development and magma underplating in the deep crust (melting stage 2) that generated the BLC. Stage 1 lmost probably occurs during the complex (including vergence changes; Pin and Paquette, 2002) subduction of Paleotethys (Stampfli and Borel 2002) and before and/or during Variscan ophiolite obduction (Berger et al. 2005b; 2006). The structuring of the lithosphere as shown by the complete log (Fig. 2D), including the underplating of the mafic-ultramafic magmatic complex and the regional granulitisation of the lower crust, was accomplished during the late- to post-orogenic period that lasted long after the subduction event.

Our model for the development of the upper mantle – lower crust (=lithosphere) in the French Massif Central would fit to stage 5 of Massonnes's (2005) general model of continent-continent collision applied to the Variscan orogen in Europe. It is also compatible with



Fig. 2. Schematic evolution of the mantle and lower crust during the 4 principal stages of the Variscan orogeny illustrated here by orthographic projection with Europe fixed in its presentday position from Stampfli and Borel (2002). The late stage (D: 260Ma) illustrates the BLC emplacement during Permian (late- to post-orogenic) basin-related tectonic event.

the conceptual model for the Paleozoic and Mesozoic lithosphere evolution of Western Europe proposed by Ziegler et al. (2004) and Ziegler and Dèzes (2005).

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MINERAL CHEMISTRY AND GEOTHERMOMETRY OF LHERZOLITE ENCLAVE WITHIN "WILCZA GÓRA" BASANITES AND ITS PETROGENETIC IMPLICATIONS

Abstract: The new whole-rocks and mineral chemistry data of lherzolite enclave within Wilcza Gora basanite are presented. The obtained results indicate, that high-temperature picritic melts were injected inside the primary fertile mantle olivine xenocrysts of primary peridotite but its impregnation as hot crystal mushes is also possible. However, the evaluated of ol-sp and opx geotemperatures can reflect equilibrium conditions, connected with adiabatic decompression during ascent of ultrabasics from the deeper litospheric levels.

Keywords: lherzolite, geothermometry, basanites.

INTRODUCTION

Ultrabasic enclaves within the Lower Silesian Tertiary Basalts Province are intensively studied. In many earlier articles, the different petrological prob-lems concerning these ultrabasites were presented, for example: results of petro-graphic studies (Białowolska 1980, Kozłowska-Koch 1981), determinations of isotopic composition for the age evaluations as well as for reconstruction of pristine source material for basalts (Birkenmajer et al. 2002, Ladenberger et al. 2005). Apart of these, the results of geophysical researches have given a many new very interesting information about the mantle heterogeneity beneath the Sudetic (ForeSudetic) crystalline basement (Puziewicz 2006 pers. com.). This study provides whole-rock and mineral chemistry data of lherzolite enclave from the basanites outcropped at the "Wilcza Góra" quarry near Wilków. The petrogenetic implications resulted of geochemistry discrimination and geothermomety are also exemplified.

GEOLOGY AND PETROGRAPHY

The Tertiary basanites near Zlotoryja belong to younger Laramian unit of Kaczawa Mts. Complex. The "Wilcza Góra" basic volcanics form steeply dipping pipe-like body (about 0.5 km in diameter) accompanied by volcanic breccias. The studied lherzolitic enclave were found at the eastern part of the "Wilcza Góra" basanite quarry. It represents yellow-green, triangle-shaped specimen (up to 10 cm in diameter), with green-patched appeareance, locally spotted by very small black points of opaque minerals. Contact between enclave and surrounding basanite is very sharp without traces of contact rims or secondary alterations.

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In thin sections, the lherzolite exhibits the equigranular, locally porphyritic structure, composed of fresh, xenomorphic olivine individuals differing in size from 1 to 4 mm. Other rock-forming are hipidomorphic prisms of clinopyroxenes (greenish) or orthopyroxenes (brownish) up to 8 mm long. The chromian spinels occur occassionally as a small, brown, rounded, translucent grains situated in the interstices between larger olivine grains. Locally, the symplectitic intergrowths consisting interfingering olivine and spinel "worms" are also visible in the back-ground (Łąk 2002).

METHODS AND SCOPE OF STUDIES

Several tens of enclave samples were taken during the field excursion and some of them were selected for geochemical studies and cutted on slabs for preparation of microprobe slides. Two specimens (lherzolite and basanite) had been analyzed by ICP-MS, INAA and XRF methods in the Activation Laboratories Ltd. (Canada). Microprobe analyses of olivine, orthopyroxenene, clinopyroxene and spinel were performed in Institute of Geological Sciences, Wrocław University, on Cambridge MK-9 microprobe. The following analytical settings had been applied: current voltage 15 kV, amperage 50 nA, counting time 15 s and ZAF correction procedure.

GEOCHEMISTRY

The studied Al-intermediate (1.64 wt % of Al_2O_3) lherzolite (#Mg =90) exhibits unusual enrichment of HFSE and LREE-MREE elements and Zr content of 37 ppm. On chondrite-normalized plot the significant LREE and MREE enrichment (100-20 chondrite value) and flattening of profile line in the range of HREE suggest very complicated conditions of lherzolite origin. The value of (Ce/Sm)_N ratio (equal to 3.24) can reflects genetic connection with slightly differentiated fertile mantle material (Rollinson 1990).

The surrounding basic volcanic rocks can be classified as a basanite (with Zr/Y ratio equal to 8), which can be regarded to typical for continental withinplate setting. On chondrite-normalized REE plot, the Wilcza Góra basanite show the higher contents of REE, but their distribution line on spiderdiagram is similar as in the case of lherzolite. It can be explained by derivation both lherzolites and basanites from the one source or variations of primary source composition involving later extensive modification of primary melt caused by fractional crystallisation, assimilation etc. (Rohrbach et al. 2005). These characteristic enrichment of LILE contents also can to evidence a melting (or adiabatic decom-presion) episode during or after ascent of ultrabasites from deep crustal regions. The flattenning of profile in the HREE range also indicates, that low-level fractional crystalization played important role in forming both lherzolites and basanites.

MINERAL CHEMISTRY AND GEOTHERMOMETRY

Olivine has forsterite content between 86.9 to 90.1 vol. % and, they can be divided on two groups: 1) low-Ca olivine with CaO below 0.1 wt % and 2) olivine, where CaO is between 0.15 and 0.34 wt %. All of studied grains have a very low TiO_2 contents (0.02-0.04 wt %) and similar NiO abundances (0.21-0.37 wt %).

Orthopyroxene is enstatite En 89.4-90.1 vol. %. Majority of samples exhibit very low Al content below 0.40 wt %; only the two individuals have Al_2O_3 content higher than 1.0 wt %. The variation ranges of NiO content is between 0.01 and 0.15 wt %, while MnO content varies from 0.14 to 0.19 wt %.

Clinopyroxene belongs to augitic diopside – diopside group. (clinoenstatite 44.9 –51.4 vol. %). The NiO abundance is constant (0.1-0.10 wt %) but MnO content varies in range from 0.08 to 0.13 wt %.

Spinel is represented by bimodal Cr-Al rich varieties with #Cr ranged from 0.39 to 0.67 and #Fe³⁺ between 0.03 and 0.07. On Stevens (1944) triangle all of them can be classified as a chromian spinels. Their NiO and MnO contents are below 0.25 wt % and two samples display very high TiO₂ abundances about 2 wt %.

The different methods was used for evaluation of lherzolite equilibrium temperatures. They include: 1) of olivine-spinel geothermometer of Fabries (1979) and geotermometer of Brey and Kohler (1990) using the Ca in orthopyroxenes. Any attempts to evaluate of opx-cpx equilibrium temperatures had finished unsucces-fully.

The ol-sp equilibrium temperatures were the same in the case of low-Ca and intermediate-Ca olivines with all coexisting spinels. The range of 784-890°C was obtained for olivine-spinel pairs, while temperatures between 897°C and 1012°C were ascertained using Ca-orthopyroxene geothermometer.

CONCLUDING REMARKS

The obtained data suggest, that Wilcza Góra lherzolites contain two generations of olivines. One, low-CaO olivines might be derived from dissagregated, fertile, litospheric (or asthenospheric) upper mantle and the second, high – Ca generation, that crystallized probably from the high-temperature picritic melt.

Enrichment of LREE and similar distribution profiles both lherzolites and basanites indicate that high temperature picritic melt was injected inside the primary fertile mantle olivine xenocrysts (microdykes?) (Schuth et al. 2005). Other possibility is impregnation of primary peridotite by high-temperature picritic lavas most likely emplaced as hot crystal mushes (Rohrbach et al. 2005). However, the obtained ol-sp equilibrium and opx crystal-lization temperatures reflect only the last lherzolite crystallization event, connected most probably with adiabatic decompression during ascent of crystalline ultrabasic material from the deeper litospheric levels.

The results presented above, suggest, that the Wilcza Góra lherzolites were primarily products of low degree of partial melting of peridotites at the spinel stability field which were probably modified by intereaction with high-temperature picritic melt.

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PETROGENESIS OF THE LATE MIOCENE TO QUATERNARY ALKALINE BASALTIC VOLCANISM IN THE PANNONIAN BASIN

Abstract: Neogene to Quaternary volcanism of the Carpathian-Pannonian Region is part of the extensive volcanic activity in the Mediterranean and surrounding regions. Alkaline basaltic volcanism developed at the end of rifting stage of the Pannonian Basin (11 Ma) and continued until recently (the last eruptions occurred only a few 100 ka). Most of the mafic volcanic rocks are fairly primitive in composition and contain quite abundant lower crustal and upper mantle derived xenoliths. The post-extensional volcanism may require an influence of an anomalously hot mantle upwelling, however, we suggest that a mantle plume beneath the Pannonian Basin is highly unlikely. We propose that the mafic magmas were formed by small degree partial melting in a heterogeneous asthenospheric mantle, which has been close to the solidus temperature due to the lithospheric extension in the Miocene. Petrogenetic model calculations indicate that the difference in the trace element compositions of the magmas is mainly due to the variable degrees (1-6 %) of partial melting in the garnet-peridotite stability field with the presence of different amounts of hydrous K-bearing minerals (amphibole or phlogopite). The mantle source could have been moderately enriched relative to the primitive mantle (1.5 to 4-times primitive mantle values). Magmatism appears to have been in a waning phase for the last 2 Ma, but recent volcanic eruptions (<200 Kyr) indicate that the future volcanic activity cannot be unambiguously ruled out.

Keywords: basalts, petrogenesis, extension, mantle plume, Carpathian-Pannonian Region.

INTRODUCTION

During the Cenozoic, alkaline mafic magmas erupted in different regions of Europe (Wilson and Downes 1991). This volcanism is associated with lithospheric extension and some of them are related also to domal uplift of Variscan massifs. The Sr-Nd-Pb isotopic composition of the mafic magmas indicates a common sublithospheric mantle source (Cebria and Wilson 1995). This mantle component has a HIMU OIB affinity. The magmatism is commonly regarded as a response of diapiric upwelling of small-scale, relatively hot upper mantle (Granet et al. 1995; Hoernle et al. 1995; Wilson and Patterson 2001). Remarkably, the alkaline mafic volcanic fields in Europe are at the periphery of the Alpine-Mediterranean region, which is underlain by a positive seismic velocity anomaly in the depth range of 400-650 km (Piromallo et al. 2001). The high velocity anomaly has been interpreted as accumulation of thick, cold material, possibly subducted residual material. This can form a barrier

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against the rise of a lower mantle plume and could separate it into several smaller branches ("mantle plume fingers"), which emerge at the periphery of the cold material.

The Carpathian-Pannonian Region (CPR) has a unique situation among the alkaline mafic volcanic fields of Europe. The CPR is considered as a Mediterranean-type area characterized by arcuate, retreating subduction, formation of extensional basins within the orogen and wide range of erupted magmas for the last 20 Ma. Noteworthy, this area is underlain by a thick fast seismic velocity anomaly in the Transition Zone. Yet, the Late Miocene to Quaternary alkaline mafic volcanism resembles those occurring at the periphery of the Alpine chain. The alkaline volcanism in the Pannonian Basin took place following the main extensional phase, thus most authors invoke upwelling of a localized mantle plume beneath the area (Embey-Isztin and Dobosi 1995; Granet et al. 1995; Seghedi et al. 2004).

GEOCHEMISTRY

The Late Miocene to Quaternary alkaline suite of the CPR consists mostly of mafic rocks (nephelinites, basanites, alkali basalts and trachybasalts; Embey-Isztin et al. 1993). The oldest alkaline basaltic products of this series were formed 11-12 Ma. After a few Myr long quiescence, the paroxysm of the volcanism occurred at 4-2 Ma. The last eruptions took place only a few 100 ka. The alkaline volcanism resulted in scattered volcanic fields within the CPR (Harangi 2001).

The Mg-number of the mafic rocks varies between 0.56 and 0.76, but it is mostly between 0.63 and 0.68. This suggests that most of them underwent only minor olivine and ±clinopyroxene fractionation and compositions of the basaltic rocks are close to the primary magmas. Mantle-derived ultramafic and lower crustal granulite xenoliths are common in these rocks (Embey-Isztin et al. 2003; Szabó et al. 2004). The trace element composition of the alkaline mafic rocks resembles the intra-plate magmas and that of the Neogene to Quaternary alkaline mafic rocks in Western and Central Europe (Wilson and Downes 1991). Seghedi et al. (2004) separated more than ten groups of alkaline basalts based on their age and compositions. However, simplifying this, we distinguish here only two main compositional groups without regarding their age: the first one is characterized by stronger enrichment in incompatible trace elements and a typical negative potassium anomaly, whereas the second one has smoother trace element patterns. In the Sr-Nd isotope diagram, all of the alkaline mafic rocks fall into the depleted isotopic field, although they show a considerable scatter of Sr and Nd isotope ratios. They have also a relatively large variation in the Pb-isotope ratios. Many of the samples have relatively high ²⁰⁷Pb/²⁰⁴Pb ratio causing a vertical shift from the NHRL. The highest ²⁰⁶Pb/²⁰⁴Pb ratio is shown by the oldest alkaline basalts from the western Pannonian Basin.

PETROGENESIS AND GEODYNAMIC IMPLICATIONS

The most primitive alkaline mafic rocks (MgO>7 wt %) of the CPR show variable degrees of silica-undersaturation. The silica-saturation index (Fitton et al. 1991) correlates with the strongly incompatible trace elements suggesting that it is controlled partly by the degree of partial melting. In contrast, Y and Yb remain fairly constant, indicating that residual garnet could retain these elements at small degree of melting. The major element composition of these rocks confirms that the parental magmas could have been formed mostly in the garnet-peridotite stability field (i.e., at 80-120 km depth), whereas a minor part in the spinel-garnet stability field (i.e., at 55-80 km depth). Considering the thickness of the lithosphere during the volcanism, melt generation could take place in the asthenosphere. Another constrain on the mineralogy of the mantle source is given by the presence of negative K anomaly in the primitive mantle normalized patterns. This requires a K-bearing hydrous phase (amphibole or phlogopite) in the source region. The chemical composition of the source region of the magmas is estimated by inverse model calculation. This suggests a moderately enriched mantle source relative to the primitive mantle (1.5- to 4-times primitive mantle values). The primitive mafic magmas could generate by 4-6 % degree of melting in the garnet-peridotite stability field, whereas some of the magmas were formed by lower degree of melting, but with the presence of hydrous K-bearing minerals.

The subtle variation of the estimated trace element composition of the mantle sources as well as the relatively large variation of the Sr-Nd-Pb isotope ratios of the most primitive basalts indicate heterogeneous mantle beneath the Pannonian Basin. This could mean either an asthenospheric mantle heterogeneous even in relatively small scale or the primary magmas generated in the asthenospheric mantle were subsequently modified by chromatographic effects while they passed through the lithosphere or interaction of magma batches from different sources.

The main extensional phase of the Pannonian Basin occurred between 17 Ma and 13 Ma, or locally up to 11 Ma, while it started even earlier in the western part of the CPR (20-21 Ma). This resulted in considerable thinning of the continental lithosphere and crust. The main phase of the alkaline mafic volcanism started at 7 Ma and culminated at 2-4 Ma, resulting in monogenetic volcanic fields sporadically distributed in the Pannonian Basin. This volcanism occurred >5 Myr after the cease of the syn-rift phase, therefore the thinning of lithosphere could not be the direct reason of the melt generation. The CPR is underlain by a high seismic velocity body in the mantle transitional zone, thus, a hot mantle plume or a plume finger cannot be expected from the relatively 'cold' base of the upper mantle. The characteristic features of the mantle plumes are also missing beneath this region. However, the shallow asthenospheric mantle could be still hot enough (due to the former rifting phase) to generate melt due to some local temperature perturbance. The reason of this temperature perturbance can be only flow in the mantle, but a large-scale mantle plume is not likely. This mantle flow could be explained either by the irregular shape of the lithosphere/asthenosphere boundary or by the deflection of the presumed mantle plume beneath the Bohemian-Polish area due to the suction effect of back-arc rifting and detachment of subducted slab at the northern part of the CPR (Harangi et al. 2006).

The alkaline mafic magmas show a relatively wide compositional variation both regionally and locally. This compositional variation and the presence of the HIMU/FOZO-like isotope and trace element ratios can be explained by a heterogeneous mantle model. The long history of orogenic events (Hercynian and Alpine orogenesis) in Europe could supply vast amount of crustal material into the upper mantle resulting in geochemical heterogeneity on various scales. Partial melting of different parts of the shallow asthenospheric mantle (metasomatized, phlogopite-bearing enriched sections with HIMU-like composition and depleted MORB-mantle around them) and mixing of these melts could also explain the compositional variation in the alkaline mafic magmas of the Pannonian Basin.

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THE RUTKI BASALT (SW POLAND) - PRELIMINARY DATA

Abstract: Two types of basalt occur in the 'Rutki-Ligota' quarry (SW Poland). The basalt with clinopyroxene and olivine phenocrysts dominates whereas the basalt with olivine phenocrysts occurs only in central part of the quarry. The Ol-Cpx basalt shows petrological characteristic of welded tuff. Morphology and composition of olivine and clinopyroxene grains suggest two stages of crystal-lization: pre- and post-eruptive.

Keywords: basalt, olivine and clinopyroxene composition.

INTRODUCTION

Tertiary basalts outcropping in the active quarry "Rutki-Ligota" 6 km south-east from Niemodlin (eastern part of Lower Silesia) belong to the easternmost part of the Central European Volcanic Province (CEVP) trending from the Eifel in the west, through Germany, Czech Republic, Lower Silesia to Moravia in the east. Basalts from "Rutki-Ligota" overlain Cretaceous marls and siltstones and are covered by Tertiary and Quaternary sediments. They were dated by K-Ar method at 27.5 Ma (late Oligocene, Birkenmajer & Pécskay 2002).

In this abstract we describe field relationships, petrology and mineral composition of basalts from the "Rutki-Ligota" quarry. The quarry is divided into two separate parts: "Rutki" in the north-east and "Ligota" in the south-west. Seventy three samples were collected from Rutki and twelve from Ligota. Chemical composition of minerals was measured by microprobe at the Geological Institute, Copenhagen.

FIELD RELATIONSHIPS AND PETROLOGY

The dominating rock in the "Rutki-Ligota" quarry is basalt, marls occur in places (Fig. 1). Thickness of basaltic rocks is up to 20 meters. Two types of basalt occur: 1)basalt containing olivine and clinopyroxene phenocrysts (Ol-Cpx basalt) 2)basalt with only olivine phenocrysts (Ol basalt)

Ol-Cpx basalt dominates and occurs in both Rutki and Ligota quarries whereas Ol basalt outcrops only in the central part of the Rutki quarry, forming elongated belt trending from SW to NE (Fig. 1).

The Ol-Cpx basalt (Fig. 2a) is composed of olivine (100 μ m-4 mm) and clinopyroxene phenocrysts (100 μ m-1 mm). Matrix consists of plagioclase (50-100 μ m), clinopyroxene (10-100 μ m) and titanomagnetite (5-15 μ m), melt occurs in interstices. Olivine phenocrysts are

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euhedral or rounded, sometimes embayed with matrix minerals occurring within embayments. Characteristic feature of Ol-Cpx basalt is occurrence of aggregates of several clinopyroxene phenocrysts and larger (up to 2 mm) melt pools with clinopyroxene forming small, skeletal grains (Fig. 2b).

The Ol-Cpx basalt is heterogeneous. It contains flattened or circular small lapillae and ash particles (0.5 mm-2 cm) with matrix finer grained than that of surrounding basalt. Some of the lapillae are vesiculated in contrary to the surrounding rock. They sometimes contain fragmented grains of olivine.

The Ol basalt (Fig. 2c) is composed of olivine phenocrysts (0.5-2 mm). Matrix consists of clinopyroxene, plagioclase olivine and small oxides. Olivine phenocrysts are similar to those from Cpx-Ol basalt.



Fig. 1. The "Rutki" part of the quarry with location of Ol-basalt (light grey field) and marl (dark grey fields). Numbers in circles show the places where samples were collected.

MINERAL COMPOSITION

Ol-Cpx basalt: Forsterite content in the olivine phenocrysts changes from core (~87 %) to rim (~75 %), whereas olivine constituting the matrix is more homogenous and its forsterite content varies from 72.7 % to 74.1 %. Ca content in the olivine phenocrysts changes from centers (660-790 ppm) to margins (1700-2150 ppm). Small grains are more homogenous, their Ca content varies from 2100 ppm to 2200 ppm. Ni content in olivine phenocrysts varies in wide range from 2100 ppm in the centers to below detection limit (800 ppm) in the margins. Ni content in smaller olivine grains is below detection limit.

Mg/(Mg+Fe) ratio in clinopyroxene varies from 0.39-0.43 in centers to 0.32-0.39 in rims. The smaller the grain the lower Mg/(Mg+Fe) ratio. Ca/(Ca+Mg+Fe) ratio varies from 0.47-



Fig. 2. (a) Ol-Cpx basalt – microscope PPL, (b) BSE image of melt pool with skeletal clinopyroxene grains from Ol-Cpx basalt, (c) Ol basalt – microscope PPL, (d) BSE image of zoned clinopyroxene from Ol-Cpx basalt.

0.49 in centers to 0.49-0.52 in rims. Rims are also richer in Ti and Al compared to centers of clinopyroxene. Cores of the larger grains (>100 μ m) have Cr content above 500 ppm (up to 5000 ppm), Cr is below detection limit in all other parts of clinopyroxene grains.

Plagioclase is euhedral and usually zoned from 58 to 64 % in the core to 29-49 % in the rim.

CONCLUDING REMARKS

1) Occurrence of rounded and flattened, fine grained lapillae and ash particles containing fragmented olivine in Ol-Cpx basalt suggests that the basalt originated as tuff that was subsequently welded, probably after deposition of new tuff layers on top of the sequence. On the other hand Ol basalt is more homogenous and may represent lava flow.

2) Crystallization of Ol-Cpx basalt took place in at least two stages. First, high Fo olivine phenocrysts and high Mg clinopyroxene grains crystallized. The dominance of large olivine with subordinate smaller clinopyroxene resembles the structure and phase

proportions produced by low pressure (~ 2 kbar) crystallization experiment performed on basaltic material from Stromboli Volcano (Di Carlo et al. 2006). However, more microprobe data is needed to estimate PT conditions of this stage more accurately. The records of the second stage are crystallization of low Mg# clinopyroxene, resorption of olivine followed by crystallization of low Fo olivine rims and crystallization of skeletal clinopyroxene in melt pools. Resorption might have been triggered by rapid ascent and eruption similar to the process described by Nelson & Montana (1992) for plagioclase and clinopyroxene. Skeletal morphology of clinopyroxene in the melt pools also indicates crystallization due to rapid cooling. Thus, it is concluded that the massive crystallization of the matrix (plagioclase, low Mg, Ti, Al clinopyroxene, low Fo olivine rims occurred after eruption.

Acknowledgements. Berit Wenzell and Tod Waight are thanked for help during microprobe analyses. The work was supported by the grant 2022/W/ING/2006-14.

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ALKALINE MAGMATISM IN SW POLAND – AN EXAMPLE OF ASTHENOSPHERE-LITHOSPHERE INTERACTIONS?

Abstract: Alkaline volcanism in SW Poland occurred due to an extensional regime related primarily to the Alpine orogeny. More than 300 small intrusions found in the Lower Silesia represent undersaturated magmas with high MgO content. Melts could be derived from two separate sources: an asthenospheric and a lithospheric mantle source, or generated in the garnet-spinel transition zone of a chemically and isotopically zoned lithospheric mantle. Strong HIMU-FOZO mantle signature indicates asthenospheric source and presence of recycled oceanic crust in the mantle source. However, some interactions with continental lithosphere should be also considered.

Keywords: basalt, Lower Silesia, HIMU, FOZO, asthenosphere, lithosphere.

INTRODUCTION

Alkaline intraplate volcanism represents usually volumetrically small events in comparison to other types of intraplate magmatism such as flood volcanism. Alkaline rocks are characterised by low SiO₂ and high concentrations of Na₂O, K₂O, P, F, Cl, Zr, Nb, Ta, Ti and REE. Their origin is related to small degree melting and enrichment processes in the lithospheric mantle, often expressed by occurrence of phlogopite and kaersutite in xenoliths. Alkaline magmas can be formed in the metasomatised parts of the mantle influenced by water- and/or CO₂-rich fluids. The origin of metasomatism can be related to the recycling of subducted material and/or plume heads rising through the asthenospheric mantle. The geology of the crust also plays a role in the petrogenesis of some alkaline lavas (Faure 2001).

During the Cenozoic alkaline volcanism occurred in central Europe within the system of NNE rifts on the Hercynian platform and within the hinterland of the Alpine orogenic belt and its marginal platforms (Kononova et al. 1991). Tertiary–Quaternary volcanic activity occurred on a large area extending across western and central Europe. The volcanic belt comprising volcanic rocks from Germany, Czech Republic and Poland is defined as Central European Volcanic Province (CEVP). This volcanic province (around 750 km long) is composed of large separated volcanic fields (e.g. Vogelsberg) and groupings of smaller intrusions (pipes, necks, flows, veins) of basalts and their differentiates.

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GEOLOGICAL BACKGROUND

The Cenozoic intraplate volcanism in the Bohemian Massif is a part of the CEVP associated with a rift system which was formed in extensional regime during the Alpine orogeny. The alkaline volcanism was initiated by adiabatic decompression of updomed asthenospheric mantle developed in association with the Alpine orogeny (Ulrych et al. 1999).

The Bohemian basalts occur mainly within the Eger rift which is a 300 km long, asymmetric, ENE-WSW-striking graben structure characterised by high heat flow (Vokurka & Bendl 1992). Volcanic rocks also occur in the transverse tectonic structures such as the Labe and Odra Tectonic Zones and the Cheb-Domažlice Graben (Fig. 1). Active tectonics is manifested by the periodic occurrence of earthquakes and neotectonic crustal movements, Quaternary volcanism and emanations of CO₂ gases of mantle origin (Babuška et al. 2003).



Fig. 1. Cenozoic volcanic areas of the Bohemian Massif 1-Oberfalz, 2-Doupovske hory Mts., 3-Ceske Stredohori Mts., 4-Lausitz-Elbe volcanotectonic zone, 5-Lower Silesia (with sample locations of this study in colour), 6-Cheb Basin, 7-Bruntal.

The alkaline volcanic rocks from Lower Silesia in Poland (NE part of the Bohemian Massif) form north-eastern part of the Central European Volcanic Province (Fig. 1). Compared to the volume of magmatism found in the Eger Rift (Czech Republic) and in Germany, the Polish volcanics in Lower Silesia represent a volumetrically minor part of the CEVP. Volcanic activity started in Late Cretaceous and lasted until Quaternary. The main phase took place from Eocene to Late Miocene (Birkenmajer et al. 2002a; 2002b; 2004) and two main pulses of volcanism can be distinguished:

1. Late Oligocene (between 31 and 25 Ma);

2. Miocene phase (23–18 Ma).

A younger phase of basalts (ca. 5 Ma) are found in Lutynia and Lądek in eastern part of the Sudety Mts. (Birkenmajer et al. 2004; Badura et al. 2004).

Published data on the geochemistry and isotopic composition of the Lower Silesia basalts (LSB) are sparse. Blusztajn & Hart (1989) reported Pb, Sr and Nd data from 18 localities in the Lower Silesia and showed that the LSB have the highest Nd and Pb isotopic ratios and

lowest Sr isotopic ratios within the CEVP. Blusztajn & Hart (1989) suggested the long-term depleted mantle source for the LSB with the isotopic composition produced by a mixture of DMM, HIMU and EM mantle components.

RESULTS

47 samples were collected in SW Poland, Germany and the Czech Republic close to the border with Poland (Fig. 1). The Cenozoic volcanic rocks occur as small volcanic centres, mostly in form of plugs and lava flows. The volcanic rocks from SW Poland are mostly silica undersaturated with only few more evolved types. SiO₂ content ranges from 40 to 63 wt %, MgO from 0.50 wt % in trachyte to 17.57 wt % in basanite. According to the TAS classification basanites are most common (57 % of analysed samples), whereas basalts (15 %) and nephelinites (11 % of analysed samples) are subordinate. Trachytes and trachyandesites occur in single localities.

There is no clear correlation between geographical location and age. Generally, group of rocks from the northern part of Kaczawa Mts. and Fore Sudetic Block has younger ages. The relationship between age and chemical composition (e.g. SiO₂) is not straightforward. However, if the most evolved rocks (trachyte and basaltic trachyandesite) are excluded, there is a clear trend of increasing SiO₂ content from the older volcanic phase to the younger one. A similar trend for MgO is visible: younger rocks have lower MgO content. Volcanic rocks occurring in the Kaczawa Mts. and in the Fore Sudetic Block and belonging to the younger phase of volcanism show the highest Nd and Hf isotopic ratios in CEVP.

Volcanic rocks with high Nd and Hf isotopic ratios have also lower $(La/Yb)_N$ ratios, which can be related to a more depleted mantle source (stronger influence of DMM end-member) and different partial melting conditions. In general, $(La/Yb)_N$ ratios in the



Fig. 2. Multi-element diagram (primitive mantle normalized; Sun & McDonough 1989) for selected samples from the Lower Silesia. OIB values after Wedepohl & Baumann (1999), N-MORB after Sun & McDonough (1989), UC and LC values after Taylor & McLennan (1985).

Lower Silesia volcanic rocks are high and scattered within a range of 9.4 and 33.1 (av. 22.3) and typical of alkali basalts. Most of the rocks have Cr>300 ppm and Ni>100 ppm, which indicates their primitive characteristics. They show strong negative anomalies for K and Pb (excluding trachyte from Stromica) and less expressed negative anomalies for Sr, Rb, Yb, Lu on primitive mantle-noramalized multielement diagram (Fig. 2).

Volcanic rocks display strong positive anomalies for Nb, P and Ti (excluding trachyte from Stromica) and less significant anomalies for Ba, Ta. The REE distribution is typical of OIB magmas with rather steep slope from LREE to HREE indicating melting in the residual garnet in the magma source. The trachyte from Stromica displays a different pattern due to shallower and probably more enriched magma source. It is strongly enriched in LREE and U, Th and depleted in P and Ti.



Fig. 3. Pb isotopic ratios in the CEVP (data for Massif Central, Pannonian Basin and Germany from Jung et al. 2005, Hegner et al. 1995, Wedepohl & Baumann 1999, Schleicher et al. 1991, Wörner et al. 1996, Bogaard & Wörner 2003, Embey-Isztin et al. 1993, Wilson & Downes 1991).

The Lower Silesia Basalts (LSB) have very radiogenic ²⁰⁶Pb/²⁰⁴Pb (Fig. 3; 19.3 to 20.8) which suggest HIMU-like mantle source although not as radiogenic as HIMU samples from Tubuai with ²⁰⁶Pb/²⁰⁴Pb up to 22 (Hoffman 1997). Compared to other suites within the CEVP, the LSB have much higher ²⁰⁶Pb/²⁰⁴Pb than other lavas from CEVP (Fig. 4). Nd-Hf isotopic ratios plot below the main mantle array.

Most of the LSB samples have a restricted range in Σ Hf (+6.0 to +7.9) and Σ Nd (+3.5 to +5.0), but samples from the central region (the Fore-Sudetic Block and Kaczawa Mts.) have higher Σ Hf (+10.8 to +13.1) and Σ Nd (+5.9 to +7.4) and lower ²⁰⁸Pb/²⁰⁴Pb (for a given ²⁰⁶Pb/²⁰⁴Pb). The westernmost LSB (SW Poland, Bogatynia area) samples show lower Σ Hf (+4.7 to +5.9) and Σ Nd (+2.5 to +3.2) and higher ²⁰⁸Pb/²⁰⁴Pb and ²⁰⁷Pb/²⁰⁴Pb (for a given ²⁰⁶Pb/²⁰⁴Pb). There is general trend across the CEVP province of decreasing Sr isotopic ratios from west to east.

Measured oxygen isotope compositions show a narrow range of isotopic ratios ($\delta^{18}O=4.86-5.35$ ‰ for olivines and $\delta^{18}O=4.93-5.89$ ‰ for whole rocks), typical of values expected for mantle olivines in general (Mattey et al., 1994). Low, mantle-like $\delta^{18}O$ values are consistent with low ${}^{87}Sr/{}^{86}Sr$ (0.70326-0.7044) for the whole rock and can be taken as an evidence for uncontaminated magmas.



Fig. 4. ²⁰⁶Pb/²⁰⁴Pb variations across the CEVP. Compiled data from: Wedepohl et al. (1994), Hegner et al. (1995), Wedepohl & Baumann (1999), Kramm & Wedepohl (1990), Mengel et al. (1984), Wörner et al. (1986), Schleicher et al. (1991), Jung & Hoernes (2000), Jung et al. (2005), Bogaard & Wörner (2003), Bogaard et al. (2001), Jung & Masberg (1998), Vokurka & Bendl (1992), Ulrych et al. (1999), Ulrych et al. (2002).

DISCUSSION AND CONCLUSIONS

(1) Alkaline magmas from the Lower Silesia are the result of partial melting processes and they do not represent a single magmatic plumbing system.

(2) Crustal contamination processes did not play significant role in the origin of the Lower Silesia Basalts because of: 1. General lack of correlation between isotopic composition and MgO; 2. Low Sr and high Nd isotopic ratios; 3. The presence of ultramafic nodules indicating rapid ascent through the crust. The influence of crustal contamination exists only in more evolved rocks (trachyte, basaltic trachyandesite, tephrite) and can be due to prolonged magma residence and fractionation in shallower levels in the crust. The most evolved samples were probably contaminated by upper crust of different age in amount less than 10 %.

(3) Variations in major elements, trace elements and Sr-Nd-Pb isotopic variations cannot be explained by fractional crystallisation and crustal contamination and require polybaric melting of heterogeneous mantle sources. This involves 2-10 % melting of a shallow spineland garnet- facies mantle source. Melts from this source mixed in variable proportions with smaller degree melts (<1 %) from a deep garnet-bearing asthenospheric source.

(4) Positive values of Σ Hf and Σ Nd indicate time-integrated depletion in incompatible elements. The high Σ Hf and low Σ Nd might reflect intramantle processes like ancient melt extraction at greater depth than usual, where the garnet/clinopyroxene ratio would be high (Blichert-Toft & White, 2001). The Hf and Nd isotopic compositions of the HIMU endmember are consistent with the presence of recycled oceanic crust material. (5) Low K content in the Lower Silesia basalts can be due to a K-bearing phase (phlogopite or amphibole) being residual in the mantle during small degree of melting. The high U/Pb ratios not correlated with Pb isotopes support recent enrichment event, which did not influence isotopic composition but changed the trace element compositions. Negative Pb anomalies and positive Nb and Ta anomalies have been attributed to dehydration and melting processes during subduction, producing a Pb-depleted, Nb-enriched recycled oceanic lithosphere component, which may eventually become the source of OIB-type magmatism with HIMU or FOZO signature (Stracke et al., 2005).

(6) Low oxygen isotopic composition suggests the presence of recycled hydrothermally altered (serpentinised) oceanic crust in the mantle source.

(7) Volcanism in SW Poland is the result of three-component mixing of melts from depleted (DM) enriched mantle (EM) and HIMU-type mantle end-member (FOZO). Variations in trace element and isotopic ratios suggest a spatial change from volcanism dominated by a deeper enriched mantle source in the southern region to shallower depleted mantle source in the northern region (Kaczawa Mts. and the Fore Sudetic Block). Given the distinct trace element and isotopic signatures of each mantle end-member, melts must either be derived from two separate sources, probably an asthenospheric and a lithospheric mantle source, or generated in the garnet-spinel transition zone of a chemically and isotopically zoned lithospheric mantle. The garnet signature can be caused also by presence of silica-deficient pyroxenite veins in the spinel zone, which contain garnet and clinopyroxene and can be melted efficiently by arising hot mantle material.

Acknowledgements. This study was supported by the Marie Curie Fellowship (A.L.), Fulbright Scholarship (A.L.), research KBN projects nr 3 PO4D 014 24 (A.L.) and 3PO4D029 24 (M.M.).

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PETROGENETIC SIGNIFICANCE OF RHÖNITE IN BASANITE FROM PILCHOWICE (SW POLAND)

Abstract: The silica undersaturated volcanic rocks from southwestern Poland are mainly composed of olivine, clinopyroxene, plagioclase, nepheline and Fe-Ti oxides. However, in basanite from Pilchowice occurrence of rhönite was observed. This high Ti mineral from aenigmatite group forms abundant phenocrysts crystallising as the last in phenocrysts assemblage. **Keywords:** rhönite, Lower Silesia, basanite.

INTRODUCTION

The alkaline volcanic rocks from southwestern Poland (NE part of the Bohemian Massif) form north-eastern part of the Central European Volcanic Province (CEVP). Silica-undersaturated magmas erupted between 30 and 3 Ma years in at least three main volcanic episodes (Birkenmajer et al. 2002a, 2002b; Birkenmajer et al. 2004). Basanite from Pilchowice (SiO₂=40.87 wt %, MgO=13.71 wt %) represents small plug and lava flows which intruded within gneisses from Izera Mts. metamorphic complex (Upper Cambrian-Lower Ordovician). Basanite shows strong FOZO signature (*sensu* Stracke et al. 2005) with high Pb isotopic ratios, low ⁸⁷Sr/⁸⁶Sr and intermediate ¹⁴⁴Nd/ ¹⁴³Nd ratios (Ladenberger et al. 2004a, b).

Rhönite is one of the main constituent of basanite from Pilchowice (Fig. 1). It forms both phenocrysts and microphenocrysts. Rhönite was previously described by Smulikowski (1960). Smulikowski (1960) suggested that occurrence of rhönite in Pilchowice can be related to pseudomorphoses after hornblende.

ANALYTICAL METHODS

We obtained analyses of chemical composition of rhönite using EMPA and FES-EM-EDS. Measurements were performed in the Institute of Petrology at the University of Vienna (EMPA) and in the Institute of Geological Sciences at the Jagiellonian University in Kraków (FESEM-EDS).

RESULTS

Rhönite (Tab. 1) is a common phenocryst in basanite from Pilchowice. It forms euhedral crystals and often poikilitically encloses small inclusions of Ca-rich clinopyroxene and Fe-Ti oxides (titanomagnetite-ulvöspinel series). Rhönite belongs to the aenigma-

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tite group, and has the general formula *A2B6T6*O20, where A = Ca, Na; B = Mg, Fe²⁺, Fe³⁺, Ti; T = Si, Al (Bonaccorsi et al. 1990).

Calculated stoichiometric formulas of rhönite from Pilchowice e.g. $(Ca_{1.8}, Na_{0.2})$ $(Mg_{2.4}, Fe_{2.7}, Ti_{1.1})(Si_{3.5}, Al_{2.5})O_{20}$ corresponds to the general formula of rhönite: $Ca_2(Mg, Fe^{2+}, Fe^{3+}, Ti)_6(Si, Al)_6O_{20}$.



Fig. 1. Photograph of rhönite from Pilchowice in plane-polarized light. Rhönite occurs as semi-opaque, dark brown phenocryst.

Characteristic feature of rhönite is stable and non-variable chemical composition, i.e. low SiO₂ content, high FeO and TiO₂ content (Fig. 2, Tab. 1).

Tab. 1. Rhönite composition from Pilichowice (EMPA). Samples Kauai (alkali gabbro, Johnston & Stout 1985), Cam (ankaramite, Nono et al. 1994) and WA (pyroxenite, Grapes et al. 2003) shown for comparison.

wt %	1pilch	6pilch	8pilch	13pilch	pilchrh	Kauai	Cam	WA
SiO ₂	24.62	24.37	24.13	25.10	24.39	25.10	24.19	23.73
Al ₂ O ₃	17.67	17.77	17.78	17.07	17.74	14.75	16.27	17.62
TiO ₂	10.59	10.38	10.40	10.74	10.34	6.88	11.74	11.26
FeO	21.47	23.71	22.24	22.60	22.14	20.94	22.98	20.08
MgO	12.83	11.97	12.85	12.41	12.99	17.14	11.59	13.00
MnO	0.18	0.21	0.18	0.23	0.14	0.29	0.23	0.14
CaO	12.22	11.77	11.85	11.45	11.83	10.3	11.42	12.00
Na ₂ O	1.10	1.09	1.06	1.22	1.10	1.91	1.23	0.89
K ₂ O	bdl	0.06	0.01	0.01	0.02	0.01	0.01	0.01
NiO	0.01	0.10	0.07	0.03	.03	bdl	bdl	bdl
Cr ₂ O ₃	0.18	0.24	0.14	0.09	0.19	bdl	bdl	0.27
Total	100.87	101.67	100.71	100.95	100.92	97.32	99.66	99.00

*bdl - below detection limit

DISCUSSION AND CONLUSIONS

Based on microscopic observations, rhönite seems to be later in the crystallization sequence than clinopyroxene phenocrysts. Rhönite occurs in silica-undersaturated alkali basalt, basanite and gabbro/syenite as phenocrysts (and microphenocrysts) associated with olivine, Ti-Al augite, plagioclase, \pm K-feldspar, kaersutite, \pm nepheline, \pm leucite, apatite, Ti-magnetite \pm ilmenite (Grapes et al. 2003). Rhönite was also described from melilite-rich inclusions in carbonaceous chondrites (Simon et al. 1999). The mineral is supposed to be stable over a wide range of fO_2 , from ilmenite-wüstite (IW) to hematite-magnetite (HM) buffer conditions (Kunzmann 1999).



Fig. 2. TiO₂ versus FeO (a), SiO₂ (b), CaO (c) and Na₂O (d) in selected clinopyroxenes and rhönites from Pilchowice.

Rhönite can be the product of the breakdown of kaersutite to the assemblage of *rhönite* + *plagioclase* + *clinopyroxene* \pm *olivine* + *melt* or the breakdown product of perovskite (Nono et al. 1994). However, rhönite can crystallize in basanite and nephelinite without the presence of amphibole. It requires p<0.5 kbar, narrow range of temperature between 1000°C and 1130°C and enough H₂O to saturate the liquid (Huckenholz et al. 1988). According to Prestvik et al. (1999) rhönite can crystallize in the presence of a fluid phase at pressures below 60 MPa (<1.8 km) and temperatures between 840°C and 1200°C. These conditions may then be associated with the metasomatic activity short

prior the eruption (Grapes et al. 2003). Rhönite can also occur in areas where there has been infiltration of the continental lithospheric mantle by basanitic melts along cracks, grain boundaries and cleavage planes (Grapes et al. 2003). Additionally, rhönite may be formed during temporary residence of the xenoliths in a shallow magma chamber. Because of lack of xenoliths in basanite from Pilchowice the most possible explanation of rhönite origin is infiltration of lithospheric mantle by basanitic melts metasomatised by H_2O and/or CO_2 -rich fluids.

Acknowledgements. This study was supported by the research KBN projects nr 3 PO4D 014 24 (A.L.), and 3PO4D029 24 (M.M.). Microprobe analyses were performed thanks to CEEPUS program.

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CLINOPYROXENES FROM THE TERTIARY VOLCANIC ROCKS FROM THE LOWER SILESIA (SW POLAND)

Abstract: Olivine and clinopyroxene phenocrysts occur in the Tertiary silica-undersaturated volcanic rocks from SW Poland. Clinopyroxenes show compositional range: from diopside, salite, to ferrosalite. Occurrence of augite is rather scarce. The typical feature of clinopyroxenes is very high Ca content. Variation in chemical composition between core and rim of clinoproxene phenocrysts can be related to decrease of crystallization temperature and changes in pressure during crystallization. Keywords: Lower Silesia, basalts, phenocryst, clinopyroxene.

INTRODUCTION

The Tertiary alkaline volcanic rocks from southwestern Poland (NE part of the Central European Volcanic Province, CEVP) comprise several lithologies. The volcanic chain occurring in SW Poland is composed of volumetrically small intrusions. Radiometric ages of basaltoids show two main magmatic events: around 20 Ma and 29 Ma (Birkenmajer et al. 2002a, 2002b; Birkenmajer et al. 2004). Volcanic rocks are emplaced in various geological units and rocks of different ages and lithologies.

Samples collected from 32 localities in the Lower Silesia represent alkaline, mostly undersaturated (SiO₂=40.0-47.9 wt %) rocks. According to TAS classification they are basanite, nephelinite, basalt, trachyandesite and trachyte.

ANALYTICAL METHODS

We obtained ca. 1000 analyses of chemical composition of clinopyroxenes using FESEM-EDS (microscope HITACHI S-4700 with microanalytical system NORAN Vantage). All measurements were performed in the Institute of Geological Sciences at the Jagiellonian University.

RESULTS

Studied rocks show aphanitic textures, with quite well crystallized groundmass. Porphyritic texture with phenocrysts of olivine and more abundant clinopyroxene is very common. Main constituents of the groundmass are: plagioclase, nepheline, clinopyroxene, Fe-Ti oxides (titanomagnetite, ilmenite). Apatite and glass occur subordinately. Olivine shows intermediate Fo content (Fo_{51.85}). Clinopyroxenes occur as phenocrysts and groundmass phases (often interstitial). Clinopyroxene phenocrysts are euhedral in shape and vary from 200 μ m to 2 mm in size.

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The clinopyroxene crystals are often zoned, frequently showing hour-glass structures. The composition of phenocryst rims correspond to the composition of clinopyroxenes in the matrix. They are diopside or aluminan diopside (Fig. 1) sensu Morimoto et al. (1988). The rims often contain small inclusions of titanomagnetite. Clinopyroxenes are characterized by high CaO (CaO from 7.22 to 26 wt %; but most common value is between 18-25 wt %) and variable TiO₂ content (from 0.48 wt % in trachyte to 7.37 wt % in basanite). Mg# is enclosed within the range from 0.42 to 0.78 (common values are around 0.6). Positive correlation between Ti and Al in studied clinopyroxene phenocrysts is significant (Fig. 2).



Fig. 2. Correlation between Ti and Al in selected clinopyroxenes (values recalculated to 6 atoms of oxygen per for-mula unit).

The style of chemical zonation differs between different clinopyroxenes and it is more complex than in case of olivines. Variations in the core compositions are mostly due to variability of Na, Mg and Al contents. Inner part is usually richer in Si and Mg and depleted in Fe, Al, and Ti (Fig. 3). Rims are richer in Al and Ti and poorer in Na. Usually, Si and Fe contents increase towards rims, while Ca, Ti and Mg contents decrease. Clinopyroxenes from Bogatynia show distinct style of zonation comparing to the rest of the analyzed samples. In sample from Bogatynia Ca, Ti, Mg and Al contents increase towards rims and Si and Fe contents decrease (Fig. 3).



Fig. 3. Chemical zonation of some representative clinopyroxenes from: a) Bogatynia; b) Kowalskie; c) Pilchowice. Variable behaviour of elements can be observed. Average distance between points of analyses is 20 µm.

DISCUSSION AND CONLUSIONS

Clinopyroxene is quantitatively the most abundant phenocryst mineral in many volcanic rocks from the Lower Silesia. Major and trace element (whole rock) trends indicate fractionation of this phase e.g. strong positive correlation between MgO and Cr, CaO and Sc. Similarly as olivines, clinopyroxenes can be of different origin, i.e. magmatic or derived from xenoliths. Magmatic origin of phenocrysts can be tested if clinopyroxenes represent phases in equilibrium with the liquid. The equilibrium between clinopyroxenes and co-existing liquid was calculated based on Fe-Mg exchange. Most of the clinopyroxenes are in equilibrium. However, in rocks from Sulików, Księginki and Grodziec clinopyroxenes in equilibrium have not been found.

The studied clinopyroxenes are rich in wollastonite component (often above 50 mol %). High Ca and Ti contents in clinopyroxene are characteristic of alkaline magmas. While the pressure decreases the CaTiAl₂O₆ content in clinopyroxene increases (Scott 1976). The solubility of Ca-Tschermak component in diospide coexisting with anorthite increases with increase of pressure at constant temperatures (Aoki & Kushiro 1968).

Clinopyroxene zoning i.e. rimward enrichment in Al^{IV}, Ti and Fe, Mg, Al^{VI} depletion can be explained in three ways (Bedard et al. 1988): 1. It represents a kinetic effect; 2. It reflects a differentiation of the melt during the crystallization of minerals and the temperature decrease; 3. It reflects changes in pressure during crystallization (Spišak & Hovorka 1997). The strong deficiencies in Si in clinopyroxenes from Lower Silesia basalts cause that at high Al content most of the aluminium goes to the tetrahedral sites. That results in high Al^{IV}/Al^{VI} ratios, which supposed to indicate rather high temperature environment and high pressure conditions (Aoki & Kushiro 1968).

Acknowledgements. This study was supported by the research KBN projects nr 3 PO4D 014 24 (A.L.) and 3PO4D029 24 (M.M.).

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PETROLOGY OF ENCLAVES AND HOST BASALT FROM THE WINNA GÓRA NEAR JAWOR (SW POLAND)

Abstract: Basalt occurrence on Winna Góra near Jawor (SW Poland) belongs to Tertiary Central European Volcanic Province. Scarce mafic to ultramafic enclaves (1-5 cm) occur in the host rock. The enclaves have the compositions of: lherzolite, gabbro, websterite, clinopyroxenite and harzburgite. Chemical compositions of the enclaves' minerals is not typical for the mantle – derived ones. The enclaves are probably of cumulative origin. Gabbroic and clinopyroxenitic enclaves might be cumulates of the host basaltic magma settled in Tertiary magma chamber. Websteritic, lherzolitic and harzburgitic enclaves may be parts of late – Permian intrusion situated on the crust/mantle boundary.

Keywords: basalt, enclaves, cumulates, SW Poland.

INTRODUCTION

Basalt occurrence on Winna Góra near Jawor (Fore – Sudetic Block, SW Poland) belongs to the Tertiary Central European Volcanic Province. The lavas, tuffs and volcancelastics forming volcanic plug and lava flows, are exposed in an active quarry and. K- Ar ages 21.62 ± 0.93 and 21.96 ± 1.36 My were determined by Birkenmajer et al. (2002), what makes them one of the oldest Tertiary volcanic rocks in Poland.

Scarce greenish and blackish enclaves, varying in size from 1 to 3 cm, occur in basalt. Plagioclase euhedral megacrysts up to 5 cm were also found. In this abstract I present the microprobe based data on basalt, enclaves and megacrysts.

PETROGRAPHY AND MINERAL CHEMISTRY OF BASALT AND PLAGIOCLASE MEGACRYSTS

The Winna Góra basalt consists of plagioclase – clinopyroxene – subordinate opaque matrix containing olivine (Fig. 1a) and clinopyroxene (Fig. 1b) porphyrocrysts. Plagioclase forms lath crystals of size up to 50 μ m (Fig. 1) zoned from 65 % of An in cores to 20 % in rims.

Clinopyroxene (mostly Al – diopside sensu Morimoto et al. 1988, Fig. 1c) occurs as small (<200 μ m) crystals of Mg/(Mg+Fe) ratio 0.75 - 0.76. Clinopyroxene forms also sub- to anhedral porphyrocrysts up to 300 μ m in diameter, whose Mg/(Mg+Fe) ratio varies from 0.83 in centres to 0.75 in margins.

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Olivine occurs as subhedral to skeletal porphyrocrysts. Two types of olivine crystals occur in basalt: homogenous (Fo 70) and rare zoned crystals (Fo content from 85 % in centres to 75 % in margins).

Subhedral crystals of spinel of composition close to $Fe^{3+}_{0.36}Fe^{2+}_{1.72}Ti_{0.57}Mg_{0.18}$ $Al_{0.11}Mn_{0.02}Cr_{0.01}O_4$ and ilmenite (typically $Fe_{0.81}Ti_{0.91}Mg_{0.18}Mn_{0.02}Al_{0.04}O_3$) up to 25 µm in size are opaques.



Fig. 1. Olivine (a) and clinopyroxene (b) porphyrocrysts and the host basalt; c) pyroxenes from basalt in the diagram of Morimoto et al. (1989); d) marginal part of plagioclase megacryst (Px – pyroxene, Ol- olivine, Pl – plagioclase, Opq – opaque; BSE images).

Plagioclase megacrysts (1-5 cm) are euhedral to subhedral and contain from 14 to 28 % of anorthite. The An content is constant within single crystal, whereas the Or content varies from 7 to 21 %. Small spinel – pyroxene – plagioclase intergrowths occur in marginal parts of the megacrysts (Fig. 1). Spinel and pyroxene form minor, dot – like crystals of size up to few μ m. Spinel has the composition of ülvospinel and pyroxene is Ti, Al- diopside. Plagioclase composition in the intergrowths varies in wide range (from 15 to 68 % of An).

MINERALOGY AND CHEMICAL COMPOSITION OF ENCLAVES Scarce mafic to ultramafic enclaves (lherzolite, websterite, clinopyroxenite, gabbro and harzburgite; 1 – 5 cm) occur in the Winna Góra quarry.



Fig. 2. Apperance of olivine in gabbro. BSE image.

The majority of enclaves has a composition of **lherzolite**. Olivine crystals (0.25-1.5 mm) are anhedral and contain 75-80 % of forsterite. The NiO content varies from 0.24 to 0.30 wt %. Clinopyroxene (Na – diopside) forms anhedral crystals up to 200 μ m in size. The Cr₂O₃ content in clinopyroxene varies from 0.26 to 0.71 wt % and the Mg/(Mg+Fe) ratio is constant at 0.86. Scarce enstatite, forming anhedral crystals up to 1 mm in size, has the Mg/(Mg+Fe) ratio value of 0.82.

Gabbro is the second enclave type according to the frequency of occurrence. It consists of plagioclase and clinopyroxene with subordinate olivine. Plagioclase forms sub- to anhedral crystals up to 2 mm in size and the An content varying from 41

to 56 %. Majority of the plagioclase crystals is homogenous but in some of them the central parts are enriched in anorthite. Diopside occurs as anhedral crystals of average size of 2 mm. The Mg/(Mg+Fe) ratio varies from 0.68 to 0.78. Minute blebs consisting of olivine and plagioclase occur in clinopyroxene crystals (Fig. 2). The olivine contains 64 %-68 % of Fo, the plagioclase has variable An content ranging from 17 % to 48 %.

Websterite consists of anhedral clino- and orthopyroxene crystals up



Fig. 3. Occurrence of pyroxene in the marginal parts of websterite enclave. BSE image.

to 5 mm. Minute pyroxene crystals, perpendicular to the enclave border, occur in the marginal parts of the enclave (Fig. 3). Mg/(Mg+Fe) ratio in diopside is 0.86, that ratio in enstatite has value 0.84. Small aggregates of feldspar (An 1-44, Or 1-33) and/or olivine (Fo 71-79) occur in interstices or in the clinopyroxene.

Clinopyroxenite consists mainly of diopside (up to 3 mm, Mg/(Mg+Fe) ratio from 0.76 to 0.88). Its Cr_2O_3 content varies from 0.20 to 0.52 wt %. The enclave is strongly altered and contains abundant carbonates and unidentified silicates.

Olivine from **harzburgite** enclave forms anhedral crystals > 0.5 mm in size, containing 84 % of forsterite. Their NiO content varies from 0.20 to 0.47 wt %. Mg/(Mg+Fe) in anhedral (up to 1 mm) enstatite crystals is 0.86.

All enclave types, except the clinopyroxenite ones, contain intergrain aggregates of small (< 100 μ m) crystals of plagioclase, clinopyroxene, olivine and opaques. The composition of the crystals is similar to that of minerals forming the host enclave. The exception is the plagioclase from the aggregates, which, in comparison to the that from gabro, shows strongly variable content of Or (12-46 %) and An (0-25 %).

DISCUSSION AND CONCLUSIONS

Chemical composition of minerals forming the enclaves from Winna Góra is not typical for those mantle-derived. The forsterite content in olivine from enclaves varies from 75 % in lherzolite to 84 % in harzburgite, whereas the values typical of mantle peridotites are higher than 89 % (e.g. Yu et al. 2003 and references therein). Variation of forsterite content in olivine is greater in minute crystals: from 64 % in gabbro to 79 % in websterite. NiO content in olivine varies from 0.24 wt % (lherzolite) to 0.47 wt %



Fig. 4. Variations in chemical parameters characterizing the minerals from enclaves from Winna Góra basalts: (a) Ca/Cr in clinopyroxene; (b) NiO/Ca in olivine; (c) Ca/(Mg/[Mg+Fe]) in clinopyroxene; (c) (Mg/[Mg+Fe])^{cpx}/(Mg/[Mg+Fe])^{ol}.

(harzburgite), and is in part similar to NiO content in mantle olivines (> 0.35 wt %, e.g. Workman and Hart 2005). Cr₂O₃ content in clinopyroxene varies from 0.20 to 0.52 wt %. Temperatures of equilibration, calculated by the Brey and Köhler (1990) two-pyroxene thermometer, are 970°C for websterite and 870°C for lherzolite.

The mafic-ultramafic enclaves, if not the mantle ones, can be the cumulates of a mafic magma. Their potential source might be the host basaltic magma or late Variscan layered basic/ultrabasic intrusion located at the base of the crust, analogous to that described by Féménias et al. (2003) in French Massif Central.

Comparison of chemical composition of minerals from gabbroic and clinopyroxenitic enclaves with that from basalt shows that the three rocks may be connected with each other. Location of points representing clinopyroxene in the Ca/Cr plot (Fig. 4 a) is similar to the trend showed by points representing clinopyroxene from basalt. Similar pattern occurs on NiO/Ca in olivine diagram (Fig. 4 b). Points representing clinopyroxene from gabbro are located at the prolongation of the trend defined by those representing clinopyroxenite and host basalt on the Ca/[(Mg/(Mg+Fe)] diagram (Fig. 4 c).

Chemistry of minerals from lherzolite, harzburgite and websterite is generally different than that of minerals from basalt. Points representing clinopyroxene from these rocks form trends different from those representing minerals from basalt on Ca/(Mg/ [Mg+Fe]) diagram in (Fig. 4c). Similar relationships occur on (Mg/[Mg+Fe])^{epx}/(Mg/ [Mg+Fe])^{ol} diagram (Fig. 4 d). Only in the NiO/Ca in olivine diagram the points representing websterite are situated near the trend defined by points representing minerals from basalt and gabbro (Fig. 4 b).

Basing on the presented data it is impossible to ascertain the origin of websteritic, harzburgitic and lherzolitc enclaves. To define their source as well as to prove the connection of gabbroic and clinopyroxenitic enclaves with the host basalt further geochemical study is required.

Blebs of minute crystals occurring in almost every enclave suggest partial melting of the enclave during residence in magma chamber or during host lava ascent.

The rocks occurring as enclaves in the Winna Góra basalt are probably of cumulative origin. Some of the cumulates (clinopyroxenitic, gabbroic) may be an outcome of settling minerals from the host basaltic magma in Tertiary magma chamber. The genesis of websteritic, harzburitic and lherzolitc enclaves is not nclear, they may come from late – Permian layered intrusion located at the mantle/crust boundary.

Acknowledgements. I am grateful to Prof. Jacek Puziewicz (University of Wrocław) for numerous discussions and comments on the earlier versions of the text. The head of the "Winna Góra" quarry is acknowledged for warm hosting during field works. The results presented in this abstract summarize my MSc thesis completed in 2006, supervised and financed by J. Puziewicz (Institute of Geological Sciences, University of Wrocław grant no 1017/ING).

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PERIDOTITE ENCLAVES IN PICROBASALT FROM WOŁEK HILL NEAR NOWY KOŚCIÓŁ (SW POLAND) – PRELIMINARY DATA

Abstract: Picrobasalt from Wołek Hill (SW Poland) contains xenoliths of lherzolite and amphibole peridotite. The lherzolite consists of olivine (Fo 92), clinopyroxene, orthopyroxene and chromian spinels (#Cr up to73) which imply mantle orgin. Amphibole peridotite contains magmatic pargasite and kaersutite and may be of crustal origin.

Keywords: Tertiary picrobasalt, peridotite xenoliths, SW Poland.

INTRODUCTION

The Tertiary basaltic rocks belonging to the north-eastern part of the Central European Volcanic Province are exposed in an abandoned quarry situated on the south-eastern slopes of Wołek Hill. Wołek is located on the west banks of the Kaczawa River, about 2 km south of Nowy Kościół (SW Poland). The picrobasaltic dike cuts Permian trachybasalts and sedimentary rocks.

Juroszek (1985) described these rocks as ankaratrites. According to the TAS classification diagram (Le Bas 2000) these rocks are picrobasalt. In this paper we present primary results of microscopic examination and results of microprobe study of 2 samples (150 analyses).

PETROGRAPHY AND MINERAL CHEMISTRY

Picrobasalt is dark-gray and porphyritic, consists of olivine and amphibole phenocrysts, its groundmass is composed of amphibole, iron oxides, nepheline and – to a minor extent – feldspar (Fig. 1).

Olivine phenocrysts (up to 3 mm) are zoned from Fo 91 in cores to Fo 85 % in rims (Fig. 2); one of the phenocrysts contains from 82 % Fo in core to 85 in the rim. The calcium content in the olivine varies from 100 to 3250 ppm (Fig. 2).

In earlier descriptions (e.g. Juroszek 1985) no amphibole has been reported, neither as phenocrysts nor in the groundmass. The amphibole size (Fig. 1) ranges from 0.1 to 1 mm, they occur as laths or grain concentrations around olivine. They have zonal character with Mg-hornblende in the core and tschermakite in the rim. Both feldspar ($Ab_{55}Or_6An_{36}Cs_3$) and nepheline are subordinate components of the groundmass.

Enclaves of igneous and sedimentary rocks occur in the picrobasalt. Individual, ground-mass-coated grains of feldspar $(Ab_{30} Or_{69} An_1)$ are also to be found (Fig. 1).

Vesicles filled with calcite and quartz are common.

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Fig. 1. Picrite lava with zoned olivine phenocrysts (Ol) and abundant amphibole crystals (Amf) in the groundmass. Note feldspar (Fsp) xenocryst in the left corner of the picture. BSE image.

The size of xenoliths in the picrobasalt ranges from a few to a dozen centimetres. Two kinds of peridotite enclaves have been identified: lherzolite and amphibole peridotite.

Lherzolite consists of olivine, clinopyroxene, orthopyroxene and chromian spinel (Fig. 3). Grain size varies from 0.02 to 6 mm. The olivine contains 91 % Fo and < 100 ppm Ca. Orthopyroxene has an enstatite composition $(Mg_{1.81}Fe_{0.16}Ca_{0.02})(Si_{1.98}Al_{0.07}O_{6})$, and clinopy $roxene - (Na_{0.04}Ca_{0.93}Mg_{0.93}Fe_{0.06} Al_{0.02}Cr_{0.02})$ (Si₁₉₆Al₀₀₄O₆) is classified as diopside. The chromian spinel has variable chromium number (Cr/(Cr+Al) * 100) which ranges from 50 to 73, and $Fe^{2+}/(Mg+Fe^{2+})$ ratio rangeing

from about 0.50 to 0.67. These minerals, especially at the enclave rims, are greatly altered.

Ca ppm

Amphibole peridotite consists of olivine, clinopyroxene, chromian spinel and amphibole (Fig. 4). The olivine (Fo 85) contains from 250 to 450 ppm Ca. The amphibole has the zonal character with pargasite in the core and kaersutite in the rim. The clinopyroxene (Na₀₀₇Ca₀₈₂ $Mg_{0.85}Fe_{0.04}Al_{0.19}Cr_{0.03}$) (Si_{1.89} Al_{0.11}O₆) has a diopside composition.

The chromian spinel has a formula Fe²⁺₀₃₈ $Mg_{0.61}Cr_{0.69}Al_{1.03}Fe^{3+}_{0.24}Ti_{0.03}O_{4}$, the chromium number amount equals to 40, and $Fe^{2+}/$ $(Mg+Fe^{2+})$ ratio ranges from about 0.34 to 0.59.

Cpx

Op

Opx

Opx

Cnx



Fig. 2. Relationship forsterite and Ca contents in olivines in two different phenocrysts.



Fig. 3. Lherzolite xenolith structure composed of olivine (Ol) and orthopyroxene (Opx) with subordinate clinopyroxene (Cpx). BSE image.

Fig. 4. Amphibole peridotite xenolith. BSE image.

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DISCUSSION AND CONCLUSIONS

It may be conjectured, based on the chromium number in spinels (Cr/(Cr²⁺ +Al)=50-73) and on the Ca content in olivines, that the lherzolite may have been formed at temperature of 1100-1250°C and pressure ranging from 20 to 25 kb (O'Neill 1981, Brey & Köhler 1990, Choi et al. 2001). However, two Px thermometer gives much lower tempetatures (646-658°C) as well as Ca thermometer in Opx (784 to 825°C) at 15 to 25 kb respectively. Olivine-spinel thermometer gives temperature 1060 to 1130°C (P= 15 kb) for the amphibole peridotite (http://www.ugr.es/~jsoto/PTMafic.htm).

On the Arai (1994) diagram, based on olivine-spinel composition, the lherzolite xenolith plots in field of mantle origin, while the amphibole xenolith is out of the mantle field. The composition of olivines from the peridotite enclave (Fo>89) also indicates their mantle origin (fide Matusiak, Puziewicz 2005).

Some phenocrysts in the picrobasalt (Fo 82-85) and the amphibole peridotite accumulations may however originate from a magma chamber of lower continental crust. In order to establish the details further research is needed.

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Jacek PUZIEWICZ¹

THE LAST METASOMATIC EVENT IN THE UPPER MANTLE BENEATH SW POLAND

Abstract: The spinel peridotite enclaves occurring in the Księginki nephelinite (SW Poland, Central European Tertiary Volcanic Province) contain olivine Fo 89.2-91.5, three generations of clinopyroxene, and spinel of variable composition. The peridotites, as well as accompanying websterites, equilibrated under temperatures of ca. 1100°C. One of the wehrlitic enclaves consists of olivine Fo 86 and contains pools of decomposed melt, in which the sequence of melt-host rock phases reactions can be defined. It shows that cpx II occurring in peridotitic enclaves originated due melt infiltration under mantle conditions (Mg-Al-Cr spinel stable), whereas cpx III originated under surface conditions (Fe-Ti spinel stable). **Keywords**: Mantle peridotites, enclaves, metasomatism, SW Poland.

INTRODUCTION

Petrological information on litospheric mantle beneath eastern part of the European Variscan Orogen comes from mantle enclaves brought to the surface by Cretaceous and younger alkaline volcanic rocks, forming the Central European Volcanic Province. It is generally assumed that these enclaves did not react with the host magma and are thus good representatives of the mantle at the time of eruption. However, it is possible that the magma residing in mantle may affect chemically its host, which could be entrained into lava and brought to the surface as an enclave. If so, it is necessary to separate these metasomatic effects from the older record of mantle geological history. In this abstract I give a brief account on the study of the problem, based on the enclaves from the Księginki nephelinite (SW Poland, eastern part of the Central European Volcanic Province).

THE SUITE OF MANTLE ENCLAVES IN THE KSIĘGINKI NEPHELINITE

The suite of mantle enclaves of peridotitic and pyroxenitic composition occurs in the Księginki quarry. As elsewhere in Lower Silesia, the enclaves equilibrated in the spinel stability field and contain no garnet; no hydrous phases occur in them as well. The peridotites (wehrlites, lherzolites and harzburgites) are olivine rich and contain two or three generations of clinopyroxene of differing chemical composition. The enclaves have medium- to coarse-grained protogranular texture or consist of protogranular domains embedded in zones of medium- to fine-grained recrystallized texture. Small droplets or pools of altered glass occur in various amounts. The concise characteristics of enclaves from Księginki is given in Puziewicz (2005) and that of host nephelinite – in Puziewicz (2004).

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Chemical composition of minerals, reported in the following, was studied by a CAME-CA 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) and Ca (200 ppm). For glass analyses beam diameter was enlarged to 20 μ m, sample current lowered to 4 nA and counting times reduced to 4 sec for Na and K and 8 sec for another elements.



Fig. 1. (a) – Spongy olivine grain margins. Note the small recrystallized olivine grains in the upper part of the image. Wehrlite 2478, olivine is Fo 91, the numbers refer to Ca contents in ppm;

(b) – interstitial clinopyroxene I (homogeneous) and II (spongy) associated with spinel. Lherzolite 2483, olivine is Fo 91, spinel is homogeneous, Cr /(Cr+Al) = 0.38

The composition of olivine within individual peridotitic enclaves is practically constant $(\pm 1.5\%)$ of Fo): typically the olivine contains 89.2 to 91.5 % of Fo depending on the enclave. The grains of the mineral located in the protogranular domains contain <800 (in some enclaves <600) ppm of Ca and are commonly slightly spongy close to the margins (Fig. 1a). The content of Ca is lowest in centres, whereas in spongy margins increases to 1000 -1200 ppm. Small grains of olivine occurring in some interstices are obviously of recrystallization origin. Their forsterite content is identical to that of large grains in the enclave, but Ca content varies between 1000 and 1900 ppm. The content of NiO in olivines exceeds usually 0.30 wt %. Clinopyroxene grains typically are interstitial, associated with spinel (Fig. 1b) and in places with glass. In some of the enclaves larger (up to 2 mm) grains occur in the protogranular domains. The clinopyroxene consists of low-Ca central parts containing high Na, high and relatively constant Cr and low and constant Ti and Al (cpx I). The outer parts of those grains are spongy, locally patchy, richer in Ca, contain high, but variable Cr and low variable Al and Ti (cpx II). The margins are rich in Ca, contain low, variable amounts of Cr and high, but variable amounts of Al and Ti (cpx III). Spinel of highly variable composition (Cr/ (Cr+Al) = 0.25 - 0.62) occurs usually as rounded grains accompanying clinopyroxene.

One of the studied enclaves (wehrlite 2512) consists of protogranular olivine + subordinate clinopyroxene domains and melt pools of varying size. The olivine (86 % Fo) has con-



Fig. 2. The melt pool in wehrlite 2512. The inlet shows relationships between clinopyroxene, Mg-Al-Cr spinel and ulvospinel.

stant composition, contains typically 400 - 600 ppm Ca and between 0.26 and 0.36 wt % of NiO. The small grains of recrystallized olivine have identical Fo and NiO contents but contain 950-1350 ppm of Ca. Spinel occurs mostly in melt pools, its composition is very variable.

The relationships among grains occurring in melt pools show the sequence of mineral crystallization and replacement (Fig. 2). Cpx II and probably inner parts of cpx III rims crystallized in the stability field of spinel (Cr/Cr+Al) = 0.36 - 0.52). Outer parts of spinel contacting with the melt were replaced by ulvospinel. The crystallization of outermost parts of cpx III rims was parallel with replacement of Mg-Al-Cr spinel by the Fe-Ti one (Fig. 2, inset). The olivine was stable and its Ca content was between 900 and 2000 ppm; sparse and small grains containing 84 % of forsterite and ~3300 ppm Ca occur. The needles of Ca-rich phase and potassium-rich mineral of composition similar to titanian biotite crystallized last from the melt. The analyses of melt yield totals <90 wt %.

DISCUSSION AND CONCLUSIONS

The relationships among various generations of clinopyroxene and spinel in melt pools suggest that clinopyroxene II crystallized within the Mg-Al-Cr spinel stability field. Since the spinel composition is typical of the mantle, it is inferred that cpx II originated under mantle conditions. Clinopyroxene II contacts commonly with frozen glass, thus it supposedly originated due to melt penetration into peridotites. The highly calcic outer rims on clinopyroxene (cpx III) commenced the crystallization under conditions in which Mg-Al-Cr spinel was not stable and was replaced by Fe-Ti one. Since analogous spinel is stable in the host nephelinite groundmass and the composition of cpx III is analogous to that of

nephelinite matrix clinopyroxene, it may is inferred that cpx III crystallized in peridotitic enclaves after the nephelinite eruption.

Nephelinite contains numerous porphyrocrysts of clinopyroxene. In most complex form the they consist of irregular, spongy inner core, surrounded by outer core, both of diopside composition, surrounded by complex rim of subsilicic titanian diopside, the latter corresponding to cpx III from the enclaves. The transition from the core to the rim is usually marked by narrow zone of high Cr content, which might reflect the decomposition of Mg-Al-Cr spinel during movement of the nephelinite magma to the surface. The core parts of porphyrocrysts are chemically different, in terms of Al, Cr and Ti content, from the peridotitic cpx I and II.

The cores of some larger crystals of olivine occurring in the nephelinite have the composition corresponding to that of latest olivine in melt pools in peridotitic enclave 2512 and contain intergrowths of spinel, whose composition corresponds to that of spinel in the peridotites. This suggests that the cores of some of nephelinite olivine grains crystallized under mantle conditions.

The minimal forsterite content in olivine from mantle peridotites should not be smaller than 89.5 % (that value emerges from theoretical pyrolite composition and is supported by worldwide observations in natural enclaves, e. g. Yu et al. 2003). Since the enclave 2512 shares all other characteristics of mantle enclaves excepting olivine containing 86 % of forsterite, and contains melt pools, its olivine might have been modified by reaction with melt under mantle conditions. The enclave 2512 was heavily modified by the nephelinitic melt, whereas the other enclaves bear only small amounts of spongy clinopyroxene II, which originated due to melt penetration into peridotites.

The presented data suggest that the nephelinite melt resided before eruption in the upper mantle and penetrated interstices of peridotites. The melt induced the crystallization of spongy clinopyroxene II on the older clinopyroxene I as well as slight enrichment of olivine grain margins in Ca. The Ca content and distribution in olivine as well as occurrence and composition of spongy clinopyroxene are thus potentially reliable indicators of melt metasomatism in mantle peridotites.

Acknowledgments. I am grateful to the "Księginki" quarry owner and especially to Mr. Ryszard Miętus (Mining Section) for the help in the quarry. The study was financed by the Institute of Geological Sciences, University of Wrocław project 2022/W/ING-31 to JP.

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THE MĘCINKA BASALT (SW POLAND) - PRELIMINARY DATA

Abstract: The 21 My old basalt quarried in Męcinka (Fore-Sudetic Block, SW Poland) is a part of up to 100 m thick set of two lava flows interbedded with tuffs. Basalt matrix consists of plagioclase (An 65 cores \rightarrow An 20 margins), aluminian diopside and subordinate titanomagnetite. Olivine Fo 77 forms porphyrocrysts, locally sparse clinopyroxene porphyrocrysts occur as well. The matrix minerals compositions are similar to those of the neighbouring Winna Góra basalt, whereas the latter contains olivine phenocrysts of different forsterite content. Both basalts come probably from the same magma chamber, but from its different parts and were erupted at different stages of volcanic activity.

Keywords: Basalt, mineral chemistry, SW Poland.

INTRODUCTION

The Męcinka basalt belongs to numerous outcrops of rocks of the Central European Volcanic Province in SW Poland. The basalt occurs close to Jawor in central part of the Fore-Sudetic Block. A few km to the SE another occurrence of basalt (Winna Góra; Matusiak this volume) is located (Fig 1). Both Męcinka and Winna Góra basalts are exposed in active quarries. The K/Ar dating yielded 21.05 ± 0.5 My for Męcinka and 21.62 ± 0.93 plus 21.96 ± 1.36 My for Winna Góra (Birkenmajer et al. 2002). The Męcinka basalt was



Fig. 1. Outcrops of Tertiary basalts in the vicinity of Jawor in SW Poland (after Jerzmański 1956, simplified)

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not described in detail up to now. In this abstract we present the data on its petrography and preliminary microprobe-based description of mineral chemistry.

GEOLOGY, PETROGRAPHY AND MINERAL CHEMISTRY

The Męcinka basalt forms two lava flows, overlain and interbedded by tuffs. Tertiary sedimentary rocks, lying on the Paleozoic metamorphic schists, occur below the lower lava flow. The thickness of basaltic rocks reaches maximally 100 m (the geological data are compiled on the basis of the quarry geological documentation).

The basalt is dark- or light-gray, aphanitic with porphyrocrysts of olivine up to 2 mm in diameter. Microscope examination shows it to consist of holocrystalline plagioclaseclinopyroxene matrix with subordinate opaques (Fig. 2), embedding olivine porphyrocrysts. Scarce clinopyroxene porphyrocrysts occur in places. Fluidal arrangement of plagioclase laths occurs in the vicinity of porphyrocrysts.

The variation of basalt is due to varying size of matrix minerals, varying size of porphyrocrysts, presence/absence of red rims around olivine porphyrocrysts or occurrence of entirely reddish olivine grains, and presence/absence of clinopyroxene porphyrocrysts.



Fig. 2. BSE image of matrix of the Męcinka basalt. Plagioclase is dark- to medium-grey, clinopyroxene is brightgrey and opaques are white. Most of white grains are Timagnetite, but ilmenite occurs as well (two grains indicated by the arrows).

Chemical composition of minerals was studied at the laboratory of the Institute of Mineralogy, University of Hannover (Germany) by means of CAMECA SX100 electron microprobe working under standard conditions and applying the PAP correction procedure. The counting time for Ca was enlarged to achieve detection limit of ca. 300 ppm.

The basalt with no microscopically visible alteration of olivine was studied in detail. Porphyrocrysts of olivine are subhedral to anhedral, the latter locally strongly corroded. Typically they contain 77-78 % of forsterite, scarce grains with centres containing 84 % of Fo occur. Calcium content in olivine varies between 1000 and 2100 ppm. The clinopyroxene forms subhedral to anhedral grains of size ranging between 6 and 110 μ m (Fig. 2). It has the

composition of aluminian diopside (Mg/(Mg+Fe) = 0.7 - 0.8; Al = 0.11 - 0.27 atoms pfu, $O^{2-} = 6$) sensu Morimoto (1989). Plagioclase occurs as elongated laths of length between 100 and 20 µm (Fig. 2). It contains from 63 % of anorthite in cores to 20 % in margins. Fine Ti-magnetite grains are the most common opaque, but granular ilmenite occurs as well (Fig. 2). The Ti-magnetite is usually Cr-poor (Cr < 0.02 atoms pfu, K=3), but scarce Cr enriched (Cr ≈ 0.50 atoms pfu) grains occur too.

CONCLUSIVE REMARKS

The basaltic flow from Męcinka is located close to the Winna Góra one, which is also of basaltic composition. The age of both rocks is slightly (by ca 0.5 - 1.0 My) different and the Winna Góra basalt contains peridotitic and gabbroic enclaves and plagioclase megacrysts, which do not occur in Męcinka. The composition of matrix plagioclase (from 65 % of anorthite in cores to 20 % in margins) is similar in both rocks (for the data on Winna Góra see Matusiak, this volume), the same refers to matrix clinopyroxene. The olivine phenocrysts from Męcinka contain 77-78 % of forsterite, with sparse crystals zoned from 84 % of forsterite in cores to 77 in margins. Those from Winna Góra contain typically 70 % of forsterite, and some sparse are zoned from 85 % of forsterite in cores to 75 in margins. Thus, the matrix phases of both basalts are identical, whereas the phenocryst assemblage consists of the same minerals (olivine and subordinate clinopyroxene) but olivine has different composition in both the rocks. These data, together with approximately 3 km distance between both basalt outcrops, suggest that the Męcinka and the Winna Góra basalts come from one magma chamber, but represent different parts of that chamber, and might have been erupted during different stages of volcanic activity, as is suggested by age radiometric data.

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 JP.

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GENERAL SESSION

Robert BACHLIŃSKI¹

ELECTRON MICROPROBE U-Th-Pb DATING OF MONAZITE FROM THE KARKONOSZE-KOWARY GNEISSES (WEST SUDETES) – PRELIMINARY REPORT

Abstract: Monazite ages from Karkonosze-Kowary Gneisses were obtained with the electron microprobe U-Th-Pb method of dating. Three Th-Pb age domains were recognized: 450 ± 19 Ma, 402 ± 17 Ma and 367 ± 30 Ma. The first may correspond to regional metamorphism (?) or metasomatism (albitization) following the Cadomian orogeny. The second probably represents ultrahigh-grade metamorphism evident in the Góry Sowie Block and the Orlica-Śnieżnik Dome and the last reflects a HP metamorphic event in blueschist facies conditions in the Rychory Mountains.

Keywords: Karkonosze-Kowary Gneisses; Monazite; Electron microprobe U-Th-Pb dating.

INTRODUCTION

The rocks of granitic composition, structurally diversified, occur in the East Karkonosze Complex and are called the Kowary Gneisses (in Poland) or the Krkonoše Gneisses (in the Czech Republic). To avoid this duality of names it is suggested to use the common name Karkonosze (Krkonoše) – Kowary Gneisses (Bachliński, Smulikowski 2003). These rocks can be subdivided into four structural varieties: Kowary granites, coarse-layered and augen gneisses, medium-layered and augen gneisses, and fine-layered gneisses. The age of the intrusion has been determined by Oliver et al. (1993) and Kröner et al. (2001), using single zircon U/Pb method, as 505 to 481 Ma. The Rb-Sr study of the Karkonosze-Kowary Gneisses was reported in Bachliński and Smulikowski (2003). According to that report, the Rb-Sr whole-rock isochron based on 16 samples yields 447 ± 21 Ma and the initial ratio of 87 Sr/ 86 Sr 0.7056 \pm 0.0087.

ANALYTICAL METHOD AND SAMPLES

Monazite is a useful mineral for U-Th-Pb dating because it commonly occurs as an accessory mineral in several rock types and it contains large amounts of Th and U, has minor ²⁰⁴Pb and little elemental diffusion at high temperatures (Catlos et al. 2002). Moreover, monazite has high closure temperature (>850°C; Chernak et al. 2004) and ability to preserve multiple thermal events in elemental zones within the crystal.

In the Karkonosze-Kowary Gneisses, monazite occurs as an accessory mineral only in few from more than 20 samples. A concentrate of this mineral from one sample 548a of Kowary granite was prepared in the Kraków Research Centre, Institute of

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Geological Sciences PAS. A polished thin section was made for electron microprobe analyses which were determined by a CAMECA SX100 microprobe equipped with three WDS spectrometers in the Inter-Institute Analytical Complex for Minerals and Synthetic Substances of the Faculty of Geology of Warsaw University. CHIME (Suzuki, Adachi 1991) ages were calculated using the computer program of Kato et al. (1999). A correction factor for uranium (Scherrer et al. 2000) was not used. Th-Pb dates were plotted on relative probability diagrams using the Isoplot computer program (Ludwig 2000). To calculate domain age and error, weighted average diagrams were used.

RESULTS

60 points in 3 grains of monazite from the Karkonosze-Kowary Gneisses were analyzed. These grains are 60-80 μ m long, about 40 μ m wide, subhedral or irregular in shape and sometimes with zonation (Fig. 1). In the first grain, 21 single-spot analyses yield a weighted average Th-Pb age domain of 402 ± 17 Ma (MSWD 0.93). In the second grain, 18 single-spot analyses, and in the third grain – 21, yield weighted average Th-Pb age domains of 367 ± 30 Ma (MSWD 2.6) and 450 ± 19 Ma (MSWD 0.20; Fig. 2).

CONCLUSIONS

The oldest single-spot ages (513 Ma and 502 Ma) may represent the initial protolith crystallization of the Kowary granite and are consistent with the 505 \pm 17 Ma U/Pb zircon age reported by Kröner et al. (2001). The age of 450 \pm 19 Ma is consistent with 447 \pm 21 Ma of Bachliński & Smulikowski (2003), and may correspond rather to regional metamorphism (?) or metasomatism (albitization) than the crystallization of the intrusion. This age (about 470-440 Ma) is present in other parts of the Sudetes: Izera Massif and Orlica-Śnieżnik Dome (Bachliński 2005; Borkowska et al. 1980; 1990). The youngest age domain (the age of 367 \pm 30 Ma) represents HP metamorphic event in blueschist facies conditions (300-500°C; 0.7 – 1.0 GPa) reported by Maluski and Patočka (1997) in the Rychory Mountains by ⁴⁰Ar/³⁹Ar method on phengite. The 402 \pm 17 Ma domain probably represents ultrahigh-grade metamorphism which is evident in the western Góry Sowie Block and the Orlica-Śnieżnik Dome at c. 400 Ma by Brueckner et al. (1996), and also reported by Gordon et al. (2005) using the Th-Pb monazite ages. The youngest single-spot ages (289-303 Ma) may correspond to postmagmatic phenomena associated with the Variscan orogeny.

This study is only preliminary and in near future the author is going to analyze more grains of monazite from Karkonosze-Kowary Gneisses by electron microprobe to confirm the presented results.







Fig. 1. SEM images of individual monazite grains from sample 548a (Kowary granite) with single-spot analyses and calculated ages.



Fig. 2. Cumulative probability graphs for single-spot total-Pb ages. 'Peak' ages were calculated from weighted mean dates.

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Bogusław BAGIŃSKI¹

DIFFERENT AGES RECORDED BY ZIRCON AND MONAZITE IN CHARNOCKITIC ROCKS FROM THE ŁANOWICZE BOREHOLE (NE POLAND)

Abstract: Dating results of zircons and monazites from charnockitic rocks from Łanowicze borehole are presented. Ion microprobe analyses of zircons yielded U/Pb ages clustering at 1805±16 Ma while chemical dating on monazites provided ages at 1785±40 Ma, 1444±35 Ma and more indistinctly at 1506±40 Ma. The obtained differences are regarded to be a result of different behaviour of monazite and zircon during metamorphism.

Keywords: charnockitic rocks, zircon dating, monazite chemical dating, NE Poland.

INTRODUCTION

Zircons and monazites are the most useful minerals for age determinations in crystalline rocks, but their behaviour during the thermal history of investigated rocks is sometimes different (Williams 2001, Zeh et al. 2003). Zircons are more stable phases and widely used as geochronometers, while monazites are more sensitive on late interactions with fluids, but on the other side are more sensitive recorders than zircons, specially during thermal metamorphic events.

METHODS OF INVESTIGATIONS

The monazite crystals from selected, prepared on lead-free polishing discs, thin sections were analysed using a Cameca SX 100 electron microprobe. The analytical procedure for monazite is as follows: accelerating voltage 20 kV, beam current 50 nA; counting time (peak+background) 600 s for Pb, 400 s for U, 200 s for Th.

The X-ray lines used were UM β , Pb $M\beta$, Th $M\alpha$, Nd $L\beta$, Sm $L\alpha$, Ce $L\alpha$, La $L\alpha$, Pr $L\beta$, Gd $L\beta$, YL α . A PAP correction program was used (Pouchou, Pichoir 1991). The corrections factors were used after Scherrer et al. 2000. The calculated detection limit (2 σ) is 150 ppm for Pb and U, whereupon the absolute error is taken as 150 ppm. A systematic relative error of 2 % is considered for Th.

The standards used were crocoite (PbCrO₄) for Pb, synthetic uraninite (UO₂) for U, synthetic thorianite (ThO₂) for Th, end-member synthetic phosphates (XP₅O₁₄) for each rare-earth element (REE), YAG garnet for Y, apatite for P, and diopside for Si and Ca. As a lab inner standard, monazite crystal from pegmatite from Norway measured by SHRIMP in Canberra by Ian Williams was used.

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RESULTS

Charnockitic rocks (charnockites, opdalites and enderbites) and granites and granodiorites are the main rock types in the Łanowicze borehole – see Fig. 1 (Bagiński et al. 2001). They have been regarded as an AMCG suite member in the Mazury Complex but the latest studies (Bagiński, Krzemińska 2005) indicate that they belong to part of the crystalline basement (approx. 1,8 Ga old) and have only experienced the thermal influence of the Suwałki Anorthosite Massif (SAM).



Charnockites from the Łanowicze borehole are composed mainly of quartz, plagioclase and K-feldspar. Subordinate are biotite and hypersthene, accessories - monazite, zircon, apatite and rarely sphene. Plagioclases are often antiperthitic and myrmekites are often present. The granitic rocks do not contain hypersthene and antiperthites and myrmekites are not abundant. Boundaries between granitic and charnockitic types are not clear in the drill core.

Zircons dated from the Łanowicze borehole yielded a concordant age 1805±16 Ma (Skridlaite, Bagiński, in preparation). Additionally analogous rocks from from Lazdijai-1 borehole in Western Lithuania (Skridlaite et al. 2006) were dated at 1850±4.3 Ma and 1816±6.3 Ma (zircon cores) and 1517±11 Ma (zircon rims). The ages were determined using the Cameca IMS 1270 NORDSIM high resolution ion-microprobe at the Swed-ish Museum of Natural History.

Monazite crystals from Łanowicze show two or even three events in their history reflected by different compositions of Th, Pb and U. This is visible in BSE images (Fig. 2) – darker cores have lower Th and higher Pb contents, and brighter rims are more abundant in Th. The first event of monazite history, clearly visible in relatively big crystals (diameter above 50 μ m) as a large zone in the core (Fig. 2), was dated at 1785±40



Fig. 2. BSE images of representative monazite crystals from charnockitic rocks from the Łanowicze borehole. Choosen, representative analytical points with the calculated age are marked.

Ma. The second one, at the rim, was dated at 1445±35 Ma. Some monazite crystals from Łanowicze display additional, less pronounced zones, dated at approx. 1506±40 Ma. All results of monazite datings are calculated from microprobe chemical analyses, done using a CAMECA SX-100 at the Faculty of Geology, Warsaw University. The used computer program has been written by dr Lekki from Polish Academy of Sciences, Institute of Physics.

CONCLUSIONS

The presented results show that the ages obtained on zircons with the use of ion microprobe and on monazite based on chemical dating show not exactly the same values. The first, older magmatic stage of charnockites history is reflected in both minerals with fairly good age agreement. Monazite reflects a bit younger age what is probably connected with the slightly lower closure temperature of the latter. The next event, at approx. 1.5 Ga, has been recorded only by zircons in charnockites from Lithuania (but not in zircons from the Łanowicze borehole) and in some not clear zones in monazites from Łanowicze. This event is the evidence of thermal influence of SAM that intruded at approx. 1.56-1.52 Ga (Wiszniewska 2002). The last, third event, at approx. 1.44 Ga, recorded only by monazites, could reflect the last stages of crystalline basement formation regarded by Bogdanova (2005) as the Danopolonian orogeny. This stage is probably recorded in zircons, but very fine zones observed on the rims of the crystals, that could be the evidence, are too minute to be analysed by ion microprobe. These data indicate that even having very accurate zircon dating we can get additional information using monazite crystals, especially when the investigated rock experienced some metamorphic events.

Acknowledgments. I am grateful to dr Piotr Dzierżanowski and Lidia Jeżak from IG-MiP, Faculty of Geology, Warsaw University, for substantial help during the microprobe sessions. The research work was financially supported by National Committee for Scientific Research, project No. 3 P04D 014 23.

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FLUID INCLUSIONS STUDIES - THE ONLY KEY TO ESTIMATE THE CRYSTALLIZATION CONDITIONS OF CHARNOCKITIC ROCKS FROM SELECTED BOREHOLES FROM NE POLAND ?

Abstract: Charnockitic rocks from selected boreholes in NE Poland (Bilwinowo, Łanowicze and Wigry) have been studied in order to decipher their thermal history conditions. Application of broadly used geothermometers (feldspar ternary, two pyroxenes, hornblende-plagioclase, garnet-biotite) gave the results much lower than those typical of charnockitic rocks origin which are usually considerably above 900°C, pointing rather at the range of 700-810°C. The fluid inclusion studies revealed much higher temperatures at the range of 850-990°C. **Keywords:** charnockitic rocks, geothermometry, fluid inclusions, NE Poland

INTRODUCTION

Charnockitic rocks are:

(1) typical components of the AMCG suites all around the world (Higgins, Breemen 1996, Duchesne, Wilmart 1996, Frost et al. 2000, Bagiński et al. 2001) where they represent the most dry components of silicic members;

(2) the important constituents of many Proterozoic high grade metamorphic terranes. Under dry granulite facies conditions charnockites could be formed by metamorphism of quartzofeldspathic rocks (Bhattacharya et al. 2001) The so called metamorphic charnockites are often a result of partial melting of dry granulitic rocks (incipient charnockites) within conditions close to the granulite facies limit of temperatures reaching even 1100°C (Litvinovsky et al. 2000);

(3) the rocks that could be a result of charnockitisation process caused by CO_2 rich fluids (Kleinefeld, Olesch 2000);

(4) the main constituents of C-type magmas (Kilpatrick, Ellis 1992)

Charnockitic rocks coming from drill-cores from NE Poland are of different origins. Those coming from Bilwinowo borehole are connected with the AMCG suite (Bagiński, Krzemińska 2004) – a set of anorogenic intrusions ca. 1.51-1.54 Ga (Wiszniewska 2002) of anorthosites and associated rocks, mainly granitic (among others charnockites are important constituents). Charnockites from Łanowicze and Wigry have been dated at ca. 1.81-1.82 Ga (Bagiński 2006) and belong to the crystalline basement composed of different metamorphic rocks formed under dry granulite

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and amphibolite facies conditions. These rocks have been affected by later metamorphic events.

METHODS OF INVESTIGATIONS

All minerals used for geothermometric calculations have been analysed in thin sections using a Cameca SX 100 electron microprobe (Inter-Institutional Laboratory, Faculty of Geology, Warsaw). The analytical procedure for most of minerals was as follows: an accelerating voltage of 20 kV and a beam current 10 or 20 nA.

The standards used were natural minerals; a PAP correction program was used (Pouchou, Pichoir 1991).

Two kinds of inclusions have been studied. Polycrystalline inclusions have been investigated by quenching method described by Kozłowski (2003), while those with fluids by use of the procedure given by Roedder (1984). Inclusions have been studied in plagioclase (the main host mineral studied), orthopyroxene and in quartz.

RESULTS

In order to reconstruct thermal history of charnockitic rocks the set of common geothermometers has been used. The computed temperature results are presented in Table 1.

Borehole	Rock type	Thermometer						
		Biotite ¹	Hbl-plg ²	Gar-bio ³	Gar-opx ⁴	Cpx- opx ⁵	feldspar ⁶	
Bilwinowo	char. mang.	730- 810	780-810	400-450 610-640	560-650	645-700	<700 920 (one point only)	
Łanowicze	char. gdio.	750- 800		515-805 540-680			<700	
Wigry	char.	720- 750	770-790	510-580				

Tab. 1. Calculated temperatures yielded by various thermometers (°C)

¹Ti in biotite thermometer (Henry et al. 2005); ²hornblende-plagioclase thermometer (Blundy, Holland 1990), ³garnet-biotite thermometer (Ferry, Spear 1978), ⁴garnet-orthopyroxene geothermometer (Aranovich, Berman 1997), ⁵clinopyroxene-orthopyroxene thermometer (Fonariev, Graphikov 1991), ⁶ternary feldspar thermometer (Elkins, Grove 1990); char. – charnockite, gdio – granodiorite, mang. – mangerite.

Melt inclusion studies in charnockitic rocks in samples, coming from the boreholes: Bilwinowo, Łanowicze and Wigry, have indicated higher temperatures of homogenisation in all the studied samples (63 polycrystalline inclusions have been studied) than the results calculated by geothermometers. Detailed results are presented in Table 2. All the 49 studied fluid inclusions have contained considerable volume of CO_2 (from 30 to 100 %, mostly more than 70 %), N₂ and CH₄.

Borehole	Pools type	Inclusion in				
	коск туре	plag	opx	Q		
Bilwinowo	charnockite, Q mangerite	850-990 950-960	945-960	890-895		
Łanowicze	charnockite	875-955				
Wigry	charnockite	905-940	970-990			

Tab. 2. Measured temperatures (in °C) of inclusions homogenisation in charnockitic rocks.

CONCLUSIONS

The measured temperatures of homogenisation of the polycrystalline inclusions display most probably temperatures of the studied rocks crystallisation. The narrow range of homogenisation temperatures for quartz and orthopyroxene comes from the fact that these minerals have been not friendly hosts for fluid inclusions in the contrast with the plagioclase where wide range of the crystallisation temperatures has been displayed.

Considerably lower range of temperatures obtained from geothermometers could be the result of later reequilibration, although there are remains of the higher temperature equilibrium recorded in feldspars (see Table 1) close to temperatures yilded from fluid inclusions. The lower temperatures obtained by different geothermometers are probably the equilibrium temperatures attained during the later metamorphic events. The first one was thermal influence of anorthosite (and associated rocks) and the second one regarded by Bogdanova (2005) as Danopolonian orogeny. Both events have been recorded by monazite crystals from these rocks (Bagiński 2006).

Acknowledgments. We are grateful to Dr Piotr Dzierżanowski and Lidia Jeżak from IGMiP, Faculty of Geology, Warsaw University, for their substantial help during the microprobe sessions.

The research work was financially supported by National Committee for Scientific Research, project No. 3 P04D 014 23.

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PETROLOGY OF GRANITOIDS FROM THE POLISH PART OF THE STARÉ MĚSTO ZONE (SUDETES, SW POLAND) – PRELIMINARY RESULTS

Abstract: The Bialskie granitoids are peraluminous, high potassic with calc-alkaline affinity and are mostly classified as granodiorites. They are mylonitized to a different degree, zones of different strain are present. The presence of syndeformational chlorite and prehnite suggests that the mylonitization took place under the conditions corresponding to those of greenschist and subgreenschist facies. Numerous kinematic indicators document a non-coaxial character of deformation with the top-to-NE sense of shear. The depth of crystallization of the Bialskie granitoids was estimated at 5.5-7.0 kbar, whereas temperature of solidus at 740-765°C. **Keywords**: Staré Město Zone, Bialskie granitoids, geothermobarometry, deformation.

INTRODUCTION

The Staré Město Zone is located directly west of the Ramzova Thrust, marking the boundary between East and West Sudetes (NE Bohemian Massif). This Unit is the lowermost part of the Orlica-Śnieżnik Dome (West Sudetes), and consists of NE-SW trending lithologies (Parry et al. 1997, Štipská et al. 2001).

The top of the Staré Město Zone consists of volcano-sedimentary Hraničná unit, with underlying myllonitized gabbros. The leptyno-amphibolite complex occurs below. It was intruded by syntectonic, Variscan intrusion, dated on 339±7 Ma (Parry et al. 1997). The lenses of serpentiznized spinel peridotites occur at the base of the Staré Město Zone, marking the exact boundary between East and West Sudetes.

Small part of the Staré Město Zone is exposed in Poland, in the vicinity of Bielice (Bialskie Mts.). The Bialskie granitoids crop out as two elongated bodies. The northern one – along Kowadło-Płoska hills, and southern one - along Pasieczna-Uroczysko hills, tectonically separated by the Bialski Fault (Fig. 1). The petrography of Bialskie granitoids was previously studied by Smulikowski (1958), Borkowska (1959), Kasza (1964), Wierzchołowski (1966), Wichrowski (1973). Since the seventies, no papers on Bialskie granitoids were presented. Therefore, this paper outlines their petrography and mineral chemistry, in conjunction with microstructural observations.

RESULTS AND DISCUSSION

The petrology of granitoids cropping out within the northern body has been investigated. The Bialskie granitoids are medium- to coarse-grained. Their main constitu-

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ents are: quartz, plagioclase and K-feldspar, plus amphibole, biotite as subordinates. Accessories are pyroxene, apatite, titanite, zircon. Scarce chlorite, prehnite, epidote, and calcite are secondary phases.



Fig. 1. Geological sketch map of the Polish part of the Stare Město Zone with adjacent areas (modified after Bartz 2004).

The Bialskie granitoids are heterogeneously deformed, and exhibit mylonitic foliation of variable intensity. They are converted to mylonite within high-strain zones, located close to the contact with their metamorphic cover. Towards the centre of the intrusion, the intensity of mylonitization decreases. Locally magmatic structure is preserved in the low-strain areas. High strained granitoids exhibit strong grain-size reduction with recrystallized quartz ribbons and numerous feldspar porphyroclasts preserved. The S-C fabric is commonly observed. The C-surfaces appear as thin layers of polymineralic and recrystallized aggregate, whereas S-surfaces are defined by orientation of elongated biotite or amphibole aggregates. The C'-surfaces are less common, corresponds to structures developed within feldspar porphyroclasts such as extensional fissures filled with quartz, plagioclase, chlorite or displaced broken grains. The σ_b – assymetric feldspar tails occur in high strained granitoids. All of these kinematic indicators consequently show a top-to-NE sense of shear. The mylonitic foliation dips at low angles to NE and NW, bearing weak subhorizontal stretching lineation, which are concordant with the same structures observed in granitoids metamorphic cover (Bartz 2004).

The Bialskie granitoids plot in the granodiorite field on the QAP diagram. They are peraluminous, with silica content ranging from 54.19 wt % to 58.93 wt %. Points cluster in the high potassic field on the SiO₂ vs. K₂O diagram. The Peacock's (1931) alkali-lime index indicates the Bialskie granitoids belong to the calc-alkaline suite. The content of major elements tends to decrease with increasing SiO₂, excluding K₂O.

Plagioclase and K-feldspar form two kinds of grains: large porphyrocrysts (up to 2.0 mm) and small ones (below 0.5 mm). The small plagioclase is typically normally zoned, containing from 31-36 % anorthite in cores to 29-33 % in rims, whereas the large ones exhibit complex zonation. Cores depleted in anorthite content (34-36 %) are surrounded by mantles richer in anorthite (37-39 %). Subsequently, anorthite content decreases towards rims (31-33 %). K-feldspar is homogenous, and contains up to 10% of albite.

The biotite and amphibole commonly occur as elongated aggregates, squeezed between leucocratic minerals, or sparsely as single crystals. Intergrowths of small biotite, quartz and titanite within amphiboles typically occur. Amphibole has the composition of tschermakite (Leake et al. 1997), showing weak zonation, with Si content increase from cores (6.3 Si⁴⁺ a.p.f.u.) towards rims (6.5 Si⁴⁺ a.p.f.u.). The aluminium content in amphibole points to crystallization pressure ranging between 5.0-7.0 kbar (Hammarstrom, Zen 1986, Hollister et al. 1987, Schmidt 1992).

The solidus temperatures were estimated using hornblende-plagioclase geothermometer (Holland, Blundy 1994, Dale et al. 2001) which yields values ranging from 740 to 765°C. The biotite is often rimmed by chlorite, or entirely chloritized. It is characterised by slight increase of the Fe/(Fe+Mg) ratio and Al^{IV} from 0.40 to 0.45, and 2.4 to 2.7 a.p.f.u. respectively.

Homogenous diopside ($Wo_{45.49}En_{36.37}Fs_{15.18}$) occurs as small relics inside the large amphibole crystals. Secondary prehnite, epidote and calcite fill fissures.

The Bialskie granitoids contain abundant, oval-shaped enclaves of amphibolitic or scarce gneissic composition. Their size varies from centimetres in diameter to elongated ones, tens centimetres long. The elongation of enclaves is always parallel to observed mylonitic foliation.

Acknowledgements. The study was supported by research grant No 2022/W/ING/ 04-4. Critical comments of prof. Jacek Puziewicz improved the final version of manuscript, what is acknowledged.

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MINERALOGICAL CHARACTERISTIC OF ANCIENT MORTARS FROM THE HENRYKÓW ABBEY IN VIEW OF THEIR CONSERVATION

Abstract: Mortars from the western façade of the Henryków Abbey have been studied, concerning mineralogy of binder, as well as aggregate. Different phases were identified, using petrographical analysis, X-ray diffraction and Differential Thermal Analysis. Binder is a mixture of carbonates and variable quantities of gypsum. Four main aggregate types were distinguished: 1) crushed marble (calcite grains), 2) sand, 3) limonite (ochre), 4) charcoal. The binder/aggregate proportion ranges from 1:1 to 1:3. The design of restoration mortars could be proposed, with regards to mineralogy of studied samples.

Keywords: ancient mortars, petrography, Henryków Abbey, X-ray diffraction, differential thermal analysis.

INTRODUCTION

We present data on mortars from the western façade of the Henryków Abbey. Ancient recipes of preparation of lime mortar are almost completely lost, because of increasing use of modern cement-based one, since XIX century (Degryse et al. 2002). The latter applied as restoring mortar frequently exhibits incompatibility in mechanical proprieties, as well as aesthetics, with old masonry (Maravelaki-Kalaitzaki et al. 2003). Therefore present work is an attempt of restoring original technology, which play a crucial role in successful restoration and conservation of monuments.

SAMPLES AND METHODS OF INVESTIGATION

Five samples of mortars representing different decorative details were obtained from the western façade of the Henryków Abbey, in order to show characteristics of material. Detailed descriptions, as well as location of samples are shown in Table 1 and Figure 1.

Each sample was cut into two slices. The first one was used for preparation of thin section. Due to high porosity and friability all samples were impregnated with canadian balsam before polishing. Thin sections were investigated in transmitting light. Due to limitation in sampling of mortars and resulting small quantities of samples, sieve analysis was not applied. Instead, the aggregate/binder ratio and porosity were determined by planimetry. The second slice was pulverized and examined by X-ray powder diffraction (XRD, CuK_{a}) radiation. Additionally, the differential thermal anal-

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ysis (DTA) was performed for one sample. The temperature was raised at constant rate (10°C/min.), from ambient temperature up to 940°C.

Sample	Description and loca- tion	Colour	Aggregate type*	Binder/aggre- gate ratio
H1	decorating detail (leaf), pediment of window (ground floor)	cream	<u>calcite</u> + sand	3:1
	decorating detail, field	inner layer: grey	<u>charcoal</u> + sand	1:1
H2	of pediment of window (1 st floor)	outer layer: cream	calcite + sand	1.5:1
	fragment of frieze finial	inner layer: grey	<u>charcoal</u> + sand	1:1
H3	cornice of façade	outer layer: cream	<u>sand</u>	3:1
H4	framing of pediment of window (1 st floor)	reddish	ochre + sand	1:1
H5	red area in scrollwork, finial of window (2 nd floor)	reddish	ochre + sand	1:1

Tab. 1. Characteristics and description of mortars from the western façade of the Henryków Abbey.

* - dominant phase is underlined

PETROGRAPHY

Thin section analysis indicates the mortars are strongly inhomogeneous. They are characterised by very fine-grained binder mass, composed mostly of calcite and gypsum (Tab. 2). The appearance of numerous pure, microcrystalline calcite aggregates (lumps of inhomogenized slaked lime in binder mass) and lack of gypsum ones, implies that carbonates are dominant component, whereas sulphates are subordinate ones. This stays in good agreement with XRD data, suggesting considerable amount of gypsum for few samples (inner layer of sample H2 and H3, sample H5; Tab. 2). The predominance of calcite over gypsum is also evidenced by DTA analysis, performed for sample H5. It shows very strong weight loss, combined with endothermic peak at 830°C (due to decomposition of carbonates), and similar reaction, weakly expressed at temperature range 120-200°C (due to dehydration of gypsum).

The XRD patterns, as well as microscopic observations reveal, that aggregate comprises different components (Tab. 1, Tab. 2). It is mainly composed of calcite grains, in sample H1 and outer layer of sample H2 (Tab. 1). Numerous grains of quartz with subordinate feldspars and fragments of crystalline rocks (gneisses and granitoids) were found in large number of samples (H4, H5, and inner layer of samples H2 and H3, Tab. 1). Few samples (H4, H5) contain rounded, red limonite (ochre) aggregates (Tab. 1). They exhibit very strong relief, comparing to quartz, and very strong birefringence – typical features of goethite. Although, the latter was not identified by XRD analysis due to weak crystallinity of limonite aggregates, it reveals presence of clay minerals. They are typical constituent of ochre (Bolewski 1993) as well as organic filaments (plant roots?), which were found embedded in binder mass, within samples H4 and H5. The DTA pattern of sample H5 shows endothermic peak at 300°C, which may be attributed to dehydration of poorly crystallized hydrogoethite (Borkowska, Smulikowski 1973). Typical, well crystallized goethite, dehydrates at temperature, 400°C (op. cit.)

Tab. 2. Results of XRD analyses of mortars from the western façade of the Henryków Abbey. Mineral abbreviations after Kretz (1983).

Sample		cal	qtz	fds	gy	ms	chl	mm	goe
H1		+++	+	+	-	?	-	-	-
H2	inner layer	++	++	+	+	-	?	-	-
	outer layer	+++	+	-	?	-	-	-	-
Н3	inner layer	+++	++	+	+	-	?	-	-
	outer layer	+++	+++	+	_	?	-	-	_
H5		+	+++	+	++	-	?	+	?

+++ dominantly present

++ present

not resentpossibly present





The aggregate of inner layer of samples H2 and H3 is composed of numerous black-coloured particles. This phase is difficult to identify, both by XRD and optical microscopy. Their non-magnetic proprieties preclude employment of forge scale. It presumably represents a charcoal (Tab. 1), which was found within numerous ancient mortars and plasters (Bani-Hani, Barakat 2006).

The granulometric characterization of aggregate typically indicates a predomination of grains smaller than 1.0 mm. A few grains of diameter up

Fig. 1. Western façade of the Henryków Abbey with location of analysed samples.

to 1.8 mm were found. The binder/aggregate ratio is strongly variable, with no respect to their mineralogy (Tab. 1). Typically, it was found around 1:1, however a few samples reveal more binding material, resulting in 3:1 ratio (Tab. 1).

FINAL REMARKS

Four different types of aggregate were distinguished: 1) crushed marble (calcite grains), 2) sand, 3) limonite (ochre), 4) charcoal. The occurrence of aggregate composed of calcite, imply that it was most likely prepared by crushing marble and employed in order to enhance mortar's strength and frost resistance (Degrysse et al. 2002). The presence of ochre (limonite aggregates) may be considered as a result of addition of meadow ore, which plays a role of colorizing agent. Binder was prepared by mixing non-hydraulic calcium sulphate semi-hydrate and slaked lime, in variable proportion. The latter was prepared by calcinations of pure limestone, with no clay minerals. The hydraulic phases, like belite (larnite) C_2S , alite (hatrurite) C_3S and particularly gehlenite C_2AS , are formed during calcinations from clay minerals (Callebaut et al. 2001), nevertheless they were not found within the investigated samples.

Acknowledgements. This research was supported by grant 1017/S/ING/06-II/WB. The authors would like to thank to dr Czesław August and mgr inż. Wiola Raczek for performing DTA and XRD analyses, respectively. Prof J. Puziewicz is greatly acknowledged for his comments, which improved earlier version of this manuscript.

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KALINKA TONALITES – PETROGRAPHY AND GEOCHEMICAL CHARACTERISTIC (STRZELIN CRYSTALLINE MASSIF, SW POLAND)

Abstract: The Variscan Kalinka tonalite dyke (Strzelin Massif, SW Poland) is characterized by similar incompatible element patterns and range of trace elements contents depending on the position in dyke. The composition of minerals in dyke is variable Tonalite dyke was emplaced at shallow crustal levels (2-3 kbar), probably in several (at least two) pulses. **Keywords:** Kalinka tonalite, SW Poland, geochemistry, mineral composition.

INTRODUCTION

The Strzelin Crystalline Massif is an isolated fragment of the Variscan basement exposed in the eastern part of Fore Sudetic Block (SW Poland). Granodiorites, quartz diorites and tonalites, biotite granites and two mica granites form small bodies, mostly stocks and flat dykes, within metamorphic rocks (Oberc-Dziedzic 1999).

Kalinka tonalite occurs in the small outcrop in the Kalinka Hill (Bereś 1969) and was drilled in borehole Dobroszów-2 (Db-2) located near the Dobroszów village, 2 km to the south from the outcrop. In this paper the petrography and geochemistry of the tonalites from the borehole Db-2 are described.

METHODS

Chemical compositions of major minerals were determined using a Cameca SX100 at the electron microprobe laboratory of the Warsaw University (working under standard conditions). Whole-rock analyses of major and trace elements were performed at Activation Laboratories Ltd. and Acme Analytical Laboratories, Canada using ICP-MS techniques.

FIELD RELATIONSHIPE

The borehole Db-2 crosscuts the tonalite dyke (62 meters thick) at depths from 125 m to 187 m. The dyke is heterogeneous and forms two varieties of tonalite (dark and light with sphene). The contact between these two tonalites is sharp and irregular. Small veins of pegmatite occur in the central part of the dyke. The tonalite from borehole is similar to the Kalinka tonalite occurring on the surface.

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PETROGRAPHY

Five samples of Kalinka tonalite from borehole Db-2 (from depths 127 m, 137 m, 141 m, 143 m and 181 m) were analyzed.

The Kalinka tonalite is grey, fine- to medium-grained, consists of plagioclase, biotite, quartz, amphibole and K-feldspar. Mafic minerals and feldspar grains are clustered. Occasionally, some amphiboles contain a relic clinopyroxene. Apatite, sphene and scarce zircon are accessories. Calcite is the product of alteration of pyroxene.

Two types of plagioclase are observed in all investigated samples: (1) large (up to 1.5 mm) euhedral plagioclase exhibiting complex internal structures (Fig. 1) and (2) smaller (up to 1 mm), normally zoned (35-25 % An) plagioclase. The first type consists of core rich in An (53-68 % An), normally zoned mantle (53-35 % An) and rim (32-25 % An). The An content in core varies with position (depth) in dyke. Plagioclase from upper part of the dyke (127 m) is most anorthite rich (up to 67 % An), the lowest An content in mantles and rims is similar for plagioclase from all depths. The boundary between mantle and rim is strongly embayed (Fig. 1). The embayments contain biotite, hornblende and plagioclase with An content <40 %. The An content in the rim is almost constant (within 3 % of An) in individual grains but varies depending on the grain. The K content in plagioclases increases with decreasing An.



and corresponding traverse showing anorthite content

Biotite and amphibole form irregular clusters or occur as individual grains. The Ti in biotite varies from 0.35 to 0.57 p.f.u. with maximum content occurring in biotite from the uppermost part of the dyke (127 m). Tetrahedral aluminum varies from 2.42 to 2.55 a p.f.u., again the highest values are in biotite from 127 m. The mf ratio $(Mg/(Mg+Fe^{2+}))$ varies from 0.36 to 0.47 and the extreme values occur in tonalite from central part of the dyke (respectively 153 m and 141 m).

Amphibole consists of Mg-hornblende/Fe-hornblende cores (Mg/(Mg+Fe²⁺) varying from 0.45 to 0.6) and actinolite/Fe-actinolite rims (Mg ratio is 0.48-0.66). The amphibole from middle (153 m) and the lowest (181 m) parts of the dyke has maximum contents of Ti (0.22 at p.f.u.) and Al tot (1.8 at p.f.u.), whereas the minimum is characteristic for the 137 m depth. The relics of diopside $(Wo_{47-50}En_{28-33}Fs_{16-23})$ occur sometimes within amphibole (only at 137 depth).

The temperature estimated by Holland and Blundy thermometer (1994) is 600-660°C. The pressure calculated from Al-in-hornblende (Anderson et al. 1995) for assumed average temperature 800-900°C is 2-3 kbar.

GEOCHEMISTRY

Four samples of Kalinka tonalites were analyzed (from depth 141.5 m, 153 m, 167.3 m, 182 m, Tab. 1).

Table 1. Geochemical composition of investigated tonalites. Values normalized according to Boyton (1984).

element	sample	D141.5	D153	D167.3	DB182
SiO ₂	%	59.23	55.34	55.85	57.96
Al ₂ O ₃	%	17	17.42	17.45	15.29
Fe ₂ O3	%	6.59	8.12	7.56	6.22
MgO	%	3.18	2.72	3.43	2.91
CaO	%	5.7	6.13	5.84	8.9
Na ₂ O	%	3.37	3.42	3.7	2.71
K ₂ O	%	2.34	3.09	2.61	1.86
TiO ₂	%	1.07	1.73	1.67	1.311
P ₂ O ₅	%	0.36	0.59	0.48	0.54
MnO	%	0.09	0.11	0.11	0.108
Ba	ppm	543	1015	663.9	507.1
Υ	ppm	28.8	39.2	30.6	29.86
Rb	ppm	69.9	82	68.2	52.94
Sr	ppm	338	473	509	456
Nd	ppm	44.8	56.5	47.7	52.6
Yb	ppm	2.35	3.18	2.43	2.79
Zr	ppm	351	412	311	369
(Tb/Yb) _N		2.05	2.08	1.98	1.83
Eu*		0.77	0.75	0.75	0.84
(La/Lu) _N		15.17	11.98	13.99	16,29

All analysed samples are calcic and metaluminous. No obvious correlation between SiO_2 and other major elements is observed. Tonalites have relatively high abundances of Yb (from 2.35 to 3.18 ppm), low abundances of Sr (317-509 ppm) and low values of Sr/Y, Sr/Nd, Zr/Y and (Tb/Yb)_N (Tab. 1). Analyses show range of compositions in trace element contents, again it seems that no mutual relationships between SiO₂ and

trace element and between two trace elements exist. However, despite the observed variability of trace element contents, the incompatible element patterns are similar for all samples and characterized by Pb, Ti and slight Nb negative anomaly as well as by LILE enrichment.

Chondrite-normalized rare earth element (REE) patterns (Boynton 1984) are characterized by similar moderate concave-upward shapes. The negative Eu anomaly is relatively low (0.69-0.94). The magnitude of the negative Eu anomaly is not dependent on the SiO₂ content.

CONCLUDING REMARKS

The range of trace element concentrations and lack of correlation between mineral composition and whole rock geochemistry with position in the dyke suggest that dyke was not formed by single injection and cooling from margins to the center. Differences in An content in plagioclase cores occurring in rocks of similar major element chemistry may indicate different conditions of crystallization at different levels in the dyke (e.g. water content in magma). Since the variability is observed in early crystal-lized plagioclase cores it is not plausible that such a differentiation occurred at the emplacement level. Therefore, the dyke might have been formed by several pulses of magma from deeper seated differentiated magma chamber. It is also supported by the presence of embayments in plagioclase indicative of decompression melting after crystallization of plagioclase cores (Nelson & Montana 1992, Pietranik et al. 2006).

Acknowledgements. This work was supported by grants: 2022/W/ING/05 – 47 and 4827/PB/ING/04.

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PETROGRAPHY OF THE KUDOWA-OLEŠNICE GRANITOIDS (SW POLAND) AND P-T CONDITIONS OF ITS EMPLACEMENT – PRELIMINARY REPORT

Abstract: Meso- and microstructural analysis and chemistry of minerals in granodiorites and wall rocks indicate the conditions of empalecement and contact metamorphism of the Kudowa-Olešnice to be 7.5 kbar and 600°C. These results are in very good agreement with conditions established for D3 metamorphic event in the Stronie formation.

Keywords: Bohemian Massif, Stronie formation, granitoids, conditions of emplacement.

INTRODUCTION

The 80 km² Kudowa-Olešnice (K-O) massif is one of a group of 4 rather small Variscan granitoids bodies which occur approximately along the boundary between Orlica-Śnieżnik Dome and the Nové Město series. This boundary zone is recently interpreted by Mazur et al. (2005) as a Teplá-Barrandian/Moldanubian terrane boundary and granitoid bodies, according to these authors, play the role of stitching plutons. The western and northern border of the massif with Nové Město series, Permian and Upper Cretaceous sedimentary cover is tectonic. A sharp deformation gradient involving both brittle and crystal-plastic processes occurs within the marginal parts of the massif, at the contact with the phyllites of the Nové Město series. On other sides massif is mantled by Stronie formation series. Dykes and sills of more basic type of granitoids are abundant in the marginal part of Stronie series, especially near Lewin Kłodzki. The dykes and sills range in width from a few centimeters to ~ 3 m. The age of K-O granite is constrained by a Rb-Sr whole rock age of 331±11 Ma (Bachliński, 2000).

Since the work of Petrascheck (1909) rocks of the K-O massif have been traditionally divided into two main petrographic types: (1) grey, medium-grained basic type of biotite granodiorite, (2) red, fine- to medium-grained acid type of granodiorite. Petrographic description of both varieties can be found in papers by Gierwielaniec (1957), Borkowska (1959), Domečka & Opletal (1974), and Żelaźniewicz (1977). The main goal of this project is to determine the emplacement conditions of the pluton and relate these results to known tectonic events that have affected the region.

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METHODS OF INVESTIGATION

The samples were collected from the basic type of granodiorites dykes south of Lewin Kłodzki, between villages Lasek Miejski and Zimne Wody. Five thin sections from samples taken directly from the contact between granodiorites and mica-schists were used in order to establish P-T conditions of emplacement/contact metamorphism. Electron microprobe examinations were carried out with a CAMECA SX100 instrument at the Faculty of Geology, Warsaw University.

RESULTS

Relationship between pluton emplacement and deformation can be unravelled analysing the structural features found in and around plutons. One of the best criterions providing evidence for deformation during emplacement and crystallisation are microstructures testifying for continuous transition from magmatic- to high-temperature solid-state deformation. Macroscopically visible foliation in the granodiorites is defined by flat faces of feldspar and oriented biotite, but is diffuse and irregular. The microstructural evidence suggests that early stages of deformation involved fracture of feldspars grains. Further deformation led to increased entrainment of biotite into microfractures, which became microshear zones, which coalesced to form a foliation. Large igneous biotite grains were destroyed and smeared along developing folia. Evidence for weak ductile deformation can be found throughout the pluton, including undulatory extinction in quartz, mechanical twins in plagioclase, myrmekite in Kfeldspar, quartz-quartz grain boundary migration and variable deformation of biotite. In places, plagioclase grains show undulose extinction, deformation bands, tapered deformation twins and bent crystals, all characteristic of ductile deformation. Many of the K-feldspar crystals are microcline and lie in the foliation plane with plagioclase. The microcline grains have cross-hatch twinning, some development of flame perthite, and poikilitic inclusions of unstrained plagioclase, biotite, and guartz.

Evidence for fracturing and alteration is also present throughout the pluton. These fractures cut across all igneous mineral, and are locally occupied by white mica, chlorite, and epidote. The fracturing and alteration in the pluton may have been associated with later faulting.

Two types of structures interpreted as submagmatic (the term "submagmatic" is used here to mean a stage of crystallization with less than the critical amount of residual melt that is necessary for magmatic flow; Vernon 2000) occur in the K-O granodiorites. (1) Plagioclase show magmatic zonation with cores being An_{31} and rims An_{19} . Some of these grains are considerably deformed and shows subgrains and coarse recrystallization by subgrain rotation. In subgrain and recrystallized grains, anorthite contents are slightly lower but overlap with those in marginal, undeformed parts of the phenocrysts. This suggests that p-T conditions during plastic deformation was approximately the same as during late-magmatic growth of the phenocryst, (2) quartz and feldspar filled fractures in plagioclase indicate that the solid-state deformation occurred with migrating melt still present (Fig. 1). Deformation under high

to moderate temperatures is suggested by grain boundary migration recrystallization in quartz aggregates and by myrmekites (Simpson 1985). There is a good geometric coherence among micro-structures in granodiorites and microstructures described by Szczepański (2001) as D_3 in host rocks.



Fig. 1. Photomicrograph showing fractured plagioclase as evidence of high strain rates and formation of magmatic quartz in the fracture.

Temperatures for the igneous feldspars at the emplacement levels, at or near solidus conditions, were calculated using different ternary solution models by means of the SOLVCALC computer program (Wenk and Nekvasil 1994). The resultant temperatures in different samples are from 570°C to 640°C (mean c. 620°C). Temperature obtained using this method was then compared with thermo- and baro-metric estimates obtained from wall rocks. Measurements were carried out on mineral pairs, which share grain boundaries. Two geothemometers, garnet-biotite (Holdaway 2000), and plagioclase-muscovite (Green &Usdansky 1986) and the GPMB geobarometer (Hoisch 1990) were applied to constrain the conditions of growth of host rocks minerals occurring directly on the contact with granodiorites. Obtained results, temperature c. 600°C and pressure c. 7.5 kbar are in very good agreement with results received by Szczepański (2006) for D_3 deformation event in mica-schists.

CONCLUSIONS

Parallelism of microfabric, similar metamorphic grade all suggests that D_3 in the mica-schist and microstructures in granodiorites was more or less coeval. The D_3 event was probably already under way before the K-O granodiorites intruded, but it continued until the submagmatic stage of the granites

Acknowledgements. The study was supported from a research grant No 2022/W/ING/04.

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GEOCHEMISTRY AND PETROLOGY OF TONALITE AND GRANODIORITE FROM STRZELIN CRYSTALLINE MASSIF (SW POLAND) – COMPARISON

Abstract: Tonalites from northern (the Gęsiniec Intrusion), central (the Kalinka Tonalite) and southern (borehole material from Jasienica, Bożnowice) parts of the Strzelin Massif (SW Poland) have similar mineral and chemical composition. Tonalites from Gęsiniec and Jasienica are associated with biotite granodiorite. Chemical composition of tonalites and granodiorites suggests that they were derived from different sources. Granodiorite from Bożnowice and Dębowiec differ by higher Sr contents and lack of Eu anomaly from Gęsiniec and Jasienica granodiorite suggesting involvement of plagioclase during melting in the source or as cumulate phase.

Keywords: tonalite, granodiorite, trace elements, mineral composition.

INTRODUCTION

The metamorphic basement of the Strzelin Massif was intruded by Variscan granitoids including biotite granodiorites, biotite-hornblende granodiorites, biotite-hornblende tonalites, quartz diorites, biotite granites and two-mica granites (Oberc-Dziedzic 1999). Granitoids form isolated, small bodies, mostly stocks and dykes, up to tens of meters thick, within metamorphic rocks. However, several larger intrusions (from 0.1 to 1 km²) occur. The largest ones are located in the northern and middle parts of the massif. These are: the Strzelin granite, the Gęsiniec tonalite-diorite, the Gębczyce and Gromnik granite and the Kalinka tonalite (Oberc-Dziedzic 1991, 1999).

In this abstract we compare tonalites, diorites and granodiorites from the Gęsiniec Intrusion, the Kalinka tonalite (borehole material and samples from exposures) and tonalites and granodiorites drilled in the southern part of the Strzelin Massif (Bożnowice, Jasienica, Dębowiec).

ANALYTICAL METHODS

Whole rock trace element contents were measured by ICP-MS (Geological Institute Copenhagen and ACME laboratories). The results of this study are based on: 9 samples of the Gęsiniec bt-hbl tonalite, 6 of the Kalinka bt-hbl tonalite, 2 of Bożnowice bt-hbl tonalite, 1 of Jasienica bt-hbl tonalite, 2 of Dębowiec bt-hbl granodiorite, and

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1 sample of each Gęsiniec bt granodiorite, Jasienica bt granodiorite and Bożnowice bt-hbl granodiorite.

FIELD RELATIONSHIPS

The contact between biotite granodiorite and biotite-hornblende tonalite is observed in the Gęsiniec Intrusion and in the borehole material from Jasienica and Kalinka. The contact is usually sharp but irregular. Contacts observed near the wall of the Gęsiniec Intrusion suggest intrusion of tonalite-diorite magma into unconsolidated granodiorite (Pietranik 2006). Back veining of granodiorite into quartz diorite is observed in Gęsiniec and similar structures occur in the Jasienica and Kalinka tonalite (borehole material). The described field evidence suggests interaction between two magmas and contemporaneous intrusion of granodiorite and tonalite with granodiorite probably representing the first pulse. However, granodiorite dykes crosscutting tonalite also occur in the Gęsiniec Intrusion (Oberc-Dziedzic 1999, Pietranik et al. 2006).

TONALITES - PETROLOGY AND GEOCHEMISTRY

All types of tonalite and quartz diorite described below are hornblende and biotite bearing. Remnants of clinopyroxene were found in Gęsiniec (Oberc-Dziedzic 1999) and Kalinka (Bereś 1969). Two main types of tonalite occur: the melanocratic one, dominated by amphibole and biotite and the leucocratic one, dominated by plagioclase.

All tonalites are metaluminous (ASI: 0.76-0.94). SiO₂ content varies from 52 to 64 wt %, Na₂O content is low and varies from 1.49 to 3.7. No clear linear trends are observed, either in Harker (silica versus major and trace elements, Fig. 1), or in trace element versus trace element diagrams (Fig. 1). Differences in trace element contents occur not only between melanocratic and leucocratic types but also within types between samples of similar mineral modes. REE patterns are characterized by moderate LREE enrichment (Fig. 1) and Eu anomaly (Fig. 1). Leucocratic types are enriched in Sr and have Eu anomalies (Eu/ $\sqrt{(Gd^*Sm)}$) higher than melanocratic types (Fig. 1) in accordance with higher plagioclase content.

GRANODIORITE - PETROLOGY AND GEOCHEMISTRY

The Gęsiniec granodiorite and the Jasienica granodiorite are fine-grained and biotite-bearing, K-feldspar is anhedral and late in crystallization sequence, whereas the Bożnowice granodiorite and Dębowiec granodiorite are biotite-hornblende-bearing and contain large (up to 1 cm), euhedral K-feldspar. Granodiorites are metalumionous to peraluminous (ASI: 0.87-1.12). They contain 65 –73 wt % of SiO₂. Geochemically, granodiorites differ from accompanying tonalites by higher Th, Ba and Rb and lower Y, Yb, V, Ti, Sc and Nb contents (Fig. 1). Bożnowice and Dębowiec granodiorites have much higher Sr content and smaller Eu negative anomaly than those of Gęsiniec and Jasienica (Fig. 1).



Fig. 1. Whole rock geochemistry of tonalites (black) and granodiorites (grey) from the Strzelin Massif. La/Lu and Eu anomaly are normalized to chondrite after Anders & Grevesse (1989).

CONCLUSIONS

The geochemical characteristic of tonalites (quartz diorites) and granodiorites from the Strzelin Massif is significantly different. Lack of linear trends in element versus element diagrams, despite continuous decrease in Si content, suggests that granodiorites are not related to tonalites by simple fractional crystallization process. Tonalites and quartz diorites have too low SiO₂ and Na₂O and too high MgO contents to be derived solely from crustal source e.g. lower, amphibolitic crust. Therefore, they are probably derived from sub-continental enriched mantle. On the other hand, low Y, Yb, V and Sc contents in all granodiorites strongly suggest derivation of granodiorites from garnet-bearing crust. Similar conclusions were given in Pietranik & Waight (submitted) based on data set from the Gęsiniec Intrusion. Composition of tonalites from central and southern parts of the Strzelin Massif coincidences with that from Gęsiniec. That suggests, that all tonalites evolved by common differentiation processes. However, large scatter in chemical composition of these rocks may indicate that more than one process is responsible for their evolution e.g. accumulation of crustal material, different conditions of partial melting, magma mixing with granodiorite magma as suggetsed also for the Gęsiniec Intrusion (Oberc-Dziedzic 1999, Pietranik et al. 2006, Pietranik & Waight, submitted). Distinguishing between those processes cannot be done on basis of geochemical data only (Pietranik & Waight, submitted).

Occurrence of low-Sr (Gęsiniec, Jasienica) and high-Sr (Boznowice, Dębowiec) granodiorites suggests presence of plagioclase in the latter. Plagioclase might have been melted in the source region, e.g. due to presence of water during melting, or be accumulated during crystallization. Crystallization of high-Sr granodiorite from water rich magma is also suggested by presence of hornblende only in this type, despite similar major element composition of all granodiorites.

Acknowledgements. This work was supported by grants to JB: 2022/W/ING/05 – 47 and 4827/PB/ING/04 and Marie Curie Fellowship to AP (DLC, Copenhagen).

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ALKALINE MAFIC DYKE FROM THE MARGIN OF THE EAST-EUROPEAN PLATFORM (KŁANINO-3 BOREHOLE)

Abstract: Petrography, mineral chemistry and some aspects of geochemistry are reported for the post-Middle Devonian mafic dyke rock occurring at the very margin of the EEP. The rock has a distinctive chemical composition with low SiO_2 and high alkalis, P_2O_5 and TiO_2 , and is classified as an alkaline lamprophyre. The lamprophyre magma is assumed to be derived from an enriched mantle source and ascended via deep crustal fractures that must have formed at the margin of the EEP.

Keywords: lamprophyre, geochemistry, Teisseyre-Tornquist Zone, Poland.

The Trans European Suture Zone (TESZ) and the neighbouring marginal part of the East European Platform, as prominent geological structures in Poland, have been subject to intensive seismic examinations since 1960. In the boundary zone, called Teisseyre-Tornquist Zone (TTZ), deep crustal discontinuities rooted in the



Fig. 1. Location of Kłanino-3 borehole on the background of main geological units of Poland.

Earth's mantle were revealed (e.g. Dadlez et al. 2005). Moreover, Moho topography and lateral heterogeneity of the upper mantle are also constrained based on seismic studies. Królikowski and Petecki (2002) and Janik et al. (2002), using different geophysical methods, interpreted the occurrence of several basic rock intrusions in the upper crust of the Pomeranian section of the TESZ. Therefore, basaltic rocks which are available for direct study in the aforementioned area are of particular interest, as their geochemistry might carry information on their source, i.e. the mantle, and add petrological characteristics to seismic ones.

Several mafic dykes were recognized in boreholes drilled in Western Pomerania for petroleum prospecting (e.g. Heflik, Muszyński 1973; Muszyński, Protas 1997). In this short note, we present some aspects of mineral chemistry and major and trace element geochemistry of the smallest of them, coming from the Kłanino-3 borehole (Fig. 1).

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The dyke lies at the depth of 3946-3947.5 m and cross-cuts Middle Devonian finegrained sandstones. The core output from the borehole was not large, so only 1,5 m of the rock was available for study. However, Muszyński and Protas (1997), on the basis of gamma and neutron log data, suggested occurrence of three several meter thick dykes in the 3946-3961 m interval.

Mineral chemistry was determined in two rock samples using the Cameca SX100 electron microprobe in the Inter-Institution Laboratory of Microanalysis, Warsaw University. Major and trace elements were measured in four samples by XRF method at GFZ, Potsdam, and at Poznań University.



PETROGRAPHY AND MINERAL CHEMISTRY

Fig. 2. A — Present-day compositional spectrum of feldspars: 1-3 are ternary feldspars, 1, 2 & 4 contain considerable amounts of celsian unit. Compositions 6(?)-8 are an effect of post-magmatic alteration. B — Dark micas in Mg/(Mg+Fe) vs. Ti_{apfu} diagram. Number of cations calculated on the basis of 22 oxygen atoms.

The rock is dark grey, slightly glimmering, with fine-grained, aphyric and homogenous texture. Primary magmatic minerals are altered by deuteric or hydrothermal processes to a quite significant extend, so only relics of them could be analysed. The rock is composed of feldspars (~40 vol. %), biotite, apatite, Fe-Ti oxides and abundant secondary minerals – chlorite, anatase and dolomite.

Feldspars are plagioclases and alkali feldspars occurring at one-to-one proportion. The plagioclases are almost totally altered into either a mixture of pure K-feldspar, chlorite and dolomite, or Na-feldspar; only their lath-shaped forms suggest their primary mineralogy. The alkali feldspars form anhedral interstitial grains or rims on the plagioclase laths. A distinctive feature is presence of so called ternary feldspars – those containing more than 5 mol. % Ab, An and Or. In addition, some alkali feldspars exhibit enhanced barium concentration (up to 3.2 wt % BaO or 5.7 mol. % celsian end-member in Fsp). The present-day compositional spectrum of feldspars is shown in Fig. 2A.

Biotite forms reddish-brown, unzoned plates and flakes of euhedral to anhedral habits. A part of the crystals is altered into intensively green coloured chlorite, so, at maximum, 7 vol. % of fresh biotite was observed. The Mg/(Mg+Fe) atomic propor-
tions range from 0.55 to 0.35, which allows to classify the micas as typical biotites (Fig. 2B). However, in comparison with typical biotites from the majority of igneous rocks, the crystals studied show significantly high contents of TiO_2 (5.6 to 7.9 wt %). Moreover, some of them are enriched in barium (BaO up to 3.6 wt %).

Apatite amounts ca. 7 vol. % of the rock, which makes it important mineral component. The long-prism, euhedral apatites are evenly distributed in the rock. Almost all crystal ends have skeletal habits. The latter feature probably evidence a rapid growth of the apatites in the final stages of crystallization. Chemically, the apatites contain 2.5-3.5 wt % fluorine, therefore are classified as fluorapatites. The crystals carry substantial amounts of LREE – up to 1 wt % of the sum of La, Ce and Nd oxides were measured by a microprobe. Some apatite crystals are zoned with cores enriched in LREE in comparison to rims.



Fig. 3. A — Primitive-mantle normalised trace-element patterns of the dyke rock (Kl), average ocean island basalt (OIB) and average alkali lamprophyre (AL). Data for OIB and AL from Sun (1980) and Rock (1991), respectively. B — Kłanino rock samples in the discriminative diagram of Pearce and Cann (1973).

Fe-Ti oxides are intensively altered and non-stoichiometric. Secondary Ti oxides (anatase) are much more abundant.

Other minerals are clearly of post-magmatic origin and therefore are not described here.

GEOCHEMISTRY – RESULTS, PRELIMINARY CONCLUSIONS AND HYPOTHESES

In terms of its major element composition, the dyke rock is characterised by very low SiO₂ contents (in the range of 40-42 wt %; LOI free), high alkalis ($K_2O+Na_2O \approx wt 5$ %), and exceptionally high TiO₂ (av. 5 wt %) and P₂O₅ (av. 3 wt %). The high loss-on-ignition values (6-9 wt %) reflect the effects of secondary alteration. The rock shows alkaline geochemical signature, it is potassic ($K_2O>Na_2O$), contains high concentrations of barium (up to 1500 ppm) and other incompatible trace elements (with the exception of Sr). On the other hand, the contents of Ni (<20 ppm), Cr (<50 ppm) and Co (<80 ppm) are low. The Mg number (Mg# = 100*Mg/(Mg+Fe_{trot})) is moderately high (57-60).

Primitive-mantle normalised trace-element variation pattern (Fig. 3A) is similar to this of ocean island basalts (OIB) and – to some extend – to alkali lamprophyre (AL) one, with the exception of a marked negative Sr anomaly. The contents of some elements are even higher than in an average OIB and an average AL.

On the Zr/TiO₂-Nb/Y classification diagram of Winchester and Floyd (1977), the analysed samples plot in the centre of an alkali basalt field. Furthermore, on the discrimination diagrams of Pearce and Cann (1973) and Meschede (1986), all samples plot in the fields of within plate alkali basalts (Fig. 3B). Muszyński and Protas (1997), in their preliminary petrologic description, classified the rock as a minette. Here, we reinterpret it as a volatile-rich version of an alkali basalt, i.e. an **alkaline lamprophyre**. Indeed, the sample compositions plot in the field of alkaline lamprophyres on the CaO—SiO₂/10—TiO₂*4 discrimination diagram of Rock (1991).

On the basis of the exceptional enrichment in incompatible trace elements, OIBlike chemistry, the lack of a distinct Nb-Ta depletion, and published interpretations of the origin of different alkaline lamprophyres, we put forward the hypothesis that a primary magma was generated from an enriched mantle source. However, the moderately high Mg number, low concentrations of Ni and Cr, and the negative Sr anomaly suggest that primitive magma underwent further processes, e.g. fractional crystallization.

The deep-seated fractures in the Earth's crust seen in the seismic profiles might serve as conduits for magma ascent.

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U-Pb ZIRCON AGE OF PARTIAL MELTING IN METAPELITES FROM THE WESTERN TATRA MTS.

Abstract: Zircon crystals from the migmatitic gneiss of the Western Tatra Mts. (Tatric Superunit - Central Western Carpathians) were dated by conventional U-Pb technique. Complexities in zircon growth patterns were identified by careful cathodoluminescence (CL) and backscattered electrons (BSE) imaging. U-Pb zircon data indicate an Upper Devonian/Lower Carboniferous partial melting around 360 Ma.

Keywords: U-Pb dating, zircon, migmatitic gneiss, Western Tatra Mts.

INTRODUCTION

Zircon is a U-bearing mineral widely used for dating because it grows in a wide variety of igneous and metamorphic rocks and incorporates negligible amounts of initial Pb. Moreover zircon has a high closure temperature (>900°C), thereby remaining isotopically stable during extended periods of high-grade metamorphism and partial melting (e.g. Cherniak & Watson 2001).

This study presents results of conventional U-Pb zircon dating from amphibolitefacies migmatitic gneiss from the Western Tatra Mts. Till now there hasn't been directly proved age of migmatisation for the basement rocks of the northern part of the metamorphic envelope. Supposition about the age of this process is based on xenoliths of migmatites found in the much younger High Tatra granite (Poller et al. 2000, 2001).

To estimate the zircon growth conditions morphology, internal structures and microchemistry of zircon grains have been also analysed.

ANALYTICAL TECHNIQUES

The sample was processed using standard mineral separation techniques. Twenty to sixty grains, 50-100 μ m in diameter, were mounted with standards in epoxy and polished. Microanalyses and cathodoluminescence (CL) imaging were carried out using a CAMECA SX 100 microprobe analyser in the Inter-Institution Laboratory of Microanalyses of Minerals and Synthetic Substances at the Warsaw University. Cathodoluminescence images (CL) have been used for identifying internal structures of individual zircon grains. The operating conditions were: acceleration voltage – 20 kV, beam current – 50 nA and beam diameter – 2 μ m.

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Conventional U-Pb zircon dating was conducted on a Finnigan MAT 262 mass spectrometer, equipped with a secondary electron multiplier-ion counter system at the Geochronology Laboratory, Institute of Geology, University of Vienna. The U-Pb isotopic analyses were carried out on selected four zircon fractions (2 long-prismatic and 2 isometric). The selection was based on morphology and visible corrosion. Only transparent, clear, inclusion free zircon grains were selected by handpicking under a binocular microscope. Zircon crystals were air abraded following the method described by Krogh (1982). The procedures applied for conventional U-Pb dating are reported in detail by Parrish et al. (1987). The final ²⁰⁷Pb/²⁰⁶Pb and U/Pb ages were calculated at 2s standard deviation using the Isoplot/Ex program version 2.10 by Ludwig (1999).

GEOLOGICAL SETTING AND SAMPLE DESCRIPTION

The Western Tatra Mts. metamorphic complex is composed of schistose Lower Structural Unit (LSU) and migmatitic Upper Structural Unit (USU), forming together the inverted metamorphic zonation. Metamorphism of the Upper Unit took place in the upper amphibolite facies conditions ($T = 690-780^{\circ}C$, P = 7.5-10 kbar; Gawęda and Burda, 2004). The metamorphic envelope is cut by two types of granites: older 405 Ma granite (orthogneiss) and younger 350-360 Ma granite (Poller et al. 2001).

The sample of banded, migmatitic gneiss from the USU was taken from Smreczyński Upłaz. The banded migmatitic gneiss is composed of quartz, plagioclase (An_{21-23}) , biotite (fm = 0.604-0.612, TiO₂ = 2.75-3.3 wt %) and sillimanite. Accessory phases comprise apatite, zircon and monazite. As the secondary minerals chlorite, epidote and fine-grained muscovite were stated. The migmatitic gneiss is strongly peraluminous (A/CNK = 2.37). Muscovite dehydratation-melting textures are ubiquitous in this rock. Reconnaissance thermobarometry yields P-T conditions consistent with this observation: T > 700°C. These reinforce arguments that partial melting reactions are integral part of the metamorphic evolution of the rock under investigations.

RESULTS

There are two main morphological types of zircon present in the sample: (1) subhedral, slightly coloured (light yellow) isometric grains with aspect ratio less then 2:1 and (2) elongated, euhedral, clear, colourless grains with aspect ratio up to 6:1. CL investigations show that the isometric crystals exhibit two different domains: an internal part with sector zoning, surrounded by a younger rim with oscillatory zoning. The long prismatic crystals reveal only oscillatory zonation.

Morphology, internal structure and geochemical analyses of zircon groups were characterised in detail in previous works (Burda 2004, 2005). Long-prismatic crystals occur only in the melt minerals (feldspars and quartz) while round (isometric) zircon grains are enclosed also in the biotite flakes. The population of isometric crystals (fractions A and B) give a concordia age of 365.1 ± 2.4 Ma (Fig.1A). The group of elongated crystals (fractions C and D) define a concordia age of 360.5 ± 1.9 Ma (Fig.1B).



Fig.1. Concordia plots of U-Pb zircon data from migmatitic gneiss from the Western Tatra Mts.

CONCLUSIONS

The high-quality conventional single-grain U-Pb zircon age determinations together with careful cathodoluminescence imaging and microchemical probing provided detailed information about the evolution of migmatitic gneiss from the metamorphic cover of the Western Tatra Mts. The first group of zircon with isometric shape could crystallize in the subsolidus stage, during incipient dehydratation melting. Low Th/U ratios (<0.1) confirmed this growth stage (Burda 2005). This population gives a concordant age of 365.1 ± 2.4 Ma (Fig. 1A). The thin rims around these grains and the whole population of long prismatic zircons could represent the next stage of dehydratation melting, when melt phase appears. This group of crystals define a concordia age of 360.5 ± 1.9 Ma (Fig.1B). Summarizing, the U-Pb zircon ages derived from migmatitic gneiss lead to the conclusion that partial melts crystallized over a relatively short period of ~ 9 Ma, from about 367 to 358 Ma. Thus the partial melting within the paragneisses may be related to the Upper Devonian/Lower Carboniferous orogenic cycle. It is contemporary with magmatism in the Western Tatra Mts. which led to the formation of the younger granites (Poller et al. 2000).

Acknowledgements. This study was financially supported by Ministry of Education and Science – Project no. 2 P04D003 29 and by CEEPUS Project CII-AT-0038-01-0506.

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THE PALAEOTECTONIC ENVIRONMENT OF AMPHIBOLITES FROM THE POLISH PART OF THE DESNA AND VRBNO SERIES, OPAVA MTS, EAST SUDETES

Abstract: The geochemistry of amphibolites from the Desna and Vrbno Series in the Polish part of the Opawa Mts is presented using discrimination diagrams. The results are compared with data from neighbouring formations, and confirm the existence of a long-time volcanic episode that took place under an extentional regime and that ended before collision, the first sign of which is recorded as deformation D_1 (Visean).

Keywords: geochemistry, amphibolites, palaeotectonic environment, East Sudetes.

INTRODUCTION

The Opava Mts are located in the north-western part of Brunovistulicum, within the Moravo-Silesian zone. They were shaped by polyphase Variscan deformations, metamorphism and multiple westward thrusting (Schulmann, Gayer 2000; Mazur et al. 2006). Most of the Opava Mts belong to the Czech Republic, but the relatively small northern part is situated at the Polish side; it is called Parkowa Hill.

Parkowa Hill is composed of the Proterozoic Desna Series that consists of biotitic paragneisses, migmatites, mylonites and amphibolites (Schulmann, Gayer 2000). It is covered by quartzites, mica and quartzite schists of the Late Devonian Vrbno Series that also contains abundant marbles and metavolcanics as amphibolites, metadiabases and quartz-amphibole rocks metamorphosed under amphibolite-facies conditions. In the Opava Mts, the Vrbno Series is followed by the Andelska Hora Formation that consists of metasediments with a flysch character with greenschist lenses. The youngest flysch sediments in the Opava Mts consist of the Horni Beneszov Formation, which is Early Carboniffeous in age (Żaba et al. 2005).

Metabasite rocks of Parkowa Hill were collected from both series. The investigated region is poor in amphibolite exposures. More samples were therefore taken from relatively large (up to 1 m in diameter) loose blocks that were irregularily located within the outcrops. Taking into account the forms of the exposed amphibolite bodies (lenses and boudins), the size of the blocks, the compactness of the amphibolites, and their relatively high resistance to weathering in comparison with the paragneisses and schists, we suppose that they have a volcanic origin as sills or dykes within the sedimentary successions of the Desna and Vrbno Series.

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The aim of the present contribution is (1) to establish the palaeotectonic environment in which the metabasites of Parkowa Hill were formed, on the basis of their geochemistry and (2) to compare them with other metavolcanites from the Eastern Sudetes. XRF analyses were made in the laboratory of the Department of Earth Sciences at Keele University, UK.

MINERALOGY AND PETROGRAPHY

The amphibolites of the Vrbno and Desna Series of Parkowa Hill are mainly fineand medium-grained foliated rocks. Foliation is generally poor, and has been caused by parallel arrangement of elongated amphibole crystals. The light-mineral content is low, up to 10-20 % of the rock volume.

Two kinds of amphiboles appear to be present: (1) big, subhedral blasts frequently arranged in an ophitic texture, and (2) small euhedral amphibole blasts which fill interstices together with anhedral plagioclases. Quartz, biotite, chlorite, muscovite, ilmenite, titanite and apatite are present as accessory minerals. Most of the larger amphibole blasts are zoned: the core is composed of magnesiohornblende, whereas the rim consists of tschemakite. The small amphibole crystals are chemically homogene-ous, and have a magnesiohornblende or tschermakite composition. The zonal character of the larger amphiboles indicates prograde metamorphism during crystallization.

Plagioclases present in amphibolites found in the central and southern parts of Parkowa Hill have an andesine–labradore composition. The anorthite content in the plagioclases is highest in the northern part of the region. This is consistent with the metamorphic zonation in the amphibolites of the northern part of the Jeseník Massif in the Czech Republic as proposed by Olejniczak (2002), where the anorthite content in plagioclase increases from south to north. Olejniczak (2002) distinguishes three parallel zones: (1) oligoclase/andesine, (2) andesine/labradorite and (3) labradorite/ bytownite. A bytownite/anorthite zone should be added to this scheme as a fourth zone (Żaba et al. 2005).

GEOCHEMISTRY

The forms of occurrence and the relicts of an ophitic texture indicate an igneous origin of the investigated amphibolites. This is supported by the Zr/TiO_2 -Ni diagram, also for the amphibolites that have been sampled from loose blocks (Fig. 1). In a TAS diagram all projecting points are located within the basalt field, but in the Zr/TiO_2 -Nb/Y diagram they concentrate in the subalkaline and alkaline basalt fields. On the basis of SiO₂-Cr, SiO₂-FeO/MgO, K₂O-SiO₂, P₂O₅-Zr and the alkali index A.I.-Al2O3 diagrams it could be deduced that the protoliths of the investigated amphibolites must have been tholeitiic basalts. The projection points of amphibolite samples are concentrated within a small area in the diagrams, except for only 1-2 samples that do not fit precisely.

Together with the typical amphibolites, the chemistry of two samples of amphibole-quartz rocks (VS) were investigated. These samples were assumed to have a pyroclastic origin, but their geochemistry is so peculiar that they might rather be considered as metasediments.



Fig. 1. Diagram distinguishing igneous and sedimentary rocks (Winchester et al., 1980; vide Rollinson, 1993). D – amphibolites from Desna series, V – Vrbno.



Fig. 2. Discrimination diagrams showing geotectonical setting after Pearce, Cann, 1973; vide Rollinson, 1993. D – amphibolites from Desna series, V – Vrbno

According to the $\text{TiO}_2 - \text{Nb/3}$ - Th diagram, the amphibolites from the Desna Series fall within the field of plate margins, whereas the amphibolites from the Vrbno Series indicate a more complex tectonic history. In a Zr - Ti/100 - 3Y diagram, the projected points fall within two fields: within plate basalts and MORB (Fig. 2).

CONCLUSIONS

Metabasic rocks from the Polish part of the Opava Mts such as the amphibolites of the Desna and Vrbno Series, the greenschists (late Frasnian – early Visean) of the Andelska Hora Formation and the metabasites from the Jeseník and Sobotín Massifs (Vrbno Series) show a similar geochemical record of subalcaline, alkaline low-Ti tholeiitic basalts, in spite of different types of primary rocks, age of the host rocks, and degree of metamorphism. This implies that all these metabasites may be derived from one magmatic source with a tholeiite composition.

The geotectonical position is difficult to establish. According to Souček (1978), the metabasites of the Vrbno and Rejvíz Series in the Hruby Jeseník Mts have a mixed volcano-sedimentary origin and represent metamorphosed ocean-floor basalts and the within plate basalts (including ocean-island basalts and continental basalts), and are similar to the amphibolites from Parkowa Hill. The geochemical results of the Jeseník and Sobotín Massifs (Fiala et al. 1980) point to oceanic tholeiitic basalts and basalts from the continental crust. The metabasites from the Polish part of the Andelska Hora Formation represent volcanic products derived from the transitional zone between within-plate and N-MORB sources, comparable with enriched E-MORB (Kozdrój 2003).

Taking into account both our field observations and the similarity of the projection points for the metabasites from the Desna and Vrbno Series of Parkowa Hill on one hand and the geochemical results of the amphibolites from Jeseník and the greenschists from the Andelska Hora Formation on the other hand, in combination with presence of greywackes within the Horni Beneshov Series (Visean), we conclude that all mentioned metabasites are connected with one long-lasting volcanic episode (Middle Devonian-Early Carbonifferous). It took place under an extensional regime and came to an end before the collision of which the first sign is recorded as deformation D_1 (Visean). It means that it could be connected with Devonian rifting of eastern part of Brunovistulicum (380-360 Ma, Schulmann, Gayer 2000) and corresponds with the stage 1 (approach of continental plates) of Massonne's model (2005) for continent-continent collision.

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RARE EARTH ELEMENTS BEHAVIOUR IN THE WEATHERING PROFILE – A CASE STUDY FROM KARKONOSZE MASSIF

Abstract: A 5-step extraction scheme has been conducted on two soil profiles in order to determine the ability of REE to be released to the environment. The bedrock for the soils was Karkonosze granite. The change in REE concentration has been determined using Nesbitt and Markovics formula. The results prove, that REE could be leached. Organic matter and Fe- Mn oxyhydroxydide appears to control the adsorption of REE in the soil.

Keywords: rare earth elements mobility, weathering profile, sequential extraction.

INTRODUCTION

The evolution of Karkonosze pluton is well reflected in differentiation of REE e.g their considerable decrease with differentiation progress (the differentiation mechanism – mixing overlapped by fractional crystallization; (Słaby, Martin 2005). Rare earth elements are dispersed in many major (i.e. biotite, feldspar) and accessory (apatite, calcite) minerals. The composition of the soils usually shows some relation to the parental rock also in respect to REE. Few studies dealt with the distribution and the speciation of rare earth elements on the granite – soil boundary (e.g. Nesbitt, Markovics 1997; Cao et al. 2001, Aubert et al. 2004). The distribution of REE concentrations in the soil profile has been studied by Gouveia et al. (1993).

They noted the decrease of concentration of REE in the middle and upper part of saprolite horizon. Van der Weijden i van der Weijden (1995) suggest there are unique way of REE behaviour in soils formed on acid rocks. The aim of this work was: a) to study REE mobility on the granite – soil boundary in two profiles; b) to recognize how the mobility of REE influences the chemical composition of soils.

METHODS

Samples of fresh rock from porphyritic weakly differentiated (Michałowice quarry) and highly differentiated granite (Szklarska Poręba Huta quarry) have been collected. In addition samples of soils covering each outcrop have been collected and analysed (Galbarczyk-Gąsiorowska 2005). The investigated soils present mostly "ranker" brown, acid brown and podzols. Usually the soil profile included 3-4 horizons: humus – iron (SPH1, M1 – symbol of the samples), iron – humus (M2), illuvial (SPH2, M3)

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and weathered bedrock (SPH3a, M4). Michałowice soil profile was composed by four horizons whereas Szklarska Poręba Huta profile by three horizons.

Whole rock samples and whole soil samples (separately for each horizon) have been analysed for trace elements by means of ICP MS method. Using Nesbitt and Markovics (1997) formula the change in the REE concentration has been determined in relation to the concentration of the less mobile element in the soil horizons and in the parental rock:

% change = 100 {[
$$(X/Ti)_{p} - (X/Ti)_{s}/(X/Ti)_{p}$$
]

where Ti means concentration of Ti in the rock or soil, X – element concentration in the rock or soil, the subscripted "*s*" represents sample of weathered rock or soil, and "*p*" fresh, parent rock (covered by soil). Titanium has been chosen as the most immobile element, because in an early stage the of alteration process it is precipitated before it is transported out of the system. The mobility of REE has been calculated for each soil horizon within both profiles.

In addition sequential extraction was performed in order to identify the type of REEbearing mineral groups. Five steps procedure has been used. Sequential extraction of the <1mm fraction from each horizon sample has been carried out according to the following, stepwise procedure: step 1 – ammonium acetate extraction (the step is a fair indication of cation exchange capacity;) step 2 – dilute acetic acid extraction (an indication of acid-soluble minerals content;) step 3 – hydroxylamine / acetic acid extraction (an indication of dissolution of Fe- and Mn-oxyhydrooxide;); step 4 – hydrogen peroxide extraction (organic / sulphidic fraction); step 5 - hot concentrated nitric acid extraction. After last extraction, in the residuum only acid resistant minerals remain.

RESULTS

The results are presented by means of Nesbitt and Markovics (1997) method. They show, that rare earth elements could be considered as mobile elements in both profiles: the one from Michałowice and the one from Szklarska Poręba Huta. The mobility shown as the percentage of the change of the ratio REE/Ti confirms that soil horizons are enriched in REE if compared to rock (Fig. 1). In addition, the analysed samples from Szklarska Poręba Huta profile present systematical impoverishment in LREE in each soil horizon and simultaneously, enrichment in HREE (Fig. 1).

The biggest percentage change in the concentration of LREE and HREE in Michałowice profile has been noted in the iron – humus horizons (up to 90 % more LREE than in parental rock) and in illuvial horizons (up to 70 % more HREE than in parental rock) (Fig. 1). The smallest change in the LREE content has been observed in the fourth horizon (weathered rock level) and respectively in the HREE content in iron – humus horizon (30 %-10 % more than parental rock). (Fig. 1)



Fig. 1. Percentage changes to elemental rations REE/Ti – SPH1, SPH2, SPH3a, M1, M2, M3, M4 – soils horizons

The showed above total REE content has been determined separately in each soil horizon in order to quantify the amount of mobilised REE species in respect to REE concentration in the rock. More detailed information provides sequential extraction. Even if the rare earth elements concentrate in each horizon in different fractions, some rules are noticeable. The ion exchange fraction is REE free. REE concentration increases in reducible fraction (three step extraction) and especially in organic and sulphidic (four step extraction), and in residual one. The amount of carbonate fraction in the bedrock is negligible (Fig. 2).



Fig. 2. REE concentrations in humus-iron horizons – results of sequential extraction (numbers in the legend – fractions).

The good correlation of REE concentration with the contents of organic matter in the soil horizons is also confirmed by Nesbitt & Markovics model (1997) (look for the results for humus-iron horizons Fig. 1).

CONCLUSIONS

Soils from both profiles are enriched in rare earth elements in comparison to parental rock. Soils developed on weakly differentiated (REE enriched) and differentiated (REE depleted) granite have similar pattern of REE distribution, so the primary composition of the bedrock doesn't influence the soil composition significantly. Sequential extraction has indicated that REE are mostly concentrated in organic and Fe – and Mn – oxyhydrooxide soil fraction. During sequential extraction, REE did not react as a homogeneous chemical group since HREE appear to be more leachable than LREE. The Nesbitt & Markovics (1997) model confirms that LREE behaviour differs from that of the HREE.

This work was founded by BW 1726/13.

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CALCITE – ARAGONITE TRANSFORMATION UNDER MECHANOCHEMICAL TREATMENT

Abstract: Samples of calcite and a mixture of calcite with Cu-hydroxycarbonate were milled using planetary ball mill. The progress of mineral transformation was investigated using X-ray diffractometry, IR-spectroscopy and SEM microscopy. The results show that mechanochemical treatment was effective in the transformation of calcite into aragonite only in the presence of Cu-hydroxycarbonate.

Keywords: aragonite, calcite, Cu-hydroxycarbonate, high-energy ball milling, mechanochemical treatment.

INTRODUCTION

Structural phase transitions represent an interesting subject from the point of view of solid state physics, geology and material sciences. We chose the calcite-aragonite transformation because it is a nominally simple, yet geologically important, reaction often considered the mineralogical archetype of isochemical, reconstructive phase changes.

The polymorphic transformation of calcite to aragonite and its reverse reaction are key reactions during the high pressure-low temperature metamorphism of carbonate rocks. Most of the experiments on the calcite-aragonite system have been made in a piston-cylinder device. Our experiment was simple and not time consuming, although its correspondence to typical high-pressure experiments is unknown yet.

Calcite-aragonite transformation was the result of a mechanochemical treatment, which is defined as a mechanical activation (MA) by milling (Takacs 2002). Such process is usually carried out in high-energy devices such as vibratory or planetary ball mills where the energy transfer to the particles takes place by shearing and impact of high velocity balls with powdered reagents. Mechanical activation can cause physical and/or chemical changes in the treated materials. The first observable action of mechanical energy on the material is the breaking of its crystalline structure, which involves formation of dislocations and point defects. At the zone of collision between solids and milling balls the temperature and pressure increase considerably. Therefore, the energy accumulated in powder under mechanochemical treatment can lead to the phase transformation or may even induce complex chemical reactions, e.g. decomposition or oxidation-reduction processes.

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In this study we investigated a possibility of aragonite formation from calcite by mechanochemical treatment and the influence of hydroxycarbonate on this transformation.

METHODS OF INVESTIGATION

Materials. The starting materials used were CaCO₃ (calcite powder) and a mixture of calcite with Cu₂(OH)₂CO₃ (Cu-hydroxycarbonate).

Milling procedure. For mechanochemical treatment a laboratory planetary mill Fritsch GmbH *Pulverisette 6* with vial and balls made of tungsten carbide was used. The milling process was performed in air, using ball-to-powder mass ratio (BPR) 10:1 and the rotation of the milling vial was 550 rpm. Time of treatment was 300 min.

Instrumental investigations. X-ray powder diffraction patterns were obtained using a Philips X'Pert diffractometer (CuK α_1) in the 2 Θ range of 10-90°. The IR spectra in the 4000-400 cm⁻¹ were recorded by means of FTS 2000 Scimiter Series spectrometer using KBr pellets. Microscopic examinations were performed using field-emission scanning electron microscope Hitachi S-4700 equipped with EDX (Noran Vantage) microanalysis.

RESULTS

Two systems were studied: pure calcite and a mixture of calcite with precipitated Cu-hydroxycarbonate. The results of X-ray diffractometry (Fig. 1) and IR spectroscopy (Figs. 2 and 3) indicate that under the same conditions of mechanochemical treatment aragonite formed only in the CaCO₃ (calcite) – $Cu_2(OH)_2CO_3$ system, and not in the pure CaCO₃ system. A relative content of aragonite in aragonite-calcite mixtures was estimated by the quantitative XRD technique (using the calibration curve drawn for calcite-aragonite proportions) to be approximately 85-90 %, proving the high efficiency of the process.

Mechanoactivation brought about the decomposition of Cu-hydroxycarbonate, according to the equation: $Cu_2(OH)_2CO_3 \rightarrow 2CuO + H_2O\uparrow + CO_2\uparrow$, which was confirmed by the presence of tenorite (CuO) on the XRD patterns (Fig. 1).

The most intensive absorption band at 1420-1480 cm⁻¹ (Figs. 2 and 3) is from vibrations of carbonate groups in calcite and Cu-hydroxycarbonate. In the region of 520-590 cm⁻¹ bending vibrations from Cu-O bonds appear. The 699-712 cm⁻¹ doublet, typical for aragonite, is observed only in products of the mechanically activated CaCO₃ (calcite) - Cu₂(OH)₂CO₃ mixture. In order to determine morphology of the mechanochemically activated calcite and its mixture with Cu-hydroxycarbonate scanning electron microscopic measurements were performed. For both tested systems the particles have tendency to form aggregates, which are typical for the first steps of mechanical activation process. EDX analysis shows uniform distribution of Cu, Ca and O elements that indicates that high-energy ball milling caused strong homogenisation of the treated component mixture.



Fig. 1. X-ray diffraction pattern from a primarily CaCO₃ (calcite)-Cu₂(OH)₂CO₃ mixture, after mechanochemical treatment lasting 300 min.



Fig. 2. Infrared absorption spectra of calcite before and after mechano-chemical treatment.



Fig. 3. Infrared absorption spectra of calcite and $Cu_2(OH)_2CO_3$ mixture before and after mechanochemical treatment.

DISCUSSION

The transformation of calcite into aragonite during mechanochemical treatment of the system $CaCO_3$ (calcite) – $Cu_2(OH)_2CO_3$ is possible due to two independent factors: – the rise in gas pressure in the milling reactor as the result of $Cu_2(OH)_2CO_3$ decomposition – the defective structure of calcite.

Jump in pressure is caused by gas products from $Cu_2(OH)_2CO_3$ decomposition. The presence of CO_2 and water vapour is probably significant in our experiments. Based on their experimental results Hacker et al. (1992) suggested that transformation of calcite to

aragonite in geological time scales does not occur in the absence of volatiles at temperatures below 200°C. The influence of copper on the transformation is not clear.

By extrapolating his experimental data to natural conditions Huang (2003) calculated unusually fast transformation rates from calcite to aragonite, in contrast to those of natural samples. He suggested that the presence of deformational strain, fractures, defects or impurities in natural samples, and other factors may account for the calculated discrepancy. Also Newton *et al.* (1969) demonstrated experimentally that aragonite can be crystallized at pressures much lower than the equilibrium pressure strained calcite. In our experiment, a defective structure of calcite is caused by the simultaneous action of stroke and friction during the high-energy ball milling process. This releases the excess of strain energy stored in dislocations and is responsible for the extra-ordinary reactivity of the mechanically treated materials. This stored energy lowers the pressure requirements for calcite into aragonite transformation. Moreover the sudden release of such strain energy, energetically favours the formation of a metastable phase such as aragonite.

Most kinetic experiments on geologic materials, including ours, have been done under physical conditions quite different from the natural environment. Results from such experiments are in general difficult to apply to many natural situations. It is possible that mechanoactivation imitates shock rather than progressive metamorphism. Further studies are needed to determine how products of mechanoactivation can be interpolated to the natural conditions of the Earth.

CONCLUSIONS

It is experimentally shown that a high-energy ball milling makes the transformation of calcite towards aragonite possible, but only in the presence of other additives.

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APATITE-RICH ROCK FROM THE HIGH TATRA GRANITE, WESTERN CARPATHIANS

Abstract: The occurrence of a mafic, coarse-grained apatite-rich ultrapotassic rock with a mixed mantle-crustal signature marks a hitherto unknown magmatic episode in the Tatra Mts. history. Trace element chemistry suggest a mantle plume magma, metasomatized before the partial melting and within-plate tectonic regime of intrusion - unknown at an early stage in the Variscan consolidation of the massif.

Keywords: apatite, shoshonitic magmatism, mantle plume, within - plate regime.

GEOLOGICAL SETTING

The Tatra Mountains crystalline core is composed of four petrographic types of Variscan granitoids that intrude the metamorphic envelope: quartz-diorite, common Tatra granodiorite-tonalite, High Tatra porphyrytic granite and Goryczkowa-type granitoid (Kohut & Janak 1994, Gawęda et al. 2005). In the upper part of the Batyżowiecka Valley, at about 1950 m a.s.l. on the western slopes of Gerlach Mt. and inside the High Tatra granite, I have found a coarse-grained apatite melasyenite enclave with numerous K-feldspar phenocrysts. The melasyenite has a sharp contact with a host porphyrytic K-feldspar granite, that is only slightly altered near the contact.

ANALYTICAL METHODS

Microprobe analyses of minerals were carried out on a CAMECA SX-100 electron microprobe in the Inter-Institution Laboratory of Microanalysis of Minerals and Synthetic Substances, Warsaw. Whole-rock analyses of major and trace elements were done by XRF and ICP-MS methods in the ACME Analytical Laboratories, Vancouver, Canada. For the comparison I used the 34 analyses of granitoids from the High Tatra Mts. from my own database.

ROCK DESCRIPTION, CLASSIFICATION AND MINERALS CHARACTERISTICS

The rock is composed of K-feldspar megacrysts < 30 mm in length (39.8 %), biotite (30.7 %), apatite (13.8 %), albite (6.1 %), quartz (4.4 %) and muscovite (4.5 %). Accesories are monazite, epidote-allanite, zircon, magnetite-ilmenite-rutile intergrowths, titanite and xenotime. A weak fabric is defined by Kfs megacrysts and biotite-apatite alignment. Based on the mineral and chemical composition the rock can be classi-

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fied as quartz mela-syenite (IUGS classification) or syenodiorite (TAS classification). Similar phosphorus-rich rocks were described from Fennoscandian Shield and classified as ladogalites (2-8 wt % P_2O_5 ; i.e. Khazov 1983, Eklund et al. 1998). According to ladogalite group subdivision, the apatite-rich rock from the Tatra Mts. can be classified as mesoladogalite.

The Kfs porphyrocrysts have zonal arrangement of Ba content: from 0.034-0.024 a.p.f.u. in the core to 0.014-0.008 a.p.f.u. in the margin. Biotite (*fm*=0.644-0.598, Ti = 0.39.0.36 a.p.f.u.) is weakly zoned. The Ti content of dispersed muscovite lies in the range of 0.135-0.176 a.p.f.u. Albite $(Ab_{93}An_5Or_2-Ab_{97}An_3)$ is the only plagioclase present – mainly as the inclusions in Kfs porphyrocrystals.

Two types of apatite (0.5-2 mm Ø) were recognized: 1) apatite crystals with patchy internal structure, marked by differences in Fe, Y, Na and Mg contents and with inclusions of HREE-rich xenotime and zircon, 2) unzonal apatite, with biotite inclusions. In zircons, cores with Zr/Hf~104 and margins with Zr/Hf~58-38 can be distinguished. Zoned epidote shows a transition from allanite cores to REE-bearing epidote at margins. Secondary zoizite+titanite fringes overgrow the REE-epidote. Unzoned Ce-monazite crystals show ThO₂ coronas, suggesting some Th mobilization. Opaque minerals are represented by aggregates of ilmenite, magnetite and rutile in varying proportions, suggesting the decomposition of an original ulvöspinel overgrown by titanite and calcite coronas.

GEOCHEMISTRY

The chemistry of the melasyenite is characterised by a low SiO₂ content and by enormously high P₂O₅ content (Tab. 1). On the other hand, it is quartz and corundum normative, as biotite is a main rock-forming aluminosilicate. Ba (2538.5 ppm), Rb (180 ppm), total REE, Zr (440.8 ppm), Hf (13.6 ppm), Y (401.1 ppm) contents are high and that of Sr (384 ppm) moderate. REE fractionation is weak (Ce_N/Yb_N = 3.16). A negative Eu anomaly (Eu/Eu^{*} = 0.354) and low Sr/Sr^{*} ratio (0.135) are pronounced. Nd prevails over Th (Nd/Th = 6.526). The melasyenite plots in the shoshonitic field, K₂O/Na₂O ratio is 3.93 pointing out its ultrapotassic affinity, in contradiction to the calc-alkaline and high-K calc-alkaline host granitoid suites (Fig. 1).





Fig. 1. The plot of the apatite-rich rock (black square) in the SiO₂ versus K₂O diagram (Le Maitre et al., 1989). Fields of granite-types according to author data.

The plot of the apatite-rich rock in the Pearce et al. (1984) diagram. Fields of granite-types according to author data.

DISCUSSION AND CONCLUSIONS

Four possible alternatives for the origin of the apatite-rich rock were discussed: 1. that is a restite, 2. a cumulate, 3. a xenolith of metasedimentary rock enriched in phosforus or 4. a magmatic rock of different origin.

The lack of negative Ce-anomaly and high REE, Ba, Zr, Y and Hf concentrations and no metamorphic fabric, typical of most xenoliths in the Tatra granites, tell against a P-rich metasediment (Dorais et al. 1997). The negative Eu anomaly, the high concentration of LILE and lack of any trends characteristic of enclosing granitoids are atypical of cumulate and/or restite. Moreover, cumulate cannot contain only tectosilicate and low density minerals (quartz, feldspars).

The high REE content, the flat chondrite-normalized pattern, the high HFSE content combined with low SiO₂ and high Nd/Th ratio could point to a magmatic rock of mantle derivation. The negative Eu and Sr anomalies and high Cr/Ni (4.1) suggest a HP mantle fractionate whereas the low Zr/Y and Nb/Y ratios may indicate a mantle plume connection (Condie 2005). On the other hand, low transitional-metals contents and high LILE concentrations together with high La/Nb ratio (22.64) open the possibility of a crustal melt. In figure 2, the rock plots in the WPG field, in contrast to the VAG-related host granitoids.

Assuming the magmatic origin of the apatite-rich rock, temperatures were determined for the apatite rock and the Tatra Mts. granitoids using three methods. The method of Watson & Harrison (1983), based on Zr content in the rock gave temperatures of 752°C (apatite rock), 822-797°C (Kfs-rich megacrystic High Tatra granites), 806-736°C (biotite monzogranites - common Tatra type) and 822-753°C (quartz diorites). In case of apatite rock calculation of the Mt-Ilm equilibria (Spencer & Lindsley 1981) gave temperature range of exsolutions of 680-668°C with a low oxygen fugacity ($\log_{10} fO_2 = -16$). These values are similar to previously stated for High Tatra granitoids (Grabowski & Gawęda 1999).

The high pressure (22-32 kbar) melts are in equilibrium with eclogitic residue, giving the highly fractionated HREE depleted patterns with low Yb content, while low pressure (~ 8 kbar) melts have no garnet in residue (Luais & Hawkesworth, 1994). The observed weak REE fractionation point out rather low pressure melts. The presence of magmatic, zoned epidote with allanitic core, crystallizing after biotite but before quartz and K-feldspar suggest the pressure in the range 6-8 kbar, with temperatures not exceeding 775°C for H₂O > 9 wt % (Schmidt & Poli 2004). The lack of "dry" minerals and presence of biotite as the predominant mafic mineral suggest the high concentration of volatiles in the magma. The presence of allanite-epidote and monazite point out the change in Ca activity in the melt, steered by the apatite crystallization.

Considering the above mentioned facts, the apatite-rich rock can represent the intrusive, mantle-related magma portion, originated in a within plate regime (Fig. 2), as a result of extension (hot-spot?). The mixture of mantle and crustal chemical and mineralogical signatures may suggest a lamprophyric, late-orogenic character. As it is an enclave in High Tatra granite – predates it. Such phosphorus rich melts are usually interpreted as portions of the mantle plume, affected by carbonate metasomatism prior to partial melting (i.e. Eklund et al. 1998, Andersson et al. 2006). The volatile-rich melt, moved by adiabatic decompression, left behind the feldspar-rich (lherzolitic?) source, what resulted in Eu negative anomaly. The metasomatised mantle plume, emplaced as a crystal mush at relatively high crustal level (6-8 kbar) could bring enough heat to start melting the surrounding crust and contribute to the formation of the late (314 Ma) High Tatra granite pluton. The presence of this rock could bring the explanation for mixed I/S origin of the late Variscan High Tatra granite.

Acknowdgements. Dr P. S. Kennan is deeply acknowledged for the help in data interpretation and English correction. Dr P. Dzierżanowski and Mrs. L. Jeżak helped during microprobing. The Ministry of Sciences and Informatics grant No. 2 PO4D 05629 founded this research.

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MINERALOGY OF NOCTIS LABYRINTHUS (VALLES MARINERIS, MARS) ON THE BASIS OF SPECTROMETRIC AND IMAGING DATA

Abstract: IR spectra of the OMEGA data set from the Mars Express mission have been used to analyse the presence and diversification of minerals in rock material of the Noctis Labyrinthus region of Mars. Raw OMEGA data are corrected for the contribution of atmospheric components by an algorithm basing on differences in thicknesses of the atmospheric column content in measurements made at the top and at the bottom of Olympus Mons. The analysis of OMEGA spectra shows evidence of pyroxenes (diopsyde and augite) both in the central and western part of the Noctis Labyrinthus region. The spectra probably also include the clays components: nontronite, halloysite or illite/smectite. Evidence for proximity of volcanic material and eolian deposits with possible presence of clays on MOC image indicates strong weathering processes in this area.

Keywords: pyroxene, clay, weathering product, OMEGA spectrum, MOC image, Noctis Labyrinthus, Valles Marineris, Mars.

INTRODUCTION

The Noctis Labyrinthus province is situated in the western end of the Valles Marineris canyon and consists of a high plateau cut by a network of structurally controlled roughs (Fig. 1), which extend for 976 km along the Martian equator. This dense network of grabens, a few kilometers deep in some places, lead to forming by numerous fault dislocations in the western part of Valles Marineris (Tanaka 1997).

The investigation area is covered by multiple remote sensing data from Martian missions. The OMEGA (Observatoire pour la Minéralogie, l'Eau, les Glaces et l'Activité) spectrometric data set from Mars Express mission has been choosen to analyse the presence and diversification of minerals in the rock material of the Noctis Labyrinthus region of Mars. New data from the OMEGA instrument recently provided extensive information on the aqueous history of Mars and the mineralogical evolution of its crust (Bibring et al. 2006). The use of Mars Orbiter Camera (MOC) imaging data from Mars Global Surveyor mission is an example of using correlations between spectral data and images of rock material from camera data to analysing the Mars surface.

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Fig. 1. View on the Noctis Labyrinthus area and the course of Mars Express orbits; source of image: MOC/ MGS data.

METHODS OF INVESTIGATION

The OMEGA VIS/IR imaging spectrometer aboard Mars Express orbiter collects spectra in the 0.38 to 5.2 µm wavelength range. The spatial resolution of the spectrometer varies from over 300 m to 4.8 km/pixel. These parameters allow to use this spectrometer as a basic tool in recognizing the mineral composition of Mars surface. Only the near IR range (1.0 to 2.5 um) has been used for this study. The use of the lower range (0.38-1.0 µm) is problematic because of occuring geometric registration problems. Only 108 narrow spectral bands that can be correctly geometrically registered and well processed to obtain valuable spectra for analyses have been used in the analyses shown below.

Raw OMEGA data should be corrected for the contribution of atmospheric components before an analysis of the surface composition. There is exists for this purpose, an often used (e.g. Mustard et al. 2005), algorithm basing on differences in thicknesses of atmospheric column content in measurements made at the top and at the bottom of Olympus Mons (the highest volcano in the Solar System, over 24 km high). Slopes of Olympus Mons are composed uniformly of basaltic lavas, so the only change in an observed, in short time, pair of images should be in the atmospheric content. By taking the ratio of measurements coming from the top and the bottom of Olympus Mons slope we should get clear atmospheric "contamination". The obtained spectrum can be used to correct the remaining data.

The Spectral Angle Mapping (SAM) algorithm included in the ENVI software package has been used for this research. This algorithm bases on finding "the purest" pixels (statistically the most typical inside clusters of pixels) in a n-dimensional space. Dimensionality is equal to the number of endmembers (proposed mineral components) and usually should not be greater than 15-20. The algorithm is building e.g. a 15-dimentional space and trying to compose the analyzed pixels into 15 clusters. Each of such cluster should correspond to one of the mineral contents on the analysed image. At the end of the calculations we can show the derived endmembers and decide, which of them should be used in the process of image classification, the next step in the SAM analysis. There is a possibility to delete some endmembers, add endmembers (e.g. from a spectral library) or substituting a derived endmember we can recognize as a specific mineral or rock content by a pure content from a spectral library. At this step it allows to decide which endmember group will classify the image. The classification process assigns each image pixel to one cluster. At the last step cluster should group pixels showing areas covered by a specific type of material.

A part of the OMEGA data set from 4 representative orbits: 305, 357, 486 and 519 has been analysed. The orbits 357 and 519 cut the western part of Noctis Labyrinthus, while the orbits 305 and 486 cross the central part of this region (Fig. 1). Part of the



orbit 486 corresponds to the MOC narrow angle image S04-00657, which covers the area over 7°S latitude and 95°W longitude (Fig. 2a, b).

RESULTS AND DISCUSSION

The analysis of the OMEGA spectra shows evidence of pyroxenes both in the central and western part of the Noctis Labyrinthus region. In measurements from the central part of this area the shape of the spectrum in the range 1-2 um and the band over 2.5 µm indicates the presence of a pyroxene component - diopsyde. The characteristic absorption band of augite (over 1.5 µm) has also been observed. This result is a confirmation for the presence of augite in the PFS spectrum from this area (Gurgurewicz 2005). In measurements from the western part of the Noctis Labyrinthus an evidence of diopsyde is also present. According to the SAM classification, pyroxenes occur mainly on the plateau and in low quantity on the canyons slopes and floors. The spectra from both the western and central part of the Noctis Labyrinthus area probably include also clays components: nontronite, hallovsite or illite/smectite. Results of the SAM classification show that deposits with possible presence of clavs occur on the canyons slopes and floors. Presence of clays must be confirmed by results of ratioing a neutral spectrum and the spectrum from the possible clays-rich area.

The spatial resolution of PFS data, that have been used in the earliest analysis of the Noctis Labyrinthus region, in most cases did not allow to identify the mineral composition of particular kinds of the rock material (Gurgurewicz 2005). Use of OMEGA data to determine mineralogy makes possible to describe detailed spatial diversification of identified minerals and provides new insights into the mineralogical processes that have taken place in this area. Part of the area in the central

Fig. 2. Diversification of the rock material on the canyon slope in the central part of Noctis Labyrinthus: (A) localization of MOC image; subframe from Viking image; (B) subframe from MOC image S04-00657, center coordinates are 95.57°W, 7.23°S, image resolution is 2,99 m/pixel.

part of Noctis Labyrinthus classified by SAM algorithm corresponds to the MOC image S04-00657 (Fig. 2a, b). This representative image shows diversification and relationships of rock forms and material in the canyon. Volcanic material forming extended, several kilometers long ridges, is observed on the canvon slope (Fig. 2b). Most part of the canvon wall is covered by a large quantity of eolian material (Fig. 2b). Results of the SAM classification indicate that this is an area with possible clays components. Volcanic material is probably covered by an alteration layer which modifies the reflectance properties. Covering by eolian material and possible presence of clavs indicate strong weathering processes in this area. Evidence for proximity of volcanic material and deposits with possible presence of clavs on MOC image (Fig. 2b) might point to a hydrothermal alteration as a possible source of hydrated silicates. Occurrence of this rock material on the canvons slopes and floors points out that this is an old deposit which has been afterwards exposed through erosion. Connecting the specific endmember to an area in SAM classification means that the spectral answer of the instrument is most close to that endmember. This analysis is primarily qualitative. Quantitatively we can only conclude that areas showing up in the process of classification are mostly covered by a given type of material. Correction for the atmosphere used in this analysis is a simple method with many assumptions. These are: no changes in the mineral composition of the volcano slope, no differences in the atmospheric composition over the planet and no long period changes in the atmospheric composition (e.g. no changes of the dust content in the atmosphere). These assumptions affect the obtained spectra and we have to remember them when we analyse and interpret the data.

This research work is supported by the budget funds for science in the years 2005-2007 under the research project No. 2 P04D 020 28.

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ZIRCONS AND THE EVOLUTION OF THE CONTINENTAL CRUST: INSIGHTS FROM COMBINED HF AND O ISOTOPES

Abstract: The continental crust has an evolved composition. From the late Archaean it appears to have been generated in pulses of relatively rapid growth that occur every billion years or so. The development of improved techniques for the in situ analysis of U–Pb, Lu–Hf and O isotopes and trace element contents has revolutionized approaches to modeling the origins and evolution of the continental crust, and the petrogenesis of granite.

Keywords: continental crust, zircons, crustal evolution.

Models for the evolution of the continental crust need to reconcile the crust formation ages of material whose isotope ratios reflect involvement in the sedimentary cycle, and those that do not. Such data are now available from in situ O and Hf isotope ratios on well-dated zircons. Detrital zircons encapsulate a more representative record of igneous events than the exposed geology and their hafnium isotope ratios reflect the time since the source of the parental magmas separated from the mantle.

A number of studies have highlighted striking global peaks in juvenile igneous activity at 2.7, 1.9 and 1.2 Ga, perhaps implying rapid crustal generation in response to the emplacement of mantle "super-plumes". An initial study on samples from the Lachlan Fold belt in SE Australia revealed sharp peaks in zircon crystallization ages at 0.5 and 1.0 Ga, and ages that range back to 3.4 Ga. The Hf isotope model ages range from 1.4 to 3.6 Ga, but those with d18O of < 6.5 per mil are restricted to two peaks at 1.9 Ga and 3.3 Ga. It is argued that crust generation in this part of Gondwana was limited to major pulses at 1.9 Ga and 3.3 Ga, and that the zircons crystallized during repeated magmatic reworking of crust formed at these times.

The present data indicate that from the late Archaean continental crust has been generated in pulses of relatively rapid growth. The sedimentary record shows no such pulsed evolution, and one interpretation is that it can take up to one billion years for new crust to dominate the sedimentary record. It appears that the generation of new crust may have been less linked to the development of mountainous areas susceptible to preferential erosion, than was previously envisaged. New models for crust differentiation highlight that the residence times of elements in the lower crust is much less than in the upper crust, and that the average rates of crust generation are inferred to have been in excess of six times those in the recent geologic past. Over 4 Ga more than half the K, and one quarter of the Li in the silicate Earth may therefore have been processed through the continental crust.

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MINERALOGICAL CONTROL OF ELEMENTS DISTRIBUTION IN PODZOLIC SOILS IN THE TATRA MTS

Abstract: Removal of elements from particular soil horizons and weathering features on inherited minerals of granite in three podzolic soil profiles in the Tatra Mts. were studied. The most intense removal of elements was observed in AEes horizons but also for few elements strong weathering was observed in lowermost horizons. Variable weathering intensity observed on mineral grains surfaces in single horizon confirms suggestion of existence of differing geochemical microenvironments in soils.

Keywords: Granite, Podzols, weathering features, removal of elements.

INTRODUCTION

The Skeletic Podzols (according to World Reference Base for Soil Resources 1998) formed on granitic rocks were studied. Soils are shallow and contain a considerable amount (from 20 to 40-60 %) of gravel and stone particles (>2000 μ m). The studied profiles have characteristic coloured sequence of genetic horizons: (1) organic (Oh) and humus (Ah) horizons with *albic* (Ees) horizons - developed usually as lenses within the lower part of humus horizons (AEes) (2) *spodic* (Bhfe) horizons, and (3) parent material (C). Soil texture ranges from loamy sand to sandy loam. The studied soils are acidic in the whole profiles and their pH water does not exceed 4.5. More acidic is upper part of soil profiles. The soils can be characterized by thick humus horizons, muck-like organic matter of the alpine moder type occurs, and a high concentration of total organic carbon.

The aim of the study is to compare intensity of removal of selected elements from soil horizons with mineral resistance and observed weathering features in soils in the Tatra Mts.

MATERIAL AND METHODS

Samples were collected from three soil profiles: GR7 and GR8 (see detailed profile in Fig. 1) on the NE slope of Mt. Beskid formed on so-called Goryczkowa granite and GR1 near the Morskie Oko lake formed on the High Tatra granodiorite.

Pedological examination was executed in the Institute of Geography and Spatial Management, Jagiellonian University. Polished sections, rock fragments and mineral grains were studied using scanning electron microscope HITACHI S-4700 with energy-dispersive X-ray spectrometer (NORAN Vantage) at the Institute of Geological Sciences,

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Jagiellonian University. Major and trace element analysis were made at the Actlabs in Canada using ICP-AES and ICP-MS methods.

Calculation of weathering intensity for particular elements in subsequent soil horizons was obtained using equation proposed by Land et al. (1999):

 $\Delta m_i = ([i]_w [Zr]_/ [Zr]_w [i]_w [Zr]_-1) 100 \%$

where Δm_i denote relative mass change of element i, c and w denote C – horizon and some weathered horizon. Values in square brackets refer to concentration.

RESULTS

Majority of elements seems to be depleted in whole soil profile (GR8) in comparison to their abundance in C horizon with an exception of Ti (+80 % of enrichment), V, Cr, U, Cs, Sb. Some elements are depleted in uppermost horizons AEes or Ah and enriched in Bhfe horizons (Ni, Cu, Be, Fe) (Fig. 1).

The lowest pH values were measured in AEes horizon. The strongest depletion in AEes horizon was observed for P (-40 %), Al (-45 %), Fe (-35 %) (Fig. 1), U (-55 %), Mg (-55 %), Be (-25 %), Co (-70 %), Rb (-30 %), Cu (-10 %) and Ni (-60 %).



Fig. 1. Relative mass change of Fe, Ca, P and La in soil (GR8) horizons

Bhfe horizons, in comparison to AEes are more enriched (or less depleted) in some elements e.g. Mg (+10 %), Ca (-45 %), Al (0 %), Fe (+80 %), K (-30 %), Ti (+80 %), P (-5 %), Mn (-5 %), Ni, Zn, B, Co, Cu.

Many elements are also strongly depleted in BC1hfe horizon. Depletion can be similar to this in AEes horizon, e.g. Ca, Na, K, P, Y, V, Cr, Sc, Rb, Lu or even higher (Si, Ti, Pb, Hf, Sm, Nd, La, Ce, Th, Sb) (Fig. 1).

In some horizons both weathered and unweathered feldspars occur in similar proportions. Plagioclase seems to be less resistant than K-feldspar. Deep holes that are often developed along fractures (Fig. 2a) or small eatching pits are present in K-feldspars. It is commonly observed that biotite flakes are loosened and partly dissolved. The higher weathering resistance of chlorite was revealed (Fig. 2b). Muscovite is very rare and its dissolution in acidic conditions was not observed. Although quartz is regarded as a stable mineral, irregular hollows on its surfaces were noticed in Ah horizons. Small quartz crystals can form envelopes around some minerals, fill hollows or form spherical aggregates. These crystals originate probably from polycrystalline quartz which is common in parent rocks.

Among accessory minerals dissolution microtextures were found only on apatite grains (Fig. 2c). Almost completely dissolved grains, grains with big dissolution holes and with small irregular eatching pits were observed. Dissolved and well preserved grains can occur in the same soil horizon. Monazite crystals are very often fractured and crushed but this seems to be related to mechanical destruction rather than to weathering. Rutile and titanite crystals are not decomposed.

Precipitation of new minerals and probably of amorphous phases is observed. Inhomogenous in chemical composition aggregates composed mainly of Fe, Al and Si with minor amount of P, Mn, Ti, Ca, Mg, K and REE often form fillings within partly dissolved feldspars (Fig. 2a).

DISCUSSION

High concentration of Fe in examined soil (+20 to +80 %) in horizons from AEes to BC1hfe, Ca and Na removal, depletion of P from AEes horizon (-40 %) and BC1hfe (-20 %) correspond with microscopic observation of Fe phases precipitation and plagioclase or apatite dissolution. LREE and Th depletion in BC1hfe horizons can be related to monazite dissolution however monazite dissolution was not noticed in studied samples. Monazite dissolution was described in podzol in the Dolina Suchej Wody valley (Jerzykowska 2005). It also possible that REE was released from other minerals, e.g. plagioclases or hornblende (Harlavan & Erel 2002).

Variable weathering rate of minerals in the same soil horizon and differences between mineralogical and geochemical weathering indices can be explained as a result of occurrence of distinct geochemical microenvironments in soils (Lång 2000; Morton and Hallsworth 1999; Skiba 2003).

The most intense weathering in AEes horizon is obvious because of the lowest pH values in this horizon. Very strong weathering in BC1hfe, BC2fe horizons suggested by geochemical analysis (Fig. 1) and supported by the study of accessory minerals in soils in





Fig. 2. Weathering features: a) weathering of K-feldspar - Bhfe horizon b) weathered biotite and not dissolved chlorite – BC1hfe horizon c) initial stage of weathering of apatite – BC1hfe horizon; SEM-BSE images.

the Dolina Suchej Wody valley (Jerzykowska 2005) can be explained by percolation of water through the soil along the surface of fresh rock downwards the slopes.

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SILICATES ASSOCIATION IN NODULES OF IRON METEORITES SEELÄSGEN, MORASKO AND JANKOWO DOLNE

Abstract: In the study of iron meteorites (type IIICD or IAB) the presence of graphite-troilite and troilite nodules with minor silicate and phosphate phases has been established. Silicate phases are represented by pyroxene, olivine, alkali feldspar and silica. These are accompanied by Na, Ca, Mg and Fe phosphates. Diversity of pyroxenes suggests complex origins of silicates, a conjecture confirmed by the considerable share of kosmochlor and the presence of kosmochlor-augite, which formed in reaction of residual melt with enstatite and crystallizes within chromite. **Keywords:** silicates, nodules, iron meteorite, Seeläsgen, Morasko, Jankowo Dolne.

INTRODUCTION

Silicate inclusions (nodules) in iron meteorites occur only within the IAB and the II-ICD types. Five types of inclusions can be distinguished: a) sulphide-rich, composed primarily of troilite and containing abundant embedded silicates; b) non-chondritic, silicate-rich, comprised of basaltic, troctolitic, and peridotic mineralogies; c) angular, chondritic silicate-rich, the most common type, with approximately chondritic mineralogy and most closely resembling the winonaites in composition and texture; d) rounded, often graphite-rich assemblages that sometimes contain silicates; and e) phosphate-bearing inclusions with phosphates generally found in contact with the metallic host (Benedix et al. 2000). The Seeläsgen (Przełazy), Morasko and Jankowo Dolne iron meteorites originate probably from a single fall, although they are still not thoroughly studied and unambiguously classified. Until recently they had been considered to be type IAB, however presently their classification has been changed to type IIICD (Choi et al. 1995). Genetically, iron IAB and IIICD meteorites with nodules (inclusions) containing siltactes are related to a particular group of meteorites, namely the winonaites (Clayton and Mayeda 1996, Benedix et al. 1998, 2000).

SAMPLES AND ANALYTICAL METHODS

The material under examination comes from cut-through meteorite fragments containing nodules found in the vicinity of Przełazy (2), Morasko (20) and Jankowo Dolne (1). Material from the collection of the Institute of Geology, Adam Mickiewicz University (Poznań), from a private collection of Mr K. Socha as well as single specimens from other individual collectors were used. Microscope study of 41 specimens was done in order to find silicate phases. The essential part of examination of minerals was car-

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ried out with the CAMECA SX 100 microprobe in the Inter-Institutional Laboratory of Microanalysis of Minerals and Synthetic Substances at the Faculty of Geology, Warsaw University.

RESULTS AND DISCUSSION

Meteorites of the Morasko type contain numerous irregularly scattered oval nodules ranging from 0.n to a couple of centimetres in size. Most of the nodules are represented by the type, which might be regarded as type d) of Benedix et al. (2000) – rounded, often graphite-rich assemblages that sometimes contain silicates. From the outside the nodules are rimmed with a layer of coarse-grained schreibersite and cohenite. Nodules with the schreibersite-cohenite rim in vestigial form also occur. The nodules' interior is filled with graphite and trolite occurring in various proportions, as well as other mineral phases. Apart from these the presence of the following phases has been recorded: sphalerite, whitlockite (Dominik 1976), altaite, daubreelite, kosmochlor (Muszyński et al. 2001), albite with zones of K-feldspar, independent K-feldspar, silica (unidentified), four different pyroxene phases, olivine, chromites, native copper, Nb-rutile, pentlandite, djerfisherite and a few Na, Mg, Ca and Fe phosphates (unpublished results by the authors).

Silicate minerals most often occur as separate grains located in graphite-troilite or troilite mass. Less often larger aggregates are formed consisting of pyroxenes, alkali feld-spar and silica, accompanied by phosphates. Kosmochlor is the most common pyroxene. Its composition slightly varies within individual grains. Its occurrence was determined in nodules from Morasko, Jankowo Dolne and Przełazy. Separate grains with small troilite or graphite inclusions are the most widespread form. Kosmochlor coexisting with other pyroxenes was not recorded. The presence of Na, Mg, Cr, Ti, Fe and Ca pyroxenes with some K admixture within the chromite grains, outside of which kosmochlor occurs, was established.





Fig. 1. Q-J diagram for the nodule pyroxenes from Seeläsgen, Morasko, Jankowo Dolne meteorites.

Fig. 2. Classification of the Ca – Mg – Fe^{2+} pyroxenes from Morasko type meteorites.

Enstatites occur separately from kosmochlor, sometimes they are contacting with feldspar or phosphates. They sometimes contain numerous small inclusions of troilite or silica. In the fracture zones and in the grain rim region the reactive secretes of Mg-Ca-Na-Cr pyroxenes are formed, suggesting a reaction between enstatite and the residual melt rich in Na, Ca and Cr.

The classification of pyroxenes from the examined nodules based on the Q-J diagram (Fig. 1) indicates three types of pyroxenes: I –Ca-Mg-Fe²⁺-pyroxenes (Quad); II –Ca-Na-pyroxenes and III –Na-pyroxenes.



Fig. 3. Composition range of the Ca – Na and Na nodule pyroxenes from Morasko type meteorites.



Fig. 4. Correlation of Na + Cr with Ca + Mg (in number of atoms based on 6 O atoms) for the nodule pyroxenes from Morasko type meteorites.

Substantial part of Ca-Na pyroxenes projection points lies outside the Q+J=2 line, which indicates their atypical composition, rare among pyroxenes of earthly origins. On the En-Wo-Fs diagram (Fig. 2) the projection points of pyroxenes of the first type are within the enstatite field. Two subgroups can be distinguished: a) – with practically no ferrosilite, and b) – with approximately 10 % content of ferrosilite. These pyroxenes occur in different nodules. For the classification of pyroxenes of type II and III a modified Q – Jd – Ko diagram was used, with aegirine replaced by kosmochlor (Fig. 3). It follows from the diagram that Ca-Na-pyroxenes correspond to kosmochlor-augite and Na-pyroxenes are almost pure kosmochlores.

The linear dependence shown on the Na+Cr/Ca+Mg (a.p.f.u.) diagram (Fig. 4) indicates that the substitution prevailing in Ca-Na- and Na-pyroxenes is Ca+Mg \leftrightarrow Na+Cr³. This indicates that they belong to the solid solution of diopside-kosmochlor. Moreover, Ca-Na-pyroxenes contain a small molecule of neptunite (Na Ti⁴⁺_{0.5}(Fe,Mg)²⁺_{0.5}Si₂O₆), suggested by the linear dependence between Ti and Na remaining after the formation of kosmochlor molecules (Fig. 5).

CONCLUSIONS

The genesis of pyroxenes within nodules in Morasko type meteorites seems to be much more complex than is conjectured by Benedix et al. (2000).



Fig. 5. Correlation of Ti⁴⁺ with Na – Cr (in number of atoms based on 6 O atoms)

In our opinion two types of silicate melts occurred during pyroxene formation. The melts were rich in Na, K, Ca, Cr, Fe and phosphate ions. The first one, chemically close to aubrites, crystallized two enstatites, silica and olivine. The second one gave rise to kosmochlor. When fractionated (rich in Ca, Na and Cr), it reacted with previously formed enstatites leading to kosmochlor-augite. During the process of crystallization of chromite the residual melt led to the crystallization of another kosmochlor-augite, richer in Na and Cr.

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TRANSFORMATION OF BLAST FURNACE SLAG USED IN ROAD CONSTRUCTION

Abstract: Slags, co-products of metallurgical processes, are commonly applied as a road construction material. Slags formed in pig-iron production consist of various primary Ca-silicates like larnite, akermanite, gehlenite as dominant phases. They contain also metallic iron droplets, diopside, titanite, metallic bismuth, Mn-containing monticellite and MnS as subordinate components. Secondary minerals formed in reaction of slag with ground waters were determined in slag collected from road base in the Niepołomice Forest. Assemblage of secondary minerals present in voids and in incrustation on slag fragments margins consists of calcite, SiO₂, gypsum, alite and barite. Degree of transformation of blast furnace slag used in road construction is low and has no influence on mechanical properties of this material.

Keywords: blast furnace slag, long-term transformation of slag, secondary phases.

INTRODUCTION

Blast furnace slags formed in pig-iron production are by-products of this process. Every year tones of slag are dumped, that can cause environment impact, and occupies mass of lands (Shen, Forssberg 2002). Nowadays most of them are utilized. Because of their properties comparable to natural materials they have found a wide application in cement production, landfill cover material, civil engineering work and hydraulic engineering, agriculture, but mainly as a road construction material (Proctor et al. 2000), not only for unbound layers like road bases and sub-bases but also for bituminous bound layers like surface layers (Motz, Geiseler 2001). Utilization of slag gives an opportunity of protection of natural resources. The most characteristic mineral phases of slag are silicate of melilite group like gehlenite and akermanite; larnite, merwinite, monticellite, wüstite, and Fe, Mn, Mg, Ca oxides, metallic iron and glass (Sobczyński 1999).

The aim of the study was to observe changes in composition of blast furnace slag, used as a base material of road construction, in acid geochemical conditions caused by ground waters in the Niepołomice Forest and to determine long-term stability and durability of the slag. Although numerous papers on long-term weathering of slags on heaps are published, much less data on changes of slags in contact with acid ground waters are available.

In this study we use the term "mineral" even though it is incompatible with IMA definition.

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SAMPLES AND METHODS

The samples of slag came from unbound layers of road base, from holes in asphaltic layer of ca. 25 years old road in the centre of the Niepołomice Forest near Niepołomice (close to Karkówe, S Poland). Collected fragments were small (3-5 cm in diameter), irregular, grey coloured with abundant circular voids. For further studies we selected fragments with macroscopically visible changes at margins. Various analytical methods were used: optical microscopy, SEM-EDS, XRD.

RESULTS AND INTERPRETATION

Primary minerals (i.e. components formed before reactions with ground waters) determined in the studied blast furnace slag are: elongated crystals of akermanite (Fig. 1 and 2), gehlenite, larnite (Fig. 1) as dominant phases determined by XRD and SEM-EDS method. As subordinate components wollastonite (Fig. 1 and 3), diopside, titanite, metallic iron droplets (Fig. 2), (?) metallic bismuth, Mn-containing monticellite were determined using SEM-EDS. Component determined as MnS (Fig. 1) based on SEM-EDS results is probably also of primary origin.

Secondary minerals are present in circular voids and at margins of slag fragments. Voids are filled with elongated gypsum crystals (Fig. 3), rimmed by calcite and filled with SiO₂ phases (Fig. 4) or rimmed by Ca silicate (alite?) and calcite (Fig. 5).

Margins of slag fragments are often encrusted by calcite. Calcite layer can be from 10 to 50 μ m thick (Fig. 6).

Sulphur is present in sulphate and sulphide phases but also is dispersed in whole volume of slag. Ca. 2 wt % of sulphur is usually determined in spot analyses of silicate minerals. Barite crystals dispersed in slag were formed as secondary components in reaction of sulphate ion containing water with Ba.



Fig. 1. Larnite and MnS intergrowths and wollastonite skeletal crystals in akermanite groundmass.



Fig. 2. Metallic iron droplets in akermanite.



Fig. 3. Pore-filling gypsum in akermanite--wollastonite slag.



Fig. 4. Pore space rimmed by calcite and filled with SiO_{2} .



Fig. 5. Pore space rimmed by Ca silicate (alite?) (dark rim) and calcite (light rim).



Fig. 6. Slag margin rimmed by calcite (right edge).

CONCLUSION

Secondary minerals that can be interpreted as a result of slag transformation in reaction with ground waters (gypsum, calcite, SiO_2) are present in voids and form encrustation of surfaces of slag fragments. Most components of secondary minerals are probably leached from slag (e.g. Ca, S, Si). Presence of calcite in voids rims indicates deep penetration of slag fragments by solutions rich in carbonate anion crystallized. Presence of calcite in voids and external rims suggests that acid ground waters were neutralized in reactions with alkali-rich components of slag. External source of sulphur (atmospheric precipitation) cannot be ruled out.

The study of long-term stability of blast furnace slag used in road construction indicates that degree of transformation is low within ca. 25 years period, and probably has no influence on the mechanical properties of slag.

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CAMBRIAN STAGES OF MAGMATIC ACTIVITY IN KACZAWA METAMORPHIC COMPLEX (WEST SUDETES, SW POLAND) – NEW EVIDENCE FROM ZIRCON Pb-EVAPORATION DATINGS

Abstract: Three samples representing acid (meta)magmatic rocks from different units of the Kaczawa Metamorphic Complex (KMC) were dated using single zircon evaporation ²⁰⁷Pb/²⁰⁶Pb isotope method. The mylonitised rhyolitic metavolcanic (metatuff?) from the Bolków Unit yielded an age 540.8 \pm 5.6 Ma and undeformed, silicified metarhyolite from the Lubań Unit 527.4 \pm 9.6 Ma. These datings suggest that the volcanic succession of KMC related with initial, continental rifting is of the Early Cambrian age. The third sample of weakly deformed metagranitoid from the Cieszów Unit gave an age 492 \pm 15 Ma which documents the presence of the Late Cambrian / Early Ordovician plutonic rocks formed during c. 500 Ma thermal event.

Keywords: West Sudetes, Saxothuringian zone, Cambrian, magmatic activity, geochronology, zircon, Pb-Pb isotopes.

INTRODUCTION

The Kaczawa Metamorphic Complex (KMC) is a part of the Variscan belt located in the NE peripheries of the Saxothuringian Zone. Due to intensive orogenic shuffling and stacking the accretionary prism of KMC is composed of several subordinate units, including folded thrust-sheets, slices and melange bodies (Baranowski et al. 1990, Kryza & Muszyński 2003). Such a tectonic complexity together with scarcity of reliable fossils make it difficult to unravel the precise step-by-step development of its primary sedimentary-volcanic succession. One of important and unresolved problem – due to a lack of precise geochronological constraints – is also a time of succesive volcanic stages. Hence, whichever new datings are of crucial value for understanding geodynamic history of this part of Variscides.

RESULTS

Zircons from three samples of acid metaigneous rocks from different parts of KMC were analysed using evaporation ²⁰⁷Pb/²⁰⁶Pb isotope method at the Isotope Laboratory of the Department for Mineralogy at the TU Bergakademie Freiberg. Isotopic ratios

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were measured using a Finigan MAT 262 spectrometer basing on the studies of Kober (1986, 1987). Details on the analytical procedure are given by Görz et al. (2004).

Sample CHROS.1 represents white-yellow, finegrained, laminated metavolcanic rock collected from the Czernicka Mt (1 km SW from Janówek) in the western part of the Bolków Unit. This rock belongs to the "Osełka rhyodacites" volcanic association which occurs as interlayers in mafic eruptives (Muszyński 1994). Zircon crystals from CHROS.1 are euhedral, clear and colourless to yellowish. Most of them are of normal prismatic habit (mean elongation 2,4) and in microscopic examination show oscillatory zonning that is characteristic of magmatic zircon growth. Their morphology is strongly dominated by {100} and {101} forms. According to classification of Pupin and Turco (1972) most crystals represent S25, P5 and D types. Inclusions, mainly apatite, are present in almost all the zircons.

The weighted mean age (WMA) for nine measurements of sample CHROS.1 provides an age of 540.8±5.6 Ma, i.e. lower part of the Early Cambrian. Petrographic features indicate acid tuff as a possible protolith for the CHROS.1 rock. Nevertheless because of strong shearing and obscured boundaries with surrounding metabasites their subvolcanic, intrusive character can not be excluded. Thus, the given age may represent a minimum time of its deposition or a time of injection.

Sample RADOG.1 is a yellow-greenish, weakly deformed quartz metarhyolite (with visible quartz grains as porphyrocrystals) obtained from the vicinity of Radogoszcz in the Lubań Unit. The zircon crystals selected for Pb-evaporation dating were 100-200 µm long, mainly colourless, euhedral and normal to short prismatic (mean elongation 2.0). More than 60 % of the grains display oscillatory zoning. The {100} prism is better developed than {110} and {101} is a prevailing bypiramid. Most zircons belong to P5, P4 and S25 types. The WMA age of 527.4±9.6 Ma, based on eight measurements, suggests that the emplacement of this subvolcanic body took place in the middle part of Lower Cambrian. However, the reported result should be treated with caution due to high common-Pb content (²⁰⁶Pb/²⁰⁴Pb<2500 for most analysed zircons) and all limits of the Pb-evaporation method.

Sample CIESZ.1.1 is a weakly deformed, medium-grained albitized metagranitoid collected from the "Jaskulin element" – a part of the Cieszów Unit. The metagranitoid belongs to a suite of felsic, Na-rich rocks named by Smulikowski (1956) "cataclasites and mylonites from Cieszów" which are associated with spilites and diabases. Most zircons in CIESZ.1.1 are euhedral, yellow and small (<150 μ m in length). Mean elongation of 2.1 reflects significant percentage of short prismatic crystals in the whole population. The most frequent morphological types are P4, P5 and S19-S20. The analysed sample yielded a WMA age of 492±15 Ma which may be considered as a minimum time of granitoid emplacement.

DISCUSSION AND CONCLUSIONS

Presented new isotope data mark at least two stages of magmatic activity in the Kaczawa Metamorphic Complex (KMC): Early Cambrian and Late Cambrian / Early Ordovician.

The 540.8±5.6Ma age of acid metavolcanic inlayer enclosed in the basic eruptives of Bolków Unit places the initial stage of continental rifting at the beginning of the Early Cambrian. It may possibly represent a time-equivalent of recently identified c. 540 Ma plutons (Żelaźniewicz et al. 2004) indicating that this rifting was synchronous to late- or post-Cadomian thermal activity ongoing in adjusting geological units.

The imprecise 527.4±9.6Ma age of metarhyolite from the Lubań Unit overlaps within error limits with the age obtained for CHROS.1 sample. However we cannot rule out that it reflects middle Early Cambrian volcanism in the KMC. Comparable ages are reported from other regions of the Saxothuringian zone (i.e. Jonas et al. 2001). More detail study will be carried out in order to verify that thesis.

The age of 492±15 Ma for metagranitoid from Cieszów Unit – proves that in the transition between Late Cambrian and Early Ordovician the area of KMC, like many other Sudetic series (Oliver et al. 1993, Kröner et al. 2001, Turniak et al. 2000, Mazur et al. 2004, Kozdrój et al. 2005) was affected by input of thermal energy which caused crustal anatexis and injections of granitoid magmas.

The study was financed in 2005-2007 by the Ministry of Science and Informatization; project no. 2 PO4D 065 29.

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ZIRCON FEATURES DEPENDENT ON MAGMA TYPE AND TECTONIC DEFORMATION: EXAMPLES FROM ORDOVICIAN METAVOLCANIC ROCKS OF THE KACZAWA COMPLEX (SUDETES, SW POLAND)

Abstract: Observations based on optical microscopy, CL and SHRIMP studies of zircons from Early Ordovician metarhyodacite and metatrachyte of the Kaczawa Complex (Sudetes) indicate that zircon abundance and morphology strongly depend on the chemical type of magma: zircons in calc-alkaline rocks are larger and abundant, with common inherited cores; in alkaline rocks, they are smaller and less frequent, with very rare inheritance. Intense tectonic deformation (shearing) may cause cracking of zircon grains, allowing fluid circulation, causing disturbance of their chemical and even isotopic composition.

Keywords: zircon, SHRIMP, metavolcanic rocks, geochemistry, deformation, Kaczawa Complex, Variscides.

INTRODUCTION

Two samples of Early Ordovician metatrachyte and metarhyodacite from Mysłów (20 km east of Jelenia Góra), from the lower part of the Kaczawa Complex, have been dated using the SHRIMP II in VSEGEI, St. Petersburg. A detailed account and ages are published elsewhere (Kryza et al. 2006), here we report selected observations concerning specific characteristics of the zircons studied and their possible petrogenetic significance.

METHODS

The samples, c. 3 kg each, were crushed and sieved. Minerals were separated using the conventional heavy liquid (sodium polytungsten) procedure. Hand-picked zircons were mounted in resin, and polished sections were used for optical microscopy, CL imaging, and SHRIMP analysis (see Kryza et al. 2006).

OUTLINE GEOLOGY AND GEOCHEMISTRY

The two felsic metavolcanic rocks sampled differ in their petrographic and geochemical features and the differences seem to imply different zircon abundances and characteristics. The rocks are metamorphosed under blueschist- to greenschist facies conditions (Kryza & Muszyński 2003, and refs. therein).

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The metarhyodacites are pale-cream coloured, very fine-grained and strongly sheared rocks, composed of quartz, K-feldspar, plagioclase, sericite, minor chlorite, and abundant accessory zircon and apatite. They are calc-alkaline in composition, with negative ϵ Nd₅₀₀ values. They were interpreted to have been derived form continental crustal melts emplaced as ash-flow bodies (Furnes et al. 1994).

The metatrachytes from volcanic extrusions are pale-purple to dark gray, aphanitic rocks of massive texture, usually with no signs of deformation. They are composed of feldspars, quartz, sericite, iron oxides and, quite frequently, finely-crystalline aegirine. Rare, but symptomatic, jadeite was ascertained as small relict inclusions in feldspars (Kryza & Muszyński 2003, and refs. therein). These rocks are strongly alkaline and represent acidic members of a bimodal alkaline suite (the Lubrza Trachytes) the geochemical and isotopic characteristics of which (ϵ Nd₅₀₀ between +1.9 to +3.7) indicate a mantle source. Both the rhyodacites and trachytes were interpreted as emplaced in an initial continental rift setting (Furnes et al. 1994).

SPECIFIC ZIRCON CHARACTERISTICS

(1) Zircon abundance and morphology.

The zircon abundance and morphology in both samples studied are sharply contrasting.

The rhyodacite contains a large amount of crystals. Typically, the zircons are euhedral, short- to medium-prismatic, with dominant (100) prism and (101) pyramid (Kryza et al. 2006). Most crystals have a clear central domain, and moderately pronounced growth zoning in their outer parts (Fig. 1a). A few crystals have less regular habits: isometric, subrounded or ellipsoidal, occasionally broken; the zircons of that group are usually very bright in CL images and appear to represent inherited grains.

The zircons in the trachytes are not very abundant in spite of the high Zr contents determined in bulk chemical analyses – up to 1186 ppm (Furnes et al. 1994). Typically, the zircons in the sample analysed are euhedral, short-prismatic, with strongly dominating (100) prism and (110) pyramid. Most of them are clean and homogeneous, with only a very few displaying indistinct cores and zoning; the latter grains are usually brighter in CL images (Fig. 1b).

Interpretation: The zircon abundance in both the rock types is in contrast to their zirconium contents: 68-219 ppm in the rhyodacites, and 650-1186 ppm in the trachytes (Furnes et al. 1994). The low quantity of zircon crystals in the trachytes, their small size and scarcity of inherited cores, seem to be controlled by the strong alkalinity of the magma, zirconium undersaturation and resultant high solubility of Zr in such melts. It might well be that zirconium was consumed by other growing minerals (e.g. pyroxene), so there was not enough that element to form abundant independent mineral phase. All these features are in line with the mantle provenance of the alkaline magmas in that area. In contrast, the rhyodacites derived from continental crustal calc-alkaline melts contain large amounts of fairly big crystals, with many enclosing inherited cores from the magma precursor.







Fig. 1. Zircons from metarhyodacite, sample OK9, in transmitted plane polarized light (a) and in CL (b); zircons from metatrachyte, sample LA2, in transmitted plane polarized light (c) and in CL (d). Notice the differences in size, morphology and internal structure of the crystals.

(2) Zircon crystal cracking caused by deformation.

There is also a strong contrast between the two rocks, as far as the degree of tectonic deformation is concerned. The rhyodacites are extremely sheared, with common mylonitic fabric. The zircon grains in these rocks are very often cracked and this physical damage has caused local disturbance in their chemistry. It was notified that the data from analytical spots close to cracks show high common Pb and wide (c. 270 to 500 Ma) dispersion of ages. In contrast, again, the trachytes are very massive, often with no traces of deformation, and their zircons display much less chemical and isotopic disturbance, and define a much more distinct age cluster at around 485 Ma (Kryza et al. 2006).

CONCLUSIONS

1. Our CL and SHRIMP results have shown that zircon abundance and morphology strongly depend on chemical type of magma (alkaline vs. calc-alkaline).

2. Deformation, e.g. intense shearing, may cause cracking of zircon grains and disturb their chemical and isotopic characteristics, and consequently, influence the measured isotopic ages.

The study was supported by the internal grants of Wrocław University, 2022/W/ ING and 1017/S/ING.

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PETROLOGICAL FEATURES OF THE CIESZÓW MYLONITES (SW KACZAWA COMPLEX, SUDETES) AND THEIR PETROGENETIC SIGNIFICANCE

Abstract: Petrological and detailed zircon studies of the "Cieszów cataclasites" – felsic mylonitic rocks occurring in the Cieszów Unit (SW Kaczawa Complex, Sudetes) – show them to be derived from calk-alkaline, I-type granitic protolith, which probably was formed in an active island arc and were placed in a recent basement of the Świebodzice Basin. The rocks have experienced complex deformation of brittle-ductile type which took place under greenschist facies conditions in two deformation events.

Keywords: mylonite, zircon, ductile deformation, Kaczawa Complex.

INTRODUCTION

The contact between the Świebodzice Basin (SB) and the Kaczawa Complex (KC) is a very complicated tectonic zone where Upper Devonian to Lower Carboniferous sediments are "mixed" with epimetamorphic series consisting of diabases, phyllites and felsic cataclastic rocks (so-called "Cieszów cataclasites" – Smulikowski 1956). The relationships between both groups of rocks are important constraints for the tectonic evolution and timing of orogenic events in this part of the Variscan Belt. The epimetamorphic rocks have been interpreted variously. Bederke (1929) considered them as exposed parts of Lower Palaeozoic basement of the SB According to Teisseyre (1956), this series – called Cieszów Unit – are a nappe thrusted southward over the SB sediments. In this model, the key role is attributed to the "Cieszów cataclasites", which were recognized as products of cataclasis of the Kaczawa-type greenstone series at the base of a sliding nappe, hydrothermally altered during deformation. Bederke (1929) regarded these rocks as deformed Caledonian granites, which had been intruded into the SB basement, but according to Smulikowski (1956), lack of main components of granites (e.g. K-fsp, biotite, zircon) in these cataclastic rocks, denies such thesis.

Detailed petrological study of described rocks (Kulczyński 2006) indicates that they form a varied mylonitic series derived from a felsic igneous protolith and deformed by a combination of brittle-ductile shearing processes. Microprobe analyses documented the presence of relics of K-fsp as well as accessory zircon and apatite. The aim of this study is to present new petrological data as well as morphological and typological (after Pupin 1980) study of zircons from the felsic mylonites to define a character of their protolith precisely.

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PETROGRAPHIC AND GEOCHEMICAL FEATURES

The Cieszów mylonites can be subdivided into proto-, orto- and ultramylonites, with a gradual transition between several types (Kulczyński 2006). Domains of protomylonites contain also weakly deformed granodiorites. Both rocks are coarse-grained with preserved primary igneous structures and consist of euhedral, often fractured plagioclase laths ($An_{5\pm19}$), chlorite flakes after biotite and accessory apatite, zircon and sphene. Small aggregates of recrystallized albite and quartz, chlorite as well as epidote seal the fractures. Towards the tectonic contact with diabases, these rocks grade into narrow domains with orto- and ultramylonites, due to grain size reduction of plagioclase, accompanied with progressive ductile deformation. The Cieszów mylonites have recorded two consecutive deformation events (D1÷D2), which took place under greenschist facies conditions (op. cit.). Both mylonite types comprise of dynamically recrystallized fine-grained and laminated matrix with porphyroclasts of albite and new quartz porphyroblasts – the latter was developed as a result of plagioclase deformation via mica-producing softening reactions and subsequent replacement by quartz.

The mylonites can be geochemically classified (Nb/Y-Zr/TiO₂) as granites-granodiorites of calk-alkaline series and they range from 69 to 79 wt % in silica content. On tectonic discrimination diagrams (Nb-Y; Ta-Yb) studied rocks plot within the volcanic arc granites field, and show a variable enrichment of LREE relative to HREE [(La/Lu)_N 1.3÷5], with strong to moderate Eu depletion. Negative Y, Ta, Nb and positive Th anomalies indicate common contamination of magma with crustal material. The whole-rock analyses show a decrease in Ti, Al, P, Pb and Zr with increasing deformation, while the concentrations of Si, Na, Nb and U rise. The remaining elements do not display any well-defined trends, but fluctuations of their concentration may be remarkable (e.g. K, Rb, REE).

Temperatures of zircon crystallization from melt, calculated using chemical zirconium thermometer (Harrison, Watson 1983), range between 710÷810°C.

	SAMPLI	K10 ⁽⁰⁾	Ch1 (1)	K5C ⁽²⁾	D3 (3)	average	
quan	tity of investigated	200	180	185	115		
external crystal shape (%)		euhedral	67.0	47.2	52.4	40.0	51.7
	habit	subhedral	26.5	43.3	39.5	46.1	38.8
		rounded	6.5	9.5	8.1	13.9	9.5
	elongation *	long-prismatic	17.0	10.0	8.1	5.2	10.1
		normal-prismatic	38.0	47.8	46.5	27.8	40.0
		short-prismatic	26.5	20.6	21.6	37.4	26.5
		broken	18.5	21.6	23.8	29.6	23.4
internal crystal phenomena (%)		transparent	52.0	38.9	28.1	25.2	36.1
	transparency	weakly transparent	36.5	53.9	60.5	60.0	52.7
		opaque	11.5	7.2	11.4	14.8	11.2
	metamictisation	strong/weak	11.5/14.0	11.1/12.8	10.8/13.5	14.8/20.0	12.1/15.1
	cores	euhedral/rounded	3.5/1.0	1.1/2.8	1.6/1.6	1.7/1.7	2.1/1.8
	inc	21.0	11.1	15.1	15.1	13.6	
	zoning	25.6	17.2	14.6	14.6	17.2	

Tab. 1. Main features of zircon populations from investigated felsic mylonites.

⁽⁰⁾ weakly deformed granodiorite (<2 % vol. of recrystallized matrix); ⁽¹⁾ protomylonite ($3 \div 90$ %); ⁽²⁾ ortomylonite ($50 \div 90$ %); ⁽³⁾ ultramylonite (>90 %). * long-prismatic L/W > 3 (length/width); normal-prismatic L/W = $2 \div 3$; short-prismatic L/W < 2.

ZIRCON STUDIES

The zircons from the weakly deformed granodiorite are euhedral to subhedral, but within mylonitic domains the latter habits prevail (Tab. 1). The crystals are about $50 \div 370 \,\mu\text{m}$ (av. 150) in length and the elongation range between $1.7 \div 6.4$ (av. 2.9). Both indices decrease with increasing deformation. The zircons, generally colourless, sometimes enclose sub- to euhedral cores, aligned inclusions and oscillatory zonation (Fig. 1. B1). Some grains reveal a distinct change in habit between core and mantle probably due to contamination by Al-rich crustal material (Pupin 1980). Damage of the zircons from weakly deformed domain is mostly limited to rounding and fracturing, while metamorphic growth could not be recognized. However, with increasing deformation, crystals with corroded faces, narrow rims and disappearance of primary zonation occur. It may indicate recrystallization or dissolution, related to metamorphic fluids during mylonitisation (Connelly 2000; Fig. 1.B2). Relatively many crystals are broken (18÷30 %) and metamict (20÷35 %), probably due to due to increase of U content, and often they show brownish tinge and weaker translucence. All of the studied zircons show fairly similar typological features (sensu Pupin 1980); they are dominated by varied combinations of $\{100\} \ge \{110\}$ prisms as well as $\{211\}$ with $\{101\}$ pyramids and belong mainly to subtypes S13, S17 and S19 (Fig. 1.A).



Fig. 1. Zircons from metarhyodacite, sample OK9, in transmitted plane polarized light (a) and in CL (b); zircons from metatrachyte, sample LA2, in transmitted plane polarized light (c) and in CL (d). Notice the differences in size, morphology and internal structure of the crystals.



Fig. 2. Tectonic setting plots for the Cieszów mylonites (Kulczyński 2006 & refs. therein).

DISCUSSION AND CONCLUSIONS

Plutonic origin of all studied types of mylonites is evidenced by their zircons, which show high elongation values, euhedral habit and inclusion poor internal crystal structure, combined with clear zoning. Comparing zircons from mylonites and a wall rock it may be shown that increasing mylonitisation under greenschist facies conditions is reflected by slight changes of their habit. This is clearly seen on (Fig. 2.A&B) as decrease of the alkali index (IA) and increase of the temperature index (IT). However, observed similarities in typological and physical features can imply a common protolith for these rocks. Considering the crystals habit, the rocks were derived from calk-alkaline, I-type granite melt possibly contaminated by crustal material (Fig. 2). The geochemical features suggest that the described granitic rocks were probably situated in an active volcanic arc.

Internal features of the zircons (metamictisation, recrystallization and structural recovery) could have resulted from mylonitization what may pose a severe problem in geochronological research based on U-Th-Pb isotope system in zircon, because of the secondary loss of Pb (e.g. Connelly 2000; Cherniak, Watson 2000).

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THE ANDRADITE-OPAL PARAGENESIS FROM THE GOGOŁÓW-JORDANÓW SERPENTINITE MASSIF (THE ŚLĘŻA OPHIOLITE)

Abstract: The paper presents results of mineralogical investigations of garnet-bearing opal veins from serpentinites of the GJSM. Both chemical composition and unit-cell parameters of the garnet are typical of andradite. Textural relations and crystal forms suggest syntectonic crystallization of the garnet and the CT-opal, deposited simultaneously from hydrothermal solutions. **Keywords:** Ślęża ophiolite, andradite, CT-opal, hydrothermal solutions.

The Gogołów-Jordanów Serpentinite Massif (GJSM) is located in the eastern part of the Fore-Sudetic Block. It is composed of serpentinized mantle tectonites and ultramfic cumulates. These rocks were for the first time described by Majerowicz (1979) as a part of the larger ophiolitic sequence (the Ślęża ophiolite). The GJMS, together with similar occurrences of mafic and ultramafic bodies in the vicinity of the Góry Sowie Massif forms the Central Sudetic Ophiolite.

Serpentinization of ultramafic rocks in the GJMS was a complex process which took place in several stages. For example, Jędrysek et al. (1991) distinguished four stages: oceanic, continental, magmatic and meteoric. Dubińska et al. (2004a) suggested that the serpentinization within mid-oceanic rifts took place in the early Devonian (ca. 400 Ma) and continued within a supra-subduction zone environment. Plagioclase rodingite was formed during the early serpentinization event (Dubińska et al. 2004b), whereas boninitic rodingite was supposedly formed later in the supra-subduction setting. The habit and composition of pseudospinifex olivine from the GJSM suggest that the rocks underwent UHP metamorphism at some point of their evolution and therefore, are a part of an acretionary prism (Dubińska et al. 2005).

One of general aspects of evolution of serpentinized ophiolitic sequences is formation of chalcedony and opal veins along fractures. Their origin is still not clear. The two proposed hypotheses are: formation of the veins in hypergenic conditions or precipitation and crystallization from hydrothermal solutions (see Niśkiewicz 1987).

Samples were collected at the exposure of serpentinites in the vicinity of Jordanów Śląski (E-part of the GJSM). Three types of opal were collected: milk-white opal-I, redbrown opal-II, and transparent and translucent, grey-brownish opal-III. They all form veins in serpentinites, from several mms to several cms thick. The red-brown opal is older than the grey-brownish one since it occurs as fragmented blocks within the latter.

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Age relations between the milk-white opal and two other varieties are not known. Garnet grains occur only within the red-brown opal-II. This opal also forms thin veinlets (<1 cm), or occurs as matrix in zones of serpentinite breccias.

The garnet crystals are light yellow to light green. Their size varies from 0.05 mm to 0.1-0.2 mm and they are isometric to strongly flattened. Garnet grains often form elongated aggregates of worm-like shapes (Fig. 1). Their elongation is often perpendicular to the vein walls. The largest garnet grains occur inside the aggregates; their longer axes are perpendicular to the direction of elongation of the aggregates. The finest garnet grains occur at the ends of aggregates close to the contact between opal and serpentinite. Apart from andradite, fine inclusions of hematite sometimes are encountered within the opal.



Fig 1. Andradite aggregates in the vein of the CT-opal (II).

The serpentinite -containing opal veins is characterized by the presence interpenetratof ing flame textures. The flaky to platy antigorite is a major serpentine mineral. The antigorite grains are up to 0.2 mm in length. Bastites pseudomorphs after pyroxene (up to several mm in size) occur within the antigorite ma-

Adr-andradite, Opl-opal.

trix. The occurrence of primary cleavage in pyroxene is visible due to the presence of inclusions of secondary magnetite that along the cleavage. Thin carbonate veins (0.1-0.2 mm thick) cross-cut the serpentinite.

We analyzed more than 40 garnet grains by means of electron microprobe. These garnets are practically pure unzoned andradite with the Cr content usually below the detection limit (Tab. 1). Water content in the red-brown opal-II may be estimated at ca. 5 wt %. A small admixture of Fe2O3 (Tab. 1) in this opal probably causes red-brown colour of the variety.

The garnet unit cell parameter are a=12.059(2) Å, V=1753(1) Å³ and the values corroborate with the pure synthetic andradite (JCPDS 1983). The XRD study of three types of opal shows only reflections characteristic of cristobalite and tridymite. Therefore the all opal types might be classified as the CT-variety.

garnet	SiO ₂	TiO ₂	Al ₂ O ₃	Cr ₂ O ₃	Fe ₂ O ₃ *	MnO	MgO	CaO	Na ₂ O	total
1 core	34.84	bd	0.14	bd	31.18	bd	0.14	33.66	bd	99.96
1 rim	34.60	bd	0.12	bd	31.01	bd	0.11	33.56	bd	99.42
2 core	34.86	bd	0.20	bd	30.77	bd	0.15	33.72	bd	99.70
2 rim	34.81	bd	0.13	bd	30.13	bd	0.10	33.78	bd	98.95
	Numbers of ions on the basis of 240									
	Si ⁴⁺	A1 ³⁺	Fe ³⁺	Mg ²⁺	Ca ²⁺	Σ cat.		Prp	Adr	Grs
1 core	5.913	0.028	3.982	0.036	6.121	16.081		0.6	99.3	0.1
1 rim	5.907	0.025	3.984	0.035	6.138	16.089		0.6	99.3	0.1
2 core	5.928	0.039	3.936	0.039	6.142	16.084		0.6	99.0	0.4
2 rim	5.959	0.027	3.881	0.027	6.195	16.088		0.4	99.3	0.3
opal-II	SiO ₂	TiO ₂	Al ₂ O ₃	Cr_2O_3	Fe ₂ O ₃ *	MnO	MgO	CaO	NiO	total
1	93.77	bd	0.11	bd	1.04	bd	0.18	0.06	0.20	95.36
2	93.44	bd	0.10	bd	1.22	bd	0.23	0.08	0.16	95.23

Table 1. Representative chemical analyses of garnet and opal-II, *total Fe=Fe³⁺

bd - below detection limit.

DISCUSSION AND CONCLUSIONS

The observed textures and coexistence of opal and andradite suggest that both minerals are syngenetic. The garnet aggregates are elongated parallel to the direction of maximum incremental stretching. Such a form of their occurrence suggests syntectonic crystallization. Flattening of the garnets in the central parts of the aggregates is probably due to their rapid crystallization in preferred directions, i.e. that in which elemental concentrations were sufficiently high.

Coexistence of andradite and opal suggests that garnet also crystallized at low temperature. Coombs et al. (1977), Taylor and Liou (1978) argue that low-temperature andradite crystallizes from solutions ($X_{CO_2} \le 0.2$ at $P_{fluid} = 2000$ bars) in which SiO₂ and CaO are active, whereas Al₂O₃ is absent. Oxygen fugacity should be high enough to stabilize Fe³⁺. Quartz and iron oxides commonly coexist with garnets (Coombs et al. 1977, Gutzmer et al. 2001). Kozłowski and Sachanbiński (1984) constrained crystallization temperatures of chrysoprase from Szklary and Wiry at 40-120°C using liquid-gas inclusions, whereas temperature estimated by Skrzypek et al. (2003) on the basis of oxygen isotope thermometry isotope composition varies between 5°C and 115°C. Thus, it is probable that the andradite aggregates found at Jordanów Śląski are a product of hydrothermal crystallization. Further analyses of oxygen stable isotope ratio (δ^{18} O) in andradite and opal may bring support for this hypothesis.

Most of low temperature andradites described in literature are associated with metamorphism of the oceanic floor (Gutzmer et al. 2001). Dubińska et al. (2004b) describe an occurrence of andradite garnet in vesuvianite rodingites (boninite affinity rocks) and interpret it as a crystallization product during later stages of metamorphism, already within a subduction setting. And radite garnet can be a product of a dehydration reaction during progressive metamorphism of the serpentinite (op. cit).

It is probable that crystallization of the garnet in the investigated opal veins might have taken place during the last (meteoric) serpentinization stage. The source and the age of hydrothermal solutions are still unclear. They may be related to the Cenozoic volcanic activity within the Fore-Sudetic Block.

Acknowledgements. X-ray diffraction analyses were performed at the Department of Mineralogy and Petrology of the Institute of Geological Sciences, Wrocław University. The microprobe analyses were carried out at the Geological Faculty, the Warsaw University.

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FIRST MONAZITE DATES FROM THE ELVEFLYA FORMATION, SPITSBERGEN, PRELIMINARY RESULTS

INTRODUCTION

Spitsbergen is the largest island of the Svalbard Archipelago located in the NW corner of the Barents Sea Shelf and Eurasian Plate. Metamorphic rocks belonging to the Elveflya Formation (Hecla Hoek Succession) outcrop on the Vimsodden Peninsula and on the foreland of Werenskioldbreen, south-west coast of the Wedel Jarslberg Land, between Bellsund and Hornsund fiords. The formation is divided into four parts (Czerny et al. 1993): lower mica-carbonate-quartz schist, lower black schist with chloritoid, upper mica-carbonate-quartz schist, and upper black schist with chloritoid. These rocks are believed to be affected by Caledonian greenschist metamorphism (Czerny et al. 1993 and literature therein). To date, no dates are available from this sequence.

METHODS AND SAMPLE SELECTION

Seven rocks were selected for the study: 3 samples of mica-carbonate-quartz schists, 3 samples of black quartz-paragonite-muscovite shists with chloritoid, and one sample of quartzite. Relatively fine (<20 μ m) subhedral and anhedral monazite grains are located in the matrix (Fig. 1 and 2). Grains were selected for in situ electron microprobe analysis mostly on the basis of overall size. Very seldom the existence of multiple domains was revealed with back-scattered electron (BSE) imaging.

In situ analyses were made in polished thin sections using the electron microprobe EMP, Cameca SX-100 at the Electron Microanalysis Department of the Geological Survey of Slovak Republik in Bratislava. The age was calculated for each individual point analysis using Microsoft Excel add-in program DAMON that reads the data, calculates the model and weight averaged ages, and constructs the isochrones and histograms. Details of analytical methodology and recalculations are as described by Konecny et al. (2004). The age calculation is based on the formulation of Montel et al. (1996). The accelerating potential on standards and samples was 15 kV, beam current 80-150 nA with an electron beam estimated to be 1 μ m in diameter focused on the polished thin section coated with carbon. A counting time, analyzed elements, and correction procedures are described in Konecny et al. (2004). All errors in EMP data are reported, depicted, and discussed in this paper at the 28 level (95 % confidence limits).

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Fig.1. Typical subhedral monazite grain (left) from the black quartz-paragonitemuscovite schist with chloritoid (right, sample SP 145/85). Back-scattered electron image.





Fig. 2. Typical subhedral monazite grain (left) from the mica-carbonate-quartz schist (right, sample SP 85/86). Back-scattered electron image.

RESULTS AND DISCUSSION

Out of 84 analyses performed, 35 results were rejected based on total sum of elements concentration, analytical error, beam drift or coating charging. All the remaining 49 results were selected for interpretation and considered analytically correct.

Chemical U-Th-total Pb dating performed on monazites from rocks belonging to the Elvefya Formation yielded four distinct populations of ages (Fig. 3): 356 ± 33 Ma (V), 443 ± 16 Ma (C1), 524 ± 27 Ma (C2), and 653 ± 39 Ma (K) (the numbers represent weighted averages \pm two standard deviations, the symbols correspond to the notation in Fig. 3). This selection of age populations is strongly supported by chemical consistency of analytical results on isochrones. The oldest date of 653 ± 39 Ma is in excellent agreement with 643 ± 9 Ma yielded by monazites in the nearby Isbjørnhamna Group rocks (Majka et al., in preparation). However, these ages are sparse here and were measured on two monazite grains only.

Caledonian age of greenschist facies metamorphism is long recognized in the rocks of Hecla Hoek succession in Wedel Jarlsberg Land (Czerny et al. 1993; Manecki et al. 1998). The dates 443 \pm 16Ma and 524 \pm 27Ma (C1 and C2) can be interpreted as two pulses as observed elsewhere in Svalbard. The youngest date, 356 \pm 33 Ma (Variscan?), corresponds with Devonian/Carboniferous events.



Fig. 3. Results of Elveflya Formation monazite dating presented in the histograms of age distributions and relevant isochrons defining the populations of ages. Th* represents parent isotopes for radiogenic lead recalculated as Th equivalent.

The presence of the major Vimsodden - Kosibapasset dislocation zone (VKZ) within the distance of less than 3km from the sampling sites is probably responsible for so numerous events registered by monazites. Tectonic structures of the Elveflya Formation on Vimsodden and on the foreland of Werenskioldbreen are paralell to this dislocation and were formed gradually under the influence of tectonic movements along VKZ (Czerny et al. 1993). The four dated events can be connected with diastrophic phases distinguished by Birkenmajer (1975) in S part of Wedel Jarlsberg Land:

653 Ma event correlates well with Jarlsbergian diastrophism;

524 Ma date corresponds to Hornsundian phase;

443 Ma monazites represent NY Friesland phase;

356 Ma event correlates with Svalbardian diastrphism.

Acknowledgments: This research was funded by MEN grant 2 P04D 039 30 and AGH-UST research grant no. 11.11 140.158.

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CADOMIAN GRANITOID CLASTS DERIVED FROM THE SILESIAN RIDGE (RESULTS OF THE STUDY OF GNEISS PEBBLES FROM GRÓDEK AT THE JEZIORO ROŻNOWSKIE LAKE)

Abstract: Augen gneiss pebbles from Gródek (the Silesian Unit) were studied with use of ICP-MS, FESEM-EDS methods. LA-ICP-MS zircon dating revealed a wide spectrum of Precambrian ages (from ca. 1250 to 2740 Ma) for cores. Ages obtained from rims and tips are between 530 and 570 Ma. The studied clasts are considered as fragments of deformed Cadomian granite derived from the Silesian ridge.

Keywords: Silesian ridge, Western Outer Carpathians, gneiss, Cadomian granite, U-Pb method.

INTRODUCTION

The Silesian Ridge originated as a result of fragmentation of the European platform during Jurassic-Early Cretaceous rifting (Golonka et al., 2005). Studies of gravel size clast give information on geological structure of the Silesian Ridge (see references in Oszczypko and Oszczypko-Clowes (2006). According to Poprawa et al. (2006) the Silesian Ridge supplied to the Western Outer Carpathians pebbles with the Late Carboniferous to Permian metamorphic overprint. It corresponds with the age of emplacement of granitoids in the western part of the Silesian Ridge (Hanžl et al. 2000). Late Silurian to Middle Devonian ages are interpreted as gneiss protolith age (Poprawa et al. 2006). Mesozoic ages (mostly Triassic) noted in clast from Gródek at the Jezioro Rożnowskie Lake (monazite chemical dating) are related probably to thermal event caused by the rifting (Michalik et al. 2004). Cadomian ages were noted in the same clasts using U-Pb method on separated zircon grains (Michalik et al., 2006). Late-most Neoproterozoic to middle Cambrian ages were obtained for granite clast from the Dukla basin (CHIME monazite age; Poprawa et al. 2005). Cadomian ages were recorded in detrital monazite in the Polish Eastern Carpathians (Kusiak et al. 2004).

ANALYTICAL METHODS

Optical microscopy, major and trace elements analysis (ICP-MS), scanning electron microscopy with energy dispersive spectrometry (FESEM-EDS) were used for description of rock texture, mineral composition and chemistry of minerals determination. For zircon dating LA-ICP-MS method was used at the University of Arizona (Tucson, AZ, USA). Spot positioning was based on CL observations.

RESULTS

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The studied augen gneiss clasts are rounded, 10-30 cm in diameter. These rocks from relatively homogenous group but can differ in a degree of deformation. Quartz, K-feld-spar and plagioclase are the main constituents of the rock. Quartz often forms elon-gated ribbons. Biotite is partly replaced by Fe-chlorite. Feldspars are commonly partly sericitized. Accessory minerals assemblage is composed of zircon (often zoned), small crystals of Fe-Ca garnets (Fig. 1), epidote, allanite, monazite, thorianite, uraninite, Fe oxides, rutile, pyrite and other sulphides. Monazite is subjected to breakdown and is often replaced by apatite aggregates. Coronas of secondary monazite are accompanied by sericite or kaolinite are relatively often observed around apatite aggregates (Fig. 2) (see also Budzyń et al. 2006 – submitted).



Fig. 1. Fe-Ca garnets in augen gneiss clast. FESEM-BSE image.



Fig. 2. Monazite corona on apatite aggregate. FESEM-BSE image.



Fig. 3. Histogram of ²⁰⁶Pb/²³⁸U zircon ages.

Studied rocks are peraluminous (A/CKN from 1.03 to 1.57). SiO₂ content is within the range of 64-74 wt %. The Na₂O/K₂O ratio varies from 0.8 to 1.42. Negative Eu anomaly is only slightly marked. LREE vs. HREE enrichment is visible (La_N/Lu_N is between 12 and 27).

Zircon dating was based on 139 analyses; 63 spots from cores and 76 from rims and tips of grains.

92 dates are not interpreted to be reliable age indicator and rejected therefore. Cores yield a wide spectrum of Precambrian ages (from ca. 1250 to 2740 Ma). Ages obtained from rims and tips are between 530 and 570 Ma (Neoproterozoic – Early Cambrian). Cadomian magmatic activity event is dominant in the geochronological record (Fig. 3).

DISCUSSION AND CONLUSIONS

The studied clasts can be interpreted as fragments of deformed Cadomian granite derived from the Silesian ridge. It indicates that Cadomian granites were probably common within the ridge. Numerous Carbonifeous – Permian ages (e.g. Poprawa et al. 2006) are related to Variscan metamorphism of rocks derived from the Ridge. It indicates the presence of both Cadomian and Variscan elements within the Silesian Ridge. Paleoboundary between Variscan and Cadomian orogens in the Western Outer Carpathians basement is related to contact zone of the Silesian basin and the Silesian ridge (Poprawa et al. 2004). The Silesian ridge is regarded as fold-and-thrust belts elevated by syn-collisional compression and next subjected to erosion (Poprawa et al. 2004).

Acknowledgments. This study was supported by the Jagiellonian University research fund (to M. M.) and the MNiSzW research grant 2P04D 041 29 (to B.B.).

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Krzysztof NEJBERT¹

NEW DATA ON THE Ag-Te-Se MINERALISATION IN MAGNETITE-ILMENITE ROCKS FROM THE SUWAŁKI ANORTHOSITE MASSIF, NE POLAND

Abstract: Magnetite-ilmenite rocks from the western part of the Suwałki Anorthosite Massif (SAM) commonly contain small inclusions of hessite and clausthalite occurring in chalcopyrite, pentlandite, millerite, sphalerite, and ilmenite. Ag-Te-Se minerals grown during the oxyexsolution stage recognised in the evolution scheme of Fe-Ti oxides. Such paragenetic association probably reflects crustal contamination of the SAM rocks by hydrothermal fluids generated from rocks adjacent to SAM. **Keywords:** Ag-Te-Se mineralisation, Fe-Ti-V ores, Suwałki Anorthosite Massif.

INTRODUCTION

The Suwałki Anorthosite Massif is located in the Precambrian basement of the NE Poland and contains numerous dykes of magnetite-ilmenite rocks, recognised in the vicinity of Krzemianka, Udryń, Jeleniewo and Jezioro Okrągłe (Fig. 1). The magnetite-ilmenite rocks consist of magnetite and ilmenite (both with intergrowths of Mg-Al spinel), plagioclase, and orthopyroxene (Kubicki, Siemiątkowski 1979; Speczik et al. 1988; Nejbert 1999; Wiszniewska 2002). A small amount of sulphides, such as pyrrhotite, pentlandite, chalcopyrite, and cubanite, is a common component of the magnetite-ilmenite rocks (Fig. 2A).

The presence of the Ag-Pt-Pd-Te-Se mineralisation in the Suwałki Anorthosite Massif was first reported by Salamon, Banaś (2000), and Salamon et al. (2004). The aim of this study is to supply more data about distribution and genesis of this mineralisation. Core samples from two boreholes (Krzemianka K-40 and Jezioro Okragłe Jo2) were selected for this research (Fig. 1).



Fig. 1. Geological sketch-map of the Precambrian basement in the vicinity of the Suwałki Anorthosite Massif (Kubicki, Ryka 1982). 1. anorthosite; 2. norite, gabbro-norite, jotunite; 3. magnetite-ilmenite rocks; 4. diorites, undivided; 5. rapakivi granite; 6. small granite massifs; 7. undivided metamorphic rocks; 8. mylonitic zones; 9. faults. Location of boreholes containing the samples studied: A – Jezioro Okragłe Jo2 borehole; B - Krzemianka K-40 borehole.

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Fig. 2. Back-scattered images of sulphides recognised in magnetite-ilmenite rocks from Suwałki Anorthosite Massif: A) aggregate of magmatic sulphide (pyrrhotite, pentlandite, and chalcopyrite) within host Ti-magnetite. Note the rim of Mg-Fe-Al spinel around the sulphide aggregate, B) intergrowths of chalcopyrite and ilmenite, both originated during the oxyexsolution stage. The chalcopyrite contains numerous tiny intergrowths of hessite, C) postmagmatic aggregate of sulphides composed of pentlandite, millerite, chalcopyrite and sphalerite, D) enlarged fragment of C, showing distribution of fine clausthalite grains within pentlandite, millerite, chalcopyrite, and sphalerite. Abbreviations: Ccp – chalcopyrite, Ilm – ilmenite, Mgt – magnetite, Mi – millerite, Pn – pentlandite, Po – pyrrhotite, Sd – siderite, Se – clausthalite, Sp – Mg-Fe-Al spinel, Sph – sphalerite, Te – hessite. Fig. 2A – sample Jo2-18a; Fig. 2B – sample Jo2-18; Fig. 2C-D – sample K-51-82

RESULTS AND DISCUSSION

The Fe-Ti-V ores of the Suwałki Anorthosite Massif commonly contain hessite and clausthalite. These minerals occur as fine blebs, ranging in size from submicroscopic up to 5 μ m in diameter, and therefore all of them have been identified by means of EPMA. Most occurrences of hessite were found in chalcopyrite (Fig. 2B). In some cases hessite inclusions were also observed in ilmenite. Clausthalite commonly occurrs as intergrowths with chalcopyrite, pentlandite, millerite, and sphalerite (Fig. 2C-D). The Ag-Te-Se mineralisation was recognised in numerous samples taken from central parts

of magnetite-ilmenite dykes, and from the oxide patches (up to 5 cm in diameter), occurring within the anorthosite.

Textural relationships of the Ag-Te-Se minerals in all studied samples indicate that these minerals have grown contemporaneously with postmagmatic generations of sulphides (chalcopyrite, pentlandite, millerite, sphalerite) and ilmenite, originated during intensive oxyexsolution processes (Fig. 2B). These processes, described previously by Kubicki, Siemiątkowski (1979); Speczik et al. (1988); Nejbert (1999); and Wiszniewska (2002), were caused by an increase of oxygen fugacity as a result of interaction with fluids (e.g. hydrothermal solutions) mobilized from the crustal rocks adjacent to the Suwałki Anorthosite Massif (Nejbert 1999; Nejbert, Wiszniewska 2005). In aggregates of magmatic sulphides, commonly rimmed by thin zone of Mg-Fe-Al-spinel (Fig. 2A), the Ag-Te-Se mineralisation was not recognised. Moreover, the high-quality WDS spectra of these sulphides, recorded at 15 kV accelerating voltage and 200 nA sample current, did not reveal Ag-, Te-, or Se enrichment.

The Ag-Te-Se mineralisation is characteristic of epithermal and magmatic-hydrothermal ore-forming environments elsewhere (e.g. McPhile 1995, Xiong 2003). Ag, Au, and PGE tellurides were also noted from many mafic-ultramafic complexes as well as from numerous magmatic Ni-Cu deposits, where local remobilisation of PGE-bearing tellurides was frequently reported (e.g. Mogessie et al. 2000). The presence of the Ag-Te-Se mineralisation in the magnetite-ilmenite rocks from the Suwałki Anorthosite Massif may by interpreted either as: (I) a result of contamination of the Suwałki Anorthosite Massif rocks by hydrothermal solutions from the crustal surrounding that took place during oxyexsolution stage, or (II) remobilisation of Ag, Te, and Se from the primary magmatic sulphides. The first interpretation seems to be more accurate because of the wide distribution of Te-Se mineralisation in magnetite-ilmenite rock, the lack of Ag, Te, and Se enrichments within primary magmatic sulphides, and the textural position of the hessite and clausthalite

The author thanks Adam Pieczka, Maciej Bąbel, Piotr Dzierżanowski, Lidia Jeżak, and Grzegorz Widlicki for help. The study was supported by the research grant of the Warsaw University no. BW 1726/16.

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GEOCHEMISTRY AND GEODYNAMIC SIGNIFICANCE OF MAFIC ROCKS IN THE DAY NUI CON VOI MASSIF OF THE RED RIVER SHEAR ZONE, NW VIETNAM

Abstract: High-grade paragneisses and mica schists exposed in the Red River Shear Zone in NW Vietnam were intruded by veins of mafic rocks before 70 Ma, thus prior to India- Asia collision. Based on geochemistry, three groups of metabasites have been distinguished: alkali basalts, low-Ti tholeiites and common tholeiites. They all were metamorphosed and disrupted during shearing. The alkali basalts were derived from a dominantly asthenospheric OIB-type source, with weak crustal contamination. They were connected with magma underplating at the base of the extended and broken continental crust probably when the South China Block was being separated from Gondwana in Devonian times. The low-Ti tholeiites likely developed during pre-late Cretaceous magmatic event(s), either late Jurassic or early Triassic in age, at the continental margin setting controlled by the subducting Pacific plate below SE Asia.

Keywords: alkali basalt, low-Ti tholeiite, OIB, SE Asia, WPB.

INTRODUCTION

In NW Vietnam, the Red River Shear Zone (RRSZ) exposes multiply deformed and high-grade metamorphosed garnet-sillimanite paragneisses and mica schists of the Day Nui Con Voi Massif (DNCV) which belongs to the South China Block. Although protolith ages of these rocks are unknown (probably Proterozoic), the last ductile deformation and metamorphic overprint in the presently exposed level of the RRSZ occured between 50 and 26 Ma (Zelazniewicz et al. 2005). The metasediments comprise disrupted veins and bodies (0.1-100 m thick) of high-grade amphibolites - metadolerites and metagabbros, with some ultramafic rocks. Whether these rocks represent single or several intrusive events and what is their age remain still uncertain. Ar-Ar dating of garnet metagabbro and hornblendite from the Mau A and Bao Yen areas yielded ages between 49 Ma and 25 Ma believed to reflect timing of synkinematic intrusions (Izokh et al. 2004). These data, however, probably reflect metamorphism and cooling rather than intrusion times. Our field observations combined with U-Pb SHRIMP ages of zircons reveal that the metabasites are older than 70 Ma because they have been either cut or entrapped by felsic rocks of late Cretaceous age (Zelazniewicz et al. 2005). Therefore, mafic magmatism has to be related to some earlier evolutionary stages of the DNCV. To shed more light on the problem, we have examined

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a wide selection of mafic rocks from more than 40 localities over a distance of more than 200 km along strike. The studied metabasites can be geochemically divided into 3 groups: I – alkali basalts, II – low-Ti tholeiites and III – common tholeiites (Fig. 1).



Fig. 1. Characteristics of mafic rocks of the DNCV on the basis of A – V-Ti distributions, B – chondrite normalized REE plot, C – MORB normalized plot, D – primitive mantle normalized plot, (normalization after: Sun & McDonough 1989, Pearce 1983, Taylor & McLennan 1985, cf. Rollinson 1993).

DESCRIPTION OF MAFIC ROCKS PETROGRAPHY

The alkali basalts are represented by medium- to coarse-grained, foliated amphibolites and by aphanitic to fine-grained metadolerites, which consist of green hornblende and plagioclase, with relicts of earlier clinopyroxene blasts rimmed by amphibole. Primary igneous phases are not preserved in these rocks. Accessory titanite (up to 5 %), apatite and Fe-Ti oxides are common.

The tholeiites are foliated, fine- to medium-grained amphibolites sometimes transitional to coarse-grained hornblendite-like rocks, and consist of green hornblende and plagioclase, with frequent garnet and clinopyroxene blasts from earlier stages of metamorphism of these rocks. Accessory apatite, titanite, K-feldspar, zircon, Fe-Ti oxide and biotite are present.

GEOCHEMISTRY

A linear correlation between REE pairs and correlation between HFSE pairs permit to assume that ratios of these elements reflect the pre-metamorphic, magmatic characteristics.

The **alkali basalts** are nearly homogenous in composition all over the DNCV. They show LREE-enriched patterns (La_N/Yb_N 7.15-11.33) and plot in the WPB field on discrimination diagrams. They are generally more enriched in incompatible trace elements than tholeiites, with higher Zr, Th, Ta, Hf, Ti and P abundances similar to OIB-type basalts (Wilson 1989). These group of metabasites is characterized by high Ti/V (60-73), Ti/Y (496-573), Ti/Yb (6036-7247), Zr/Y (4.95-7.89) ratios, variable Th/Ta (1.59-3.31) and Zr/Nb (5.95-8.31) proportions and relatively low La/Nb (1.13-1.36) and La/Ta (16.50-20.83) values, with small negative Nb anomaly and variable depletions in Sr and Zr. The observed element abundances and "humped-shaped" patterns with negative slope (Fig. 1D) are similar to continental rift-related alkali basalts (Wilson 1989).

The low-Ti tholeiites are characterized by the low Ti (TiO₂=0.45-0.85 wt %) contents and low Ti/Y (170-239) ratios (see Farmer 2003). The low-Ti tholeiites are generally depleted in incompatible trace element abundances (Zr, Nb, Ta, Hf, REE, Ti and P) and display relatively flat chondrite-normalized REE patterns (La_N/Yb_N =2.06-3.85). They are characterized by the low Ti/V (11.79-22.28), Zr/Y (1.12-3.70), Ti/Yb (1389-2299) ratios, high Th/Ta (4.67-11.43), La/Nb (1.86-2.39) and La/Ta (26.81-37.30) ratios and variable, but relatively high Zr/Nb (10.36-18.33) values. Negative Nb, Ta and Ti anomalies and elevated Th and LREE shown on the spidergrams are characteristic features of these rocks (Fig. 1C, D), whereas depletions in Sr and Zr are less common. This group of rocks shows affinity to volcanic arc basalts, with similar or slightly lower HFSE and HREE as compared to N-MORB (Fig. 1C), but they are distinguished from N-MORB by their slightly fractionated REE patterns and relative enrichment in LREE and LILE.

The common tholeiites are characterized by the high Ti/Y (400-526), low Zr/Y (2.82-3.71), Ti/Yb (4994-5976), Th/Ta (1.25-2.18), Zr/Nb (6.33-7.80), La/Nb (0,85-0.94) and La/Ta (12.35-13.81) ratios and medium Ti/V (30.47) values (Fig. 1A), the lack of negative Nb, Ta and Ti anomalies, and the depletion in Zr and Sr. The common tholeiites are depleted in Zr, Th, Ta, Nb, REE, Ti and P as compared to the alkali basalts and plot in the fields of WPB or E-MORB. The low REE contents and La_N/Yb_N (3.30-3.77) resemble the low-Ti tholeiites, but the common tholeiites are enriched in Ta, Nb, Ti and P. They are enriched in more incompatible elements such as Th, Ta, Nb, P and LREE relative to N-MORB and have Zr, Hf, Sm, Y and Yb contents similar to N-MORB (Fig. 1C).

INTERPRETATION

The chemistry of the **alkali basalts** (small Nb anomaly, high La_N/Yb_N Ti/Yb and low Zr/Nb, Th/Ta, La/Nb, La/Ta ratios) indicates that they were formed in a within-plate environment connected with extension of the rifted continental crust. They were derived from an enriched source, resembling an asthenospheric mantle of OIB-type (Wilson 1989), with signs of little contamination of the melt by continental lithosphere constituents and

with weak subduction signature. This might have occurred due to underplating of mafic magma from the mantle wedge at the extensional environment when the South China Block separated from Gondwana in Devonian times (Metcalfe 1996) as prompted by field relationships.

The **low-Ti**, quartz-normative **tholeiites** have traits common for both continental tholeiites with crustal contamination and for magmatic arc products. However, the Th/Ta (~10) values and the low Ti/V ratios in these rocks (in addition to high La/Ta and La/Nb) suggest that they come from a depleted mantle source which experienced a previous melt extraction event in the arc-system, followed by the enrichment in LILE and LREE via fluids from the subducting slab (Pearce et al. 1996). They likely developed during late Jurassic or early Triassic (or both) magmatic events, at the continental margin setting controlled by the Pacific plate subducting below the SE Eurasian plate.

The **common tholeiites** geochemistry (lack or negative Nb and Ta anomalies, low La/Ta and La/Nb ratios) indicates that they probably originated via melting of an asthenospheric mantle source and the parent magma had not been contaminated by continental crust. Low trace element contents in these tholeiites imply their derivation from depleted mantle source, yet more enriched than the source for the low-Ti tholeiites. They might represent further stages of magma underplating heralded by the alkali basalts.

The Polish State Committee for Scientific Research (KBN grant No. 3 P04D 052 25) is gratefully acknowledged for funding.

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APATITE CHEMISTRY IN TONALITIC ROCKS FROM THE GĘSINIEC TONALITE (STRZELIN CRYSTALLINE MASSIF, SW POLAND)

Abstract: Apatite from 5 tonalite types from the Gęsiniec Intrusion (SW Poland) has various major and trace element contents. Differences between each type are due to crystallization conditions such as: presence of fluid phase, oxygen fugacity, and sequence of crystallization of accessory minerals.

Keywords: tonalite, apatite, magma differentiation.

INTRODUCTION

The trace element and isotopic composition of accessory minerals is recently widely studied and provide us with information on geochronology and petrogenetical processes (Poitrasson et al. 2002). Several studies showed that chemistry of apatite is the indicator of origin of igneous rocks (e.g. Sha & Chappell 1999) and a tool to discriminate between different granite types (Sha & Chappel 1999).

The aim of this abstract is to show chemical variability in apatite from 5 types of tonalite from the Gęsiniec Intrusion (Strzelin Massif, NE Bohemian Massif). We provide evidence that the chemistry of apatite is a useful tool informing us about magma chemistry at late stage of crystallization. The chemistry of apatite is discussed in context of processes revealed by plagioclase chemistry and zonation (Pietranik & Waight 2005, Pietranik 2006, Pietranik & Waight submitted).

PETROLOGY AND PREVIOUS RESEARCH

The Gęsiniec Intrusion consists predominately of calc-alkaline tonalitic to dioritic rocks that intrude into scarce granodiorities and older metamorphic cover. Detailed description of the field relationships and lithologies is given in Oberc-Dziedzic (1999), Pietranik (2006) and Pietranik & Waight (submitted).

Apatite from 5 tonalite types was analysed: leucocratic poikilitic tonalite (LPT), leucocratic, coarse grained tonalite (LCGT), melanocratic tonalite (MT), leucocratic, medium grained tonalite (LMGT) and melanocratic coarse grained enclave (MCGE). MCGE occurs as ~10 cm enclave within LMGT, the contacts are diffused. All tonalites are composed of plagioclase, amphibole, biotite and quartz. Apatite, zircon, titanite and ilmenite are dominating accessories. Rare allanite (LCGT, MCGE) and monazite (MT) occur. The apatite grains in LCGT, MT, LMGT and MCGE are ap-

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proximately 120-400 μ m wide and up to 1700 μ m long, their aspect ratio varies from 0.2 to 0.5. The apatite in these types occurs as interstitial grains or is enclosed in outer portions of major minerals, mainly plagioclase and quartz. Apatite in LPT and diorites is smaller (20-100 μ m) and has lower aspect ratio (~0.1). It occurs predominately as numerous needles within biotite and amphibole grains.

RESULTS

Minor and trace elements in apatite were measured by laser-ablation inductively coupled plasma mass spectrometry (ICPMS, University of Copenhagen), in combination with the electron microprobe (University of Hannover). LPT apatite was not analysed by LA-ICPMS due to small size compared to the size of the laser beam. The agreement between LA-ICPMS and microprobe data is excellent. Zonation in apatite was examined by cathodoluminescence and back scattered electron images.

No zonation is observed in LCGT, LMGT, LPT and MCGE apatites, whereas small irregular patches occur scarcely in centres of MT apatite (Fig. 1B). Compositional zonation is observed within individual grains, however, only outermost rims differ significantly from interior of apatite. Variations between grains in one type of tonalite,



Fig. 1. (a) Cl vs F in apatite, (b) BSE images for apatite in LCGT and MT, MT: irregular patches in apatite core (see text), (c) contents of trace elements in apatite (black line is average composition and box shows 2SD), (d) chondrite normalized (Anders & Grevese 1989) REE patterns in apatite.

and within individual grain, are usually smaller than variations in apatite composition between different tonalite types. Only patches in MT type have significantly different composition compared to all apatite grains measured. The ptches are characterized by low Ce, Na and Si content (mostly below detection limit of microprobe which were 950 ppm, 160 ppm and 100 ppm respectively) and high CaO content (~56 wt %) compared to outer parts of MT apatite (Ce= 2000-4000 ppm, Na= 310-770 ppm, Si= 630-1000 ppm and CaO = 54.8-55.4 wt %).

Apatite from different tonalite types plots in distinct compositional fields (Fig. 1). The most pronounced variations are visible in Cl, F and REE content (Fig. 1). Cl is the highest in MT and range from 0.38 to 0.92. F content varies from grain to grain in LPT and LMGT apatite, whereas Cl content is constant within individual grain (it is observed in Fig. 1A as separate fields for apatite from those tonalites).

MT apatite is also characterized by the most pronounced LREE enrichment (Fig. 1C,D) and the highest Na and Pb (4-6 ppm) contents. MCGE and LMGT apatite have almost identical composition; only Sr and Pb contents are higher in LMGT apatite and similar to those of MT apatite. LPT and MT apatite have Fe contents usually above 700 ppm (up to 2000 ppm) whereas LCGT, LMGT and MCGE apatite has Fe below 700 ppm. LCGT apatite has the lowest Th contents (< 9 ppm) compared to other apatites (> 12 ppm). Si contents are similar in all apatites. S contents are always below detection limit (~80 ppm). Eu anomaly (Eu/ $\sqrt{\text{Sm}^{*}\text{Gd}_{ch}}$) varies fom 0.3 to 0.5 in all apatites and it is lower than in whole rocks (0.57-0.8).

DISCUSSION AND CONCLUSIONS

- (1) Composition of apatite in tonalitic rocks from the Gęsiniec Intrusion coincides broadly with that of I-type granites from the Lachlan Fold Belt (Sha & Chappel 1999). However, each of tonalite defines its own compositional field for several major and trace elements, thus, providing detailed information on their individual crystallization histories.
- (2) Sulphur contents lower than in apatite from the Gęsiniec Intrusion than in I-type apatites described by Sha & Chappel (1999) suggest that oxygen fugacity was lower in tonalitic magmas.
- (3) Eu/Eu* ratios in apatite lower than whole rock ratios suggest late apatite crystallization (after majority of plagioclase) and at low oxygen fugacities (Sha & Chappel 1999). Differences in LREE, Y and Th in apatite between tonalite types are probably due to different sequences of crystallization of accessory minerals as allanite (early in LCGT) and monazite (late in MT).
- (4) Similarity of apatite composition occurring in MCGE and LMGT suggests crystallization from the melt of similar chemistry. Since MCGE occurs within LMGT it is probable that late melts from those rocks equilibrated after incorporation of MCGE "enclave" by LMGT.
- (5) Composition of MT apatite is in agreement with the record in plagioclase that suggests that MT is a mixture of restite and a new melt rich in plagioclase component,

formed after fluid-present partial melting. MT apatite is rich in highly soluble elements like Cl and Pb and elements occurring abundantly in plagioclase like Sr and Na. Patches are probably products of metasomatism by water rich fluid (Harlov & Förster 2003) since their composition differs from that typical for magmatic apatite (Sha & Chappel 1999).

(6) *Acknowledgements.* Jürgen Koepke and Magnus Johansson (University of Hannover) are thanked for help with microprobe analyses. Analyses of apatite were done thanks to KBN project no 3 P04D 005 24.

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REPLACEMENT OF IRON SULPHIDES BY OXIDES IN THE DINOSAUR BONE FROM THE LANCE FM. (WYOMING, USA) – PRELIMINARY STUDY

Abstract: A unique aggregate of framboidal pyrite and iron oxides was found in the vascular canals of dinosaur bone from the Lance Fm. and was studied using SEM/EDS. Various types of pyrite, massive and framboidal, and their subsequent oxidation and replacement by iron oxides are described. The proposed sequence of events is as follows: 1: formation of pyrite framboids and framboidal aggregates; 2: infilling of the interstices between pyrite crystals by massive pyrite; 3: oxidation of former sulphides.

Keywords: dinosaur bones, pyrite, iron oxides, framboids, replacement.

INTRODUCTION

Pyritized organic remains are common in the sedimentary record. Pyrite and iron oxides generally fill open voids, and can replace organic matrix or "soft parts". Pyrite can adopt various forms, from massive to aggregated, euhedra, or framboids. Excellent descriptions of the mechanisms for fossil pyritization were given, for example, by Canfield and Raiswell (1991) and Raiswell et al. (1993). Infillings by iron oxides are quite common, although detailed studies are rare (Pfretzschner 2001 a,b). Pawlicki and Nowogrodzka-Zagorska (1998) and recently Schweitzer et al. (2005) suggested that small mineral structures could be exceptionally preserved blood which stirred an especially hot discussion on the possible implications. Schweitzer and Horny (1999) presented iron and oxygen-rich microstructures in the bone tissues of Tyrannosaurus rex but rejected the structures as framboids due to their composition of iron oxides. This paper documents various stages of framboidal pyrite replacement by oxides in dinosaur bone.

SAMPLING AND METHODS OF INVESTIGATIONS

Four to five cm size fragments of large dinosaur long bones most likely from Hadrosaur or Triceratops were collected from the dark shales of the Lance Formation near the town of Lance Creek (Wyoming, USA). Several small (0.2-0.7 mm) pieces, were fractured from the bone, mounted and carbon coated for analysis. Equipment used was a field-emission SEM (HITACHI S-4700), equipped with YAG (BSE) detector and EDS analyzer (NORAN Vantage).

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RESULTS

This study revealed the common occurrence of iron oxides in the vascular canals. Iron oxides are relatively common in all dinosaur bones examined from this location. On the contrary, the presence of iron sulphides was extremely rare but can help to understand the diagenetic processes that occurred in the bone. The internal voids were filled with 250x100 um iron (hydroxy)oxides and subordinate pyrite microcrystals (Fig. 1a). Massive iron oxides surround the embedded pyrite framboids (Fig.1b) and scattered uniform pyrite microcrystals (Fig.1c, e). The embedded framboid in figure 1b is irregular in outline suggesting replacement by a massive iron oxide. The pyrite 1-2 µm crystals are octahedral with the smaller size typical of framboid microcrystals.

Fig. 1c shows various typical microstructures. Visible in the left side of figure 1c, uniform pyrite microcrystals and imprints are embedded in the iron oxides. The smaller pyrite sub-crystals in Fig. 1e are also observed in the massive iron oxides. Fig. 1d is a magnified view of the framboid interstitial iron oxide network. Some secondary iron oxide microcrystals are preserved, whereas others are partly or totally dissolved or dislodged. Dissolution, leaving intact outer shells, is especially active in the cores of the microcrystals (Fig. 1f) with several small pyrite microcrystals remaining in the iron oxide network (Fig. 1d). Irregular barite aggregates are visible in the massive iron oxides on the right side of Fig. 1c. Note that the latter are locally highly dissolved. Pyrite crystals analyzed under EDS were found to have a generally stoichiometric FeS₂ composition. The EDS analyses of iron oxides show the range of various Fe:O ratios which can be comparable with Fe₂O₃ (lighter in BSE image) and FeOOH (darker) compositions.

DISCUSSION AND CONCLUSIONS

Pyritization of biogenic remains and the occurrence of isolated iron oxides in fossils is common (e.g. Canfield, Raiswell 1991; Sawlowicz 2000; Hubert et al. 1996) in dinosaur bones whereas the co-occurrence of both iron minerals is relatively rare. This unique aggregate of framboidal pyrite, iron oxides and their subsequent oxidation, has allowed us to trace the formation of various types of iron oxide replacement. No massive pyrite was preserved, only massive iron oxides. Based on the similar co-occurrences in many ore deposits, we suggest that the pyrite preceded the iron oxides. The proposed sequence of events is as follows: 1/ formation of pyrite framboids and framboidal aggregates; 2/ infilling of the interstices between pyrite crystals by massive pyrite, with partial replacement of the former framboidal pyrite; 3/ oxidation of former sulphides: a/ replacement of massive pyrite, followed by b/ replacement and/ or dissolution of framboidal pyrite microcrystals.

With no clear indications when these stages occurred, the timing of boundary events can only be suggested. Pfretzschner (2001a) proposed two mechanisms, the first early stage involving dissolved ferrous ions reacting with sulphides released from the decaying bone. The second is sulphate reduction to sulphide by sulphate reducing bacteria (SRB). The latter process requires the presence of organic matter which



Fig. 1. SEM (BSE) images of the void (cross-section of the vascular canal) in the dinosaur bone, filled with framboidal pyrite and massive Fe (hydroxy)oxides: a/ a void filled completely with iron minerals; b/ irregular (partly destroyed?) framboid, built of regularly arranged pyrite octahedral microcrystals (light), embedded in the massive iron oxides (darker); c/ various microstructures of iron oxides (grey), with embedded pyrite microcrystals (light); d/ details of c photograph – note different stages of the dissolution of iron oxides octahedra; e/ details of the left part of c photograph – some pyrite crystals seem to be built of very fine microcrystals (left arrow), similar granular texture is also seen in the imprint after pyrite crystal (right arrow); f/ details of d photograph, interstitial network is typically composed of better crystallized iron oxides (lighter)) than iron oxides octahedra and their remains (darker). Symbols: FeOx – Fe (hydroxy)oxides; Py – pyrite, CaP– Ca phosphate; Ba – barite.

would be easily metabolized by SRB. We suggest that pyrite framboids and aggregates of framboidal pyrite were formed at this stage. The second mechanism proposed by Pfretzschner (2001a) is a precipitation of external ferrous sulphide as the result of rising pH values due to buffering by phosphates in the bone matrix. We would advocate the formation of massive pyrite by this process. Filling both cancelous bone and replacing the phosphatic bone by iron oxides is common in the Lance formation (ms in prep.). Pfretzschner (2001b) lists three different processes of iron oxide formation in bones, i.e.: 1/ redox-precipitation of ferric hydroxide; 2/ a pH-precipitation of ferrous and/or ferric hydroxides; 3/ oxidation of pyrite. Although the two first mechanisms occur in other iron-oxide-rich bones, in the studied case oxidation of pyrite seems to be most plausible. We suggest that the oxidation of former iron sulphides (see also Canfield and Raiswell 1991) took place during later diagenesis, when the reducing conditions related mainly to the decomposition of organic matter were no longer dominant and the influence of generally oxidized host rocks was predominant.

This study suggests the possibility that some of the iron-rich microstructures found in dinosaur bones may result from generally inorganic oxidation of former pyrite framboids.

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GĂTAIA LAMPROITE (SW ROMANIA)

Abstract: The lamproite rock occurrence, south of Gătaia consists of a lava cone, resulted by a sequence of vesicular lava and by some intercalations of fall-out scoria deposits. The rocks dated at 1.3 Ma is situated at the south-eastern margin of Pannonian Basin and at the western margin of the South Carpathians unit, along an important NE-SW faults system. Its petrography and the major and trace element geochemistry attests that the rock is a typical lamproite, a unique occurrence in Carpathian-Pannonian Region. The source for Gătaia lamproite was probably a lherzolite-harzburgite lithospheric mantle, which has subsequently been metasomatized in an ancient event via alkaline mafic melts, as a necessary requirement due to its high content in incompatible trace elements as Ba, Sr, Rb and Zr.

Keywords: lamproite, SW Romania, mantle metasomatism, petrogenesis.

INTRODUCTION

Major and trace element, Sr–Nd isotope data are presented for post-collisional ultrapotassic lamproite from Gătaia (SW Romania), with K/Ar age at 1.3 Ma (Seghedi et al. 2006) in order to constrain its source region. The lamproite occurrence, as a lava cone, is situated ca. 5 km south of Gătaia (Banat) and was considered up to now as an alkali basaltic occurrence. The Şumiga hill (198 m above sea lavel) lava cone, constituted by a sequence of vesicular lava and by some intercalations of fall-out scoria deposits. The lamproite sample belongs from a ca. 10 m thick lava flow pierced by an exploration drilling at the peak area.

The lamproite magma gets into relatively undeformed flat-lying Miocene sedimentary rocks at the margin of the Pannonian Basin along an important NE-SW faults system. The lava cone overly an Pleistocene terrace deposit and older crystalline basement that experienced intense lithospheric deformation and orogeny during Cretaceous. The Gătaia (Şumiga hill) lamproite represent a short lived magmatic episode, which was generated in similar time interval with other contemporaneous volcanic activity, but at 50-150 km toward N-NE, along the South Transylvanian fault system (Lucareț alkali basalts, Uroiu shoshonites), but also with other ultrapotassic occurrences in the Pannonian Basin (Bar) (Seghedi et al. 2004; Harangi et al. 1995). The rock is fresh and has a slightly porphyritic texture with phenocrysts of high-Mg olivine and microphenocrysts of euhedral leucite, in a glassy matrix, which contain microcrysts of olivine, armalcolite, apatite, sanidine, low Al-diopside, fluor-bearing ti-

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tanium phlogopite, fluor-bearing amphibole and as accessory chrome spinels (mostly included in olivines) and rare titanomagnetite. Ba-sulphate aggregates fill small vesicles. Rare Al-phlogopite, surrounded by secondary spinels, is enclosed by leucite aggregates, which suggest formation at high pressure in an earlier event.

MAJOR - AND TRACE ELEMENT GEOCHEMISTRY

The major and trace element geochemistry attests that the rock is a typical lamproite, close to Leucite Hills and Gaussberg lamproites compositions. The rock is characterized by high Mg# (75.7), high abundances of Ni (478 ppm) and Cr (539 ppm), as well as high primary K_2O contents (8.67 wt %) and K_2O/Na_2O values (6.84). Its place in the lamproite clan is given by relatively low contents of Al_2O_3 (9.34 wt %) and CaO (3.43 wt %) in combination with high abundances of Rb (205 ppm), Ba (2750 ppm), Sr (868 ppm) Zr (1243 ppm), La (134 ppm) and Ce (253 ppm). Slight depletions of Nb relative to Ba and La and high ratios of Ba/La may suggest a metasomatically enriched lithospheric mantle source.

GEOCHEMICAL ASSUMTIONS

Higher Rb/Sr and to higher Rb/Ba for Gătaia lamproite, as compared with the most basalts, including MORB and OIB, reveal an enrichment of Rb relative to Ba and Sr, demonstrating that partial melting of a similar source to that seen in other lamproites occurrences, which reflect a style of an enrichment closer to anorogenic lamproites, then orogenic ones, which show an increasing trend of Rb/Sr ratio (e.g. SE Spain) (Fig. 1). According to this diagram the source of our rock is closer to phlogopite-bearing peridotites.



Fig. 1. Ba/Sr vs. Rb/Sr ratios in igneous rocks, including MORB (Pearce 1983), OIB and PM (primitive mantle) (Sun &McDonough 1989), garnet peridotites (Gar Per; Erlank et al. 1987) result in a trend with narrow limits of 0.03 and 0.1 of Rb/Ba ratio; In contrast, the ultrapotassic lavas from phlogopite peridotite xenoliths (Erlank et al. 1987), from SE Spain (Venturelli et al. 1984) and from W Australian lamproites (Mitchell & Bergman 1991), Gătaia lamproite and Bar leucitite are characterized by an enrichment of Rb relative to Ba and Sr.

Melting of phlogopite veins in a harzburgitic substrate, may explain the fact that the Gătaia lamproite have very low CaO/Al₂O₃ (0.36), low CaO (3.43 wt %) and Sc contents (14 ppm). As well, liquidus and near-liquidus studies on various lamproite compositions (e.g. Edgar & Vukadinovic 1992) suggest that the Gătaia lamproitic magma may have been resulted by partial melting of a phlogopite-bearing mantle source. Using La/ Yb vs. Yb that can distinguish mantle melting processes, it is suggested that Gătaia lamproite was generated in at low degree of partial melting of a phlogopite - garnet lherzolite source. The Sr-Nd isotopic composition (0.70571; 0.51257) is quite primitive as compared with other lamproites in Mediterranean area (Prelevic et al. in press), however closer to Bar leucitite, attributed, as well to a phlogopite-bearing mantle source (Harangi et al. 1995), that agree with a lithosphere-metasomatic enrichment, though different from orogenic lamproites.

CONCLUSIONS

We conclude that the source of Gătaia lamproite, as it is generally envisioned, was probably a lherzolitic-harzburgitic lithospheric mantle (Mitchell & Bergman 1991, Foley, 1992), which has subsequently been metasomatized in an ancient event, as a necessary requirement due to its high content in incompatible trace elements as Ba, Sr, Rb and Zr. However, even the Gătaia lamproite is situated at the western edge of the Carpathian unit, a typical subduction related environment, our data are not conclusive that subduction-related H_2O -rich fluid have been involved in metasomatic processes. The large presence of fluor-bearing minerals suggests, as well, that the source was F-rich. Gătaia lamproite had probably a limited available source volume for melting in direct relationship with the ambient thermal regime in a typical post-collisional tectonic setting, during the Late Neogene to Quaternary tectonic evolution, that indicate surface uplift and erosion, marking the collapse of the Alpine orogen.

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AGARDITE-(La)–DUFTITE AND SCORODITE–KÖTTIGITE-LIKE MINERAL PARAGENESIS FROM SUPERGENIC ZONE OF THE MIEDZIANKA DEPOSIT (RUDAWY JANOWICKIE MTS., POLAND) – PRELIMINARY REPORT

Abstract: The paper presents two different parageneses of secondary minerals from separate parts of the Miedzianka polymetallic deposit. The first of them comprises agardite- (La), duftite and chrysocolla, whilst the second one is represented by scorodite, Cu-bearing köttigite-like mineral and unidentified Fe- and Zn-bearing arsenate phase. A source of REE is discussed. **Keywords:** agardite-(La), Cu-bearing köttigite, duftite, Miedzianka.

INTRODUCTION

The Miedzianka deposit is located about 12 km to the E of Jelenia Góra in the Rudawy Janowickie Mountains. It belongs to a group of few small ore deposits connected with the Karkonosze pluton and situated within its eastern metamorphic cover. The deposit is developed in the form of scarn-metasomatic ore lens lying in the contact zone between the Karkonosze granite and amphibolites of the Kowary- Czarnów Unit, or as polymetallic veins which cut amphibolites and schists (Zimnoch 1978). A supergenic zone of the Miedzianka deposit contains an extensive assemblage of secondary minerals (Lis, Sylwestrzak 1986; Pieczka et al. 1988; Holeczek, Janeczek 1991; Ciesielczuk, Bzowski 2003; Ciesielczuk et al. 2004; Siuda, Kruszewski 2006).

METHODS

Samples of selected supergenic minerals were examined using JEOL JSM-6380LA scanning electron microscope equipped with EDS system (accelerating voltage 20 kV; Faculty of Geology, Warsaw University) and AMRAYX 1830 I/t6 scaning electron microscope with EDAX PV 9800 ED spectrometer (Department of Petrology and Geochemistry, Faculty of Science, Eötvös University, Budapest).

DUFTITE-AGARDITE-(La)-CHRYSOCOLLA PARAGENESIS

Minerals of the paragenesis were found in cracked skarns on dumps of the Einigkeit old mine (the west ore-exploitation field). Duftite, relatively rare component of supergenic zone of the polymetallic deposits, occurs here as tiny, aggregated masses of

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Fig. 2. Sprays of needle-like agardite-(La) covering masses of duftite. SEM image.

tabular microcrystals, apple-green in colour. These masses grow on chrysocolla. The mineral hitherto was not identified from the Miedzianka deposit. Apart from Miedzianka it also occurs in Rędziny (Gołębiewska 2005), representing the second locality of the mineral in Poland.

The second mineral forming this paragenesis is agardite-(La). It occurs as needle-like, strongly elongated crystals, up to 0.2 mm in length (Fig. 1). The crystals are light green in colour and form sprays or radial aggregates,

that grow on duftite and chrysocolla. Semiquantitative EDS analysis of the mineral showed La and Nd (La>Nd) as main REE but lack or only traces of Ce. Presence of Nd suggests, that the mineral is an indermediate phase between La-rich and Nd-rich members of the agardite group. Agardite-(Nd) has been described as a new mineral by Frost at al. (2005). Unlike many other Ladominant agardite samples (e.g. Kunov et al. 2002), the one from Miedzianka does not contain Ca or Pb. The Miedzianka localization is the first finding in Poland of a mineral belonging to the agardite group.

PARAGENESIS OF Fe, Zn AND Cu ARSENATES

Secondary arsenates of Fe, Zn and Cu occur in small cavities of weathered polymetallic ores containing chalcopyrite, tetrahedrite, tennantite, safflorite and löllingite. Samples of these minerals were collected on a dump located the in eastern ore-exploitation field of the Friedrike Juliane old mine area.

Scorodite is the most common mineral of the paragenesis. It occurs as honeyyellow crust on the surface of weathering As-bearing ores. Scorodite covers consist of idiomorphic, tabular, intergrown microcrystals. Different unidentified Fe, Zn and Cu arsenates also grow on its surface.

On the top of scorodite crust light pink tufts and single balls of a Zn- and Cubearing arsenate mineral occur. Its crystals show monoclinic symmetry and tabular habit making them similar to those of erythrite. Hour-glass-like aggregates are also present (Fig. 2.). The EDS analyses of all above mentioned forms allow to classify them as a Cubearing köttigite-like mineral. A light pink mineral of similar symmetry was recently reported by Ciesielczuk et al. (2004), as a Co-bearing köttigite. Mineral investigated here is highly enriched in Cu and in turn depleted in Co. Probably traces of Co cause the light pink colour of the mineral.

During SEM observations, small (up to 0.05 mm in diameter) cubic (or pseudocubic) crystals were also found (Fig. 3). The EDS analyses of these crystals show they are composed of an Fe- and Zn-bearing arsenate. Such chemical composition could be

attributed to a mineral close to metaköttigite, mapimite, ojuelaite or wilhelmkleinite. However, all mentioned minerals have different crystal habit.



-bearing köttigite. SEM image.

Fig. 2. Hour-glass-like aggregates of the Cu- Fig. 3. Crystals of an unidentified Zn- and Fe--bearing arsenate mineral. SEM image.

CONCLUSIONS

Diversity of the investigated paragenesis reflects variable geochemical conditions in different parts of the Miedzianka deposit. Crystallization of duftite- agardite-(La)-chrvsocolla paragenesis occurred in a zone where Cu, Pb, REE and As ions were present. Cu, Pb and As were derived from ore minerals in course of their alteration. The source of REE is uncertain. Agardite-(La) was found only in material from Einigkeit old mine. The mine is located at the contact of the deposit with Karkonosze granitic pluton. Close vicinity of the pluton and presence of granitoid blocks on the dump of the Einigkeit old mine point at the Karkonosze granite as possible source of REE. This granite, as well as its pegmatites, contain certain amounts of REE-bearing minerals (Lis 1970; Pieczka, Gołębiowska 2002). These minerals were also found near Miedzianka, in the eastern part of the Karkonosze pluton (E. Słaby, pers. comm.). Weathering of such minerals (e.g. allanites) may result in release of REE (Gieré, Sorensen 2004). Discharged REE can migrate with ground water out of the pluton and participate in reactions occuring in its cover.

Parental solutions for the minerals of the secondary paragenesis were enriched in Fe, Zn, Cu and As, originated from alteration of polymetallic ore mineralization. Presence of scorodite shows, that pH of the crystallization environment was not as high as 2.5 (Dove, Rimstidt 1985).

Acknowledgements. This research was supported by the Faculty of Geology of Warsaw University grant No. BW 1683/13 and by Consultation Council on Students Affairs (Warsaw University, Poland).

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RECORD OF MAGMA DYFERENTIATION IN APATITE FROM KARKONOSZE HYBRIDS - PRELIMINARY RESULTS

Abstract: Apatite growth under magma mixing regime has been investigated. The crystals have been collected from Karkonosze hybrids. They show complex chemical zoning. LREE and Y were estimated in crystal cores and zones. Apatite growth textures and composition reflect mechanisms of magma evolution as well as heterogeneity of magmatic flow field during their crystallization.

Keywords: apatite, magma evolution, mixing, fractional crystallization, complex zoning, Karkonosze.

INTRODUCTION

Early evolution of Karkonosze pluton (NW extremity of Bohemian Massif, SW Poland) is considerably influenced by mixing-mingling of mantle- and crust-related magmas (Słaby, Martin 2005). The process resulted in porphyritic granite formation. Porphyritic granite comprises many hybrids of different composition, shape and volume. These are: microgranular magmatic enclaves, large (up to few kilometres in diameter) lenticular bodies and dikes. According to IUGS classification the hybrids mainly constitute diorite-granodiorite. Mixed-mingled magmas leading to their formation are characterised by contrasting composition (Słaby et al. 2006). Mantle-related, lamprophyritic magma shows considerable enrichment, whereas crust-related, felsic magma considerable impoverishment in LILE. Growth morphology and composition of some of the minerals crystallizing under mixing regime precisely reflect heterogeneity of the magmatic flow field appearing due to mechanical stirring as well as due to partial chemical exchange between interacting magmas (Słaby et al. 2006; Słaby, Götze 2004). One of the most sensitive phase is alkali feldspar. Its complex-, zoned growth morphology as well as complex chemical zoning can be precisely attributed to changes in magma composition during hybridization (Słaby et al. 2006). Cathodoluminescence (CL) study on minerals from Karkonosze hybrids revealed also zoned apatite crystals. Larger equant crystals show distinct growth zoning pointing to at least two compositionally different crystallization environments. The change of the melt composition displays pulsating character, so the core and some surrounding it zones show the same luminescence. The blue-violet luminescing zones can probably be related to more alkaline conditions which favour the incorporation of REE, whereas

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the greenish-yellow CL points to more acidic environment (e.g. Kempe, Götze 2002). The effect of repeated change of the melt composition is detectable in both: apatite from granodiorites and from granites.

The aim of the present study is to show the chemical composition of those crystals and to discuss, whether the observed zoning could result from magma mixing-mingling, the prevailing mechanism of the differentiation during early pluton formation but subordinated during late evolution. Decreasing role of mixing is balanced by increasing importance of fractional crystallization, which prevails in late stages of pluton crystallization.



Fig. 1. Apatite growth morphology – granodiorite from Fojtka (Czech Republic).

APATITE GROWTH MORPHOLOGY

Apatite from granodioritic hybrids shows complex zoning. Fig. 1 illustrates one of the examples. Dark, patchy core is mantled by simply discordant zoning. The zoning has often fine or coarse oscillatory character with variable brightness. The zones are rounded or embayed. They appear also as discontinuous patches. Many crystals show syneusis texture.

APATITE COMPOSITION

Chemical point analyses of apatites were performed at the Faculty of Geology, Warsaw University (Inter-Institute Analytical Complex for Minerals and Synthetic Substances) using a Cameca SX-100. Concentrations of major elements and some traces (LREE, Y), in apatite were determined using an accelerating voltage of 20 kV, a beam current of 50 nA and a beam diameter 5 µm. Applying the Monte Carlo simulation, the interaction depth of the electron beam with the sample was less than 5 µm. The apatites have been collected from granodiorites (early hybridization event), composite dikes (late hybridization event), porphyritic granite. For comparison some grains from equigranular granite have been analysed. Fractional crystallization became dominant in the evolution of the last granite facies (Słaby, Martin 2005). The composition of apatite from early, granodiorite hybrids is similar to that from porphyritic granite. Cores of the apatites are LREE-rich and Y-poor. The zones show alternating enrichment and impoverishment in LREE. They are however all relatively poor in Y. Apatite grains from equigranular granite are depleted in LREE in comparison to those from early hydrids and from not evolved porphyritic granite. They are rich in Y. Selected data - trace element composition has been plotted on Fig. 2.



Fig. 2. Chemical characteristics of apatites (white double squares – porphyritic granite, dark grey diamonds – early hybrids, white squares – equigranular granite, light grey diamonds – composite dikes).

DISCUSSION – MELT EVOLUTION REFLECTED IN APATITE COMPOSITION

Apatite composition generally reflects the chemistry of its crystallization environment. The apatite composition could be however changed by intracrystalline diffusion. Tepper and Kuehner (1999) point to the diffusion as to additional mechanism changing core and zone composition in the apatite crystallized under magma mixing regime. They conclude: "even apatite zones or cores that appear sharply bounded in backscattered electron images may not retain their original chemical traits". REE diffusion in apatite is relatively slow. That is why the present discussion is simplified and focused only on record of the melt heterogeneity during apatite crystallization, putting aside the intracrystalline diffusion effect.

Apatite from granodioritic hybrids and from porphyritic granite show, that the crystals grew from compositionally variable magmas. Small scale oscillatory zoning could be explained by kinetic effect triggered by slow diffusion (Dempster et al. 2003). Such an effect can't account for more significant changes in apatite chemistry. These changes imply crystal movement. One of the reasons could be convection as a result of repeated thermal inputs into magma chamber. The thermal effect alone can't explain observed chemical heterogeneity of the crystal zones. Dynamic stirring process with partial chemical exchange of compositionally different magmas close to growing crystal surface could be another explanation. If the composition of the zones composition of the zones composition is related to chaotic advection of nutrients from commingled magmas, the zones composition

should show affinity to both magmas. The composition of apatite cores from granodiorite and some porphyritic granites are considerably LREE-rich and Y-poor. The same range of enrichment occurs in some zones. Those parts of apatite could be correlated with growth process, where the nutrients are provided by mafic-like magma. The cores and zones enriched in LREE are not present in the apatites collected from equigranular granite and composite dikes. The range of LREE concentration in those apatites is rather small. Very probably it represents LREE concentration in crust-related, uncontaminated or poorly contaminated melt. On the plot, those grains take intermediate position between crystals parts enriched and depleted in LREE. Therefore mixing can't be the only process triggering magma evolution. The other one supposed is fractional crystallization.

Apatite from granodiorite (early hybrid) and porphyritic granite are depleted in Y. On the contrary apatite from late hybrids and from evolved granite are enriched in Y. Similarly marginal parts of some crystals from evolved porphyritic granite show yt-trium enrichment. The range of enrichment points to late-magmatic or post-magmatic interaction with fluids. This interaction is noticeable in composite dikes and could present three-component (evolved crust-related melt, evolved lamprophyritic melt and fluids) interaction (Słaby et al. 2005).

This work was founded by BW 1726/13.

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BIOLEACHING OF PYRITE IN MICRONODULES FROM THE MIDDLE JURASSIC ROCKS (KRAKOW-CZESTOCHOWA UPLAND, POLAND)

Abstract: Pyrite micronodules, related to biogenic remains in the Middle Jurassic clays, were studied using SEM-EDS. Most of them revealed different leaching patterns but only on the external crystals. These patterns, formed by bacterial leaching, can be explained by different historical euhedra formation, possibly via a framboidal stage.

Keywords: pyrite, microconcretions, bioleaching, bacteria.

INTRODUCTION

The kinetics and mechanisms of microbial oxidation of sulphide minerals, mainly pyrite, have been the focus of considerable experimental attention. This is due to the economic importance of bioleaching (hydrometallurgy), and the environmental damage associated with alteration of pyrite-rich ore (AMD). Most studies have been conducted with the iron-oxidizing acidophiles, *Leptospirillum ferrooxidans and Thiobacillus ferrooxidans*. Overall stoichiometry of the bacterial leaching is:

 $2\text{FeS}_2 + 7\text{H}_2\text{O} + 7.5\text{O}_2 \rightarrow 2\text{Fe}(\text{OH})_3 + 4\text{SO}_4^{2-} + 8\text{H}^+.$

Examples of pyrite bioleaching in nature are rare, especially regarding descriptions of pitting patterns. In this study we present different examples of leaching and attempt to tie them with the specific history of pyrite euhedra growth.

MATERIALS AND METHODS

The studied micronodules come from the Middle Jurassic clays of the Krakow-Czestochowa Upland. They were extracted from rock samples using standard micropalaeontological techniques. Microscopic observations were performed using fieldemission SEM Hitachi S-4700, equipped with EDS (Noran Vantage).

DESCRIPTION OF MICRONODULES

In all the studied Middle Jurassic clays, micronodules exclusively built of pyrite were common. The sizes varied from 70 to 300 μ m and their shape was usually irregular, rarely ideally spherical, and sometimes 2-3 micronodules were overgrown. In contrast to typical micronodules, which are composed of intergrown euhedra, crystals of the studied micronodules (usually octahedra, 10-15 μ m in size), were closely-packed (Fig. 1A) and

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very rarely intergrown. In some micronodules individual framboids (with sizes similar to euhedra) are recorded in place of euhedra (Fig. 1F). Rarely, smaller framboids were found in the interstices between euhedral crystals. Similarities of micronodules from the studied rocks, to those forming internal molds of bivalves (Fig. 1A) and other skeletons suggest that some of the pyritic micronodules could be molds. Whereas the internal crystals in micronodules are octahedra with sharp edges, the crystals forming the most external zone are strongly modified, typically having flat outside faces, as though they grew in the limited space of the shells (Fig. 1B). Only those external crystals showed specific alterations. Two different patterns were distinguished: 1/ single and irregular deep holes or pits (Fig. 1C) whose enlargement can subsequently lead to removal of the crystals outer shells (Fig.1E); 2/ numerous pits of very different depths, especially dense in the center of the crystal, showing dendritic branching (Figs. 1D, F). At this stage we cannot conclude if the first type occurs only in the molds and the other in "free" micronodules in the rock.

DISCUSSION

Bacterial leaching of pyrite is much more efficient than abiotic leaching and can usually be distinguished from the latter by a specific pattern. The most common bioleaching is by acidic iron-oxidizing bacteria. Relatively low pH conditions in the hosting sediment, indicated by the dominance of kaolinite, could enhance pyrite bioleaching in the studied micronodules. The microenvironments where micronodules formed could also have supported other physiologic groups, e.g. neutrophilic Fe-oxidizing or sulphate-reducing bacteria (Edwards et al. 2003). Pitting morphology, pit density and wall dimensions changed gradually as leaching progressed, with some individual pits merging to form dissolution channels (Ndlovu, Monhemius 2005). Bacterial attack can also be increased by factors such as cationic substitutions, particle size, crystal defects, crystallographic directions (e.g., Martello et al. 1994; Ndlovu, Monhemius 2005) or bacterial strain. Boon et al. (1999) found that the Leptospirillum bacteria were able to oxidize both euhedral and framboidal pyrite, whereas T. ferroxidans was able to oxidize only framboidal pyrite. In the case of cells attached to the surface, leaching patterns may vary significantly depending on bacterial cell morphology (rods, cocci, filamentous forms) (see Edwards et al. 2003). Single small pits may also result from the action of filaments of Streptomyces-like bacteria and fungi (Wilkinson 2003).

We speculate here that the pattern of bioleaching also depends on the history of pyrite euhedra formation. Some micronodules may have evolved from polyframboids (Sawlow-icz 1993). Pyrite euhedra may be the final stage of transformation from framboids, either by continuous growth or by a supply of additional pyrite (see Sawlowicz 1993, 2000 and references therein). Growth and future susceptibility of euhedra would depend on the primary arrangement of crystals in the framboid. The arrangement of uniform microcrystals varies from random, linear or concentric to polygonal (see Sawlowicz 2000 and references therein). The regular arrangement, including specific icosahedral pattern was earlier described from the same samples (Sawlowicz, Szczepanik 2005). This style of growth, continuous vs. additional supply, could decide which leaching pattern develops.

In case of pyrite euhedra that are supposedly composed primarily of continuously growing framboidal microcrystals, pitting follows the boundaries between microcrystals (Figs. 1B, D, E). The specific dendritic pattern seems to mimic the interstices in the former framboid (see Fig.1F). Its form depends on the regularity of the microcrystal arrangement, which can vary from chaotic to very regular, with the latter found in samples from the same localities (Sawlowicz, Szczepanik 2005).



Fig. 1: A – pyritic internal mold of bivalves similar to micronodule; B – micronodule builds of octahedra, crystals of the most external zone are strongly modified; C – crystals with irregular deep holes or pits; D, F - crystal faces showing dendritic branching; E – crystals with the removed outer shells.

We suggest that the leaching pattern, observed in figs. 1A and C, results from the action of individual bacteria or their colonies or fungi. Subsequent removal of the external layer (Fig.1E) is due to the growing bacteria population, perhaps in the form of biofilm. The external layer which transformed framboid to euhedra could be built of additional pyrite with different susceptibility. Subsequent leaching patterns depend on the layering in the primary framboid.

Whereas the size of *T. ferroxidans* is about 1-2 μ m, they often form biofilms that are between 30 and 50 μ m thick (Crundell 1996). Formation of biofilms with a thickness comparable to or bigger than the dimensions of crystals could explain the presence of leaching pits only on the most external crystals and their absence on the internal crystals of micronodules.

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P-T CONDITIONS OF METAMORPHISM IN THE STRONIE SERIES AT THE CONTACT ZONE OF THE ORLICA-ŚNIEŻNIK MASSIF AND THE NOVÉ MĚSTO UNIT (WEST SUDETES) – PRELIMINARY REPORT.

Abstract: The metapelites from the Orlica-Śnieżnik Massif (SW Poland) at the contact with the Nové Město Unit bear a record of relatively high temperature metamorphism which peak P-T conditions were estimated at ca. 7 kbars and 600°C. Obtained results are interpreted as a record of metamorphism related to the deformation event responsible for formation of a regional-scale shear zone at the contact between the Orlica-Śnieżnik Massif and the Nové Město Unit. **Keywords**: Bohemian Massif, Orlica-Śnieżnik Massif, metapelites, amphibolite facies metamorphism.

INTRODUCTION

Western flank of the Orlica-Snieżnik Massif (OSM) comprises a large orthogneiss body (the Śnieżnik orthogneiss) mantled by the Stronie formation composed mainly of mica schists, paragneisses, basic and acid metavolcanics and marbles. The emplacement age of a protolith of the Śnieżnik gneiss was dated, using single grain evaporation zircon method at 491-510 Ma (Kröner et al. 2001). On basis of micropaleontological data supracrustal rocks of the Stronie formation, originally forming metasedimentary cover of the orthogneisses protolith, is believed to be of Late Proterozoic or Early Paleozoic age (Gunia & Wierzchołowski 1979). On the western limb the OSM is bordered by the Nové Město Unit (NMU) composed mainly of phyllites, greenstones and amphibolites of unknown age. By comparison to the Teplá-Barrandian domain, they are believed to be of Late Proterozoic age (Chaloupský et al. 1995). Recently, the boundary of the NMU and the OSM was interpreted by Mazur et al. (2005) as a contact zone between the Teplá-Barrandian and Moldanubian terranes. Importantly, the zone is underlined by two, relatively large, late-tectonic Olešnice and Kudowa granitoid plutons (Domečka & Opletal 1971).

The Stronie formation recorded a sequence of five deformation events (Szczepański 2001). The oldest D_1 structures are represented by the S_1 foliation preserved as inclusion trails mainly within plagioclase blasts. Subsequently, the S_1 foliation was deformed by F_2 isoclinal folds. The new S_2 foliation developed parallel to axial planes of these folds. Structures originated during the first two events are obliterated by results of younger deformations and preserved only locally. The following D_3 deformation phase was associated with reactivation of the older S_2 foliation. The newly formed complex

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 $\rm S_{2=3}$ foliation, being the main planar structure visible in the rocks of the OSM, dips steeply to W or SW. On the $\rm S_{2+3}$ planes the NNW-SSE trending $\rm L_3$ mineral lineation is developed. Kinematic indicators show top-to-the-NNW asymmetry. They document noncaoxial shear being the main component of the $\rm D_3$ event. The $\rm D_3$ episode was connected to the dextral non-coaxial shearing which produced a regional-scale shear zone at the boundary of the OSM and the NMU (Mazur et al. 2005). Finally, east-west trending $\rm F_4$ kink-folds were formed by brittle-ductile deformation at a shallow crustal level.

METHODS OF INVESTIGATION

The present study is based on petrological investigation of 35 thin sections. In order to establish P-T conditions of metamorphism mineral chemistry data from selected 2 thin sections were used. The analysed samples (s109 and s112) were collected south of Lewin Kłodzki near village Lasek Miejski and come from the the Stronie series of the OSM.

RESULTS

Metasediments of the Stronie series are characterised by plagioclase showing compositional zonation from albite in the core $(An_{1.0.1.3})$ up to andesine in rims $(An_{1.85.350})$. Garnet grains from sample s109 show fairly complicated compositional zonation. Both spessartine and grossular contents drop from outer to inner rim and then increase toward the core. This is accompanied by the slight decrease of almandine content from core to rim. Thus, the composition of the described garnet grains is as follows: outer rim - Alm₇₁Py₁₂Spe₇Gr₆, inner rim Alm₆₆Py₁₅Spe₄Gr₂ and cores - Alm₆₁Py₇Spe₁₀Gr₁₇. Garnet grains from sample s112 show a slightly different zonation scheme differing mainly in behaviour of grossular content and may be characterised as follows: outer $rim - Alm_{70}Py_{10}Spe_4Gr_8$, inner rim $Alm_{68}Py_{11}Spe_1Gr_{15}$ and core $-Alm_{65}Py_{10}Spe_3Gr_{16}$. The rest of the mineral assemblage constitutes muscovite, biotite (only sample s109), chlorite and quartz. Apatite, zircon, tourmaline, chlorite, rutile and opaque minerals occur as accessories. Thus, core and inner rim of the analysed garnets show normal compositional zonation related to the fall of temperature during its crystallisation. It is suggested that they formed during early stages of deformation $(D_1 \text{ or } D_2)$. Conversely, outer garnet rims must have crystallized during a significant thermal episode related to the last ductile deformation recorded in the rocks of this area (namely the D_3 deformation). Thus, the mineral assemblage related to the D_3 deformation event is composed of rims of plagioclase, garnet, muscovite and biotite.

Temperatures calculated for investigated samples using rims of the grains by garnet-muscovite (Green & Hellman 1982) and garnet-biotite geothermometers (Holdaway 2000) yielded values of $630\pm20^{\circ}$ C and $600\pm20^{\circ}$ C, respectively, while pressures obtained from GPMB (Hodges & Crowley 1985, Hoisch 1990) geobarometer were calculated at 7.6±0.5 kbar and 7.0±1.0 kbar, respectively. Fengite geobarometer (Massone and Schreyer 1987) gave considerably lower pressures 4.3 kbars at 630°C (sample s109) and 5.0 kbar at 600°C (sample s112). However, at the lack of phlogopite this should be treated as a minimal value.

DISSCUSSION AND CONCLUSIONS

Analyzed samples from the OSM recorded metamorphism related to the D₃ deformation responsible for the formation of a regional-scale shear zone at the contact between the OSM and the NMU. In the investigated northern part of the OSM the PT conditions of this event were evaluated at 7.0-7.6 kbar and 600-630°C. Additional available data from other segments of the contact zone show similar conditions of metamorphism T=600-620°C and P=8.4-9.5 kbar both on the OSM and the NMU side of the contact zone (Mazur et al. 2005). The timing of this event is roughly constrained by ⁴⁰Ar³⁹Ar and ⁸⁷Rb⁻⁸⁶Sr geochronological data from the OSM, showing that the last ductile deformation in this area took place in between c. 340 and 330 Ma (Marheine et al. 2002; Lange et al. 2002). This corresponds well to the c. 330 Ma cooling age of late deformation Kudowa granite (Bachliński 2000). This intrusion and several smaller granitic bodies (among them the Olešnice granite) distributed along the contact zone were most probably responsible for heating and temperature increase during the D₃ event.

Acknowledgements. The study was supported from a research grant No 2022/W/ING/05.

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REMARKS ON OXIDATION IN A GALENA - SPHALERITE SYSTEM ("POMORZANY" Zn-Pb MINE, POLAND)

Abstract: Microscopical study, optical and SEM with EDS, of moderately advanced oxidation zone in the "Pomorzany" Zn-Pb mine allowed to recognize basic modes of micro-oxidation of galena, associated with sphalerite. We describe here two forms of galena oxidation product cerusite and propose ways of their formation. Early stages of galena oxidation at the contact with non-altered sphalerite are explained in terms of galvanic couplings. Later stages involved oxidation of both galena and sphalerite, probably in presence of carbonate-rich fluids, and possibly of ferric iron and bacteria.

Keywords: galena, sphalerite, cerusite, galvanic couplings, oxidation, Zn-Pb deposits.

INTRODUCTION

Oxidised and non-sulphide Zn-Pb ores are currently intensively studied as their importance in the world mining grows. They were formerly mined in the Silesian-Cracovian ore deposits and are still found at depths, together with non-altered Pb and Zn sulphides (Cabała 1996). Better understanding of oxidation processes in Zn-Pb sulphide deposits is necessary in the search for new ore and for exploration around known orebodies. Oxidation of sulphides is also a significant problem in flotation processes and acid mine drainage (AMD).

In this study we present preliminary results of investigations of the oxidation in a galena-sphalerite system and suggest possible explanations of that process, including bacterial action, recognized as an important factor in the ore-deposit formation.

SAMPLING AND METHODS

All samples were taken from the "Pomorzany" mine from the ore horizon at a depth of about 300 m. For the purpose of this study we selected samples with only macroscopically moderately advanced oxidation. Special attention was paid to galena, its contact with sphalerite and its oxidation products.

Samples were initially examined in universal thin sections under the polarizing microscope, using reflected and transmitted light. Specific mineral assemblages were further studied using a field-emission SEM (HITACHI S-4700), equipped with YAG (BSE) detector and EDS analyzer (NORAN Vantage). We used FTIR

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spectrometer (BIO-RAD FTS 135, KBr pellets) to confirm the presence of cerusite and anglesite.

RESULTS

Cerusite (PbCO₃) was found to be the most important product of galena oxidation. Anglesite (PbSO₄) occurs in smaller amounts.

Two morphological forms of cerusite were observed in different spatial positions. Fine-crystalline (a few μ m in size) cerusite fills small veinlets along the cleavage in galena crystals and further replaces galena in an irregular manner (Fig. 1). Coarse-crystalline (size > 200 μ m) cerusite usually occurs as the final stage of galena replacement and/or fills wider open fractures (Fig. 2a, b, c). In both cases relics of galena are observed, although they are rarer or absent in coarser cerusite.



Fig. 1. a/ contact of galena with sphalerite. Fine-crystalline cerusite fills cleavage fractures in galena and irregular veinlets in sphalerite (transmitted light, 1N) (white rectangle corresponds with image "b"); b/ cerusite extensively replaces galena and fills irregular veinlets in sphalerite (reflected light, 1 N). Note grains of galena inside the veinlets (SEM-BSE);

Oxidation of galena and formation of cerusite in its cleavage fractures is especially common at the contact with non-altered sphalerite (Fig. 1a). Thin irregular veinlets of cerusite, with relics of galena, are observed in sphalerite, emanating outwards, away from galena crystals which are themselves partly replaced by cerusite (Fig. 1b).

Locally aggregates of galena, cerusite and anglesite, surrounded by cerusite, are observed at galena crystal margins (Fig. 2c, d). Iron oxides are sometimes observed at the contact of smithsonite and/or cerusite with galena or with mentioned aggregate (Fig. 2b). Oxidation of iron sulphides is common in the studied samples.

DISCUSSION

The relatively large amount of cerusite in the Silesian-Cracovian Zn-Pb deposits has been explained by different processes, ranging from a primary formation to an oxidation of galena at surface and in deeper ore horizons (e.g. Żabiński 1960; Cabała 1996). Our observations, based on detailed microscopic study, suggest two stages of galena-sphalerite oxidation and replacement. The first stage is characterized by a significant alteration of galena and a negligible alteration of sphalerite. It begins from cleavage fractures and leads to significant replacement of galena by cerusite, and also to the formation of thin veinlets within sphalerite.



Fig. 2. a/ dilated cleavage fracture in galena filled with cerusite; smitsonite locally replaces sphalerite at the contact with galena (white rectangle corresponds with images "b" and "c"; transmitted light, 1N); b/ and c/ aggregates of galena, cerusite and anglesite, surrounded by cerusite, at galena crystal margins; coarse-crystalline cerusite fills dilated fracture. Note local concentrations of Fe (hydroxy)oxides (b-transmitted light, 1N; c-reflected light); d/ small particles of galena inside the aggregate. Symbols: gal-galena, crst-cerusite, agls-anglesite, sph-sphalerite, smsn-smithsonite, Fe_{ar}-iron (hydroxy)oxides.



Fig. 3. Galvanic coupling between galena and sphalerite (based on: Herbert 1999; da Silva et al. 2003)

Occurrence of significantly oxidised galena together with unchanged sphalerite may be explained in terms of galvanic couplings made between the

two sulphides (galena and sphalerite) (Fig. 3). This process is well known and has been observed also in experiments in microbiological medium carried out by da Silva et al. (2003). These authors measured the rest potential of sphalerite and galena, 375 i 325 mV, respectively. In such coupling the sulphide with lower free potential is oxi-

dised, while the one with higher free potential is not affected by significant addition or loss of electrons (passivated).

The reactions are as follows:

As the result galena is efficiently oxidised, while sphalerite remains almost unchanged. Depending on a fluid composition, especially relative activities of CO_3^{2-} and SO_4^{2-} ions, Pb carbonate and/or Pb sulphate are formed.

The next major stage of oxidation occurred probably after decay of galvanic couplings. It involved both galena and sphalerite because Zn sulphide was not passivated any longer. As the final product, cerusite occurs in larger amounts especially in open spaces (veins) (Fig. 2a, b, c), and sphalerite is replaced by smithsonite (Fig. 2a). Due to large quantities of carbonates we assume that the process had to be related to fluids with high activity of $CO_3^{2^2}$.

The characteristic co-occurrence of carbonates and iron (hydroxy)oxides (Fig. 2b) could be the evidence of an influence of Fe-rich solutions, originating probably from oxidation of FeS₂. Galena (and sphalerite) would be oxidised by Fe³⁺. Ferric iron is a very effective oxidant, being stable in a solution with pH below 3.5 (Herbert 1999). At higher pH, as for example in contact with carbonates, Fe³⁺ hydrolises and could form iron oxides/hydroxides visible on Fig. 2b.

 $PbS + 2Fe^{3+} \rightarrow Pb^{2+} + S^0 + 2Fe^{2+};$ S^0 is further oxidised to SO_4^{2-} .

 Fe^{2+} may be further oxidated by bacteria (e.g. *Tiobacillus ferrooxidans*, Espejo et. al., 1988) or inorganically by O₂: $Fe^{2+-} \rightarrow Fe^{3+}$ and oxidation of sulphides can continue. Timing of the microbial process can not be defined as bacteria can be active in Zn-Pb deposits from their formation up to recent (Labrenz, Banfield 2004).

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Pb-EVAPORATION ZIRCON AGES OF POST-TECTONIC GRANITOIDS FROM THE STRZELIN MASSIF (SW POLAND)

INTRODUCTION

The Strzelin Massif (SM) is situated in the eastern part of the Fore-Sudetic Block (NE Bohemian Massif). It comprises Precambrian-Palaeozoic metasedimentary and metaigneous rocks intruded by Variscan granodiorites, quartz diorites, tonalites, biotite- and finally - two-mica granites. The igneous component forms isolated bodies, mostly stocks and flat dikes, predominantly up to tens of metres thick, within metamorphic rocks (Oberc-Dziedzic 1991, Oberc-Dziedzic et al.1996).

The biotite and two-mica granites were dated with Rb-Sr at 347 ± 12 Ma and 330 ± 6 Ma, respectively (Oberc-Dziedzic et al. 1996). The most recent Rb-Sr ages obtained for tonalite range from 293.8 ± 0.3 Ma to 296.7 ± 0.7 Ma (Pietranik & Waight, submitted). K-Ar cooling ages for granitoids, from 278 to 288 Ma (Depciuch & Lis 1972), in general are similar to Ar-Ar results obtained for white micas from Jegłowa metasediments of the massif (279.4 ± 1.8 to 284.6 ± 2 Ma; Szczepański 2002).

The Rb-Sr data set is inconsistent with existing interpretation of field data of Oberc-Dziedzic (1991) according to which diorites and tonalities are older than biotite- and two-mica granites. Our study provides new Pb-Pb zircon ages to better constrain the emplacement of granitoids cropping out in the SM.

SAMPLES AND ANALYTICAL METHODS

Three samples collected for geochronological studies represent main granitoid varieties previously dated by Rb-Sr method: tonalite (GT-Gęsiniec quarry), finegrained biotite granite (GBTDR – Strzelin quarry) and fine-grained two-mica granite (GGDW). The latter comes from a several metres thick dike crosscutting the tonalite exposed in the Gęsiniec quarry.

Zircons were extracted from rock samples and investigated by transmitted light microscopy using NIKON E-600POL microscope at the Institute of Geological Sciences Wrocław University. SE images were taken at the Laboratory of Field Emission Scanning Electron Microscopy and Microanalysis at the Institute of Geological Sciences of the Jagiellonian University using HITACHI S-4700 SEM. Zircon evaporation analyses on selected crystals were carried out at the Isotope Laboratory of the Department for Mineralogy at the TU Bergakademie Freiberg using a Finigan MAT

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262 basing on the studies of Kober (1986, 1987). Details on the analytical procedure are given by Görz et al. (2004). All weighted mean ages were calculated using the Isoplot/Ex2.06 (Ludwig 1999).

RESULTS

The accessory zircon crystals from the fine grained biotite granite are mostly euhedral, transparent, colourless and of normal prismatic habit. Some of them show oscillatory zoning and/or rounded cores under optical microscope. According to the classification of Pupin and Turco (1972), they vary in morphology from G1-P1 to S22-S23 types. Six zircons (about 100-200 μ m in length) of the GBTDR sample gave similar results that permit age calculation. The weighted mean age (WMA) is 301±7 Ma (Fig. 1). Two zircon grains yielded older, probably mixed ages of 418.9±8.1 Ma and 326.3±9.1Ma.

The tonalite from the Gęsiniec quarry contains large (up to 1 mm) clear, colourless normal to long prismatic zircons with bypiramid {211} better developed than {101}. They vary in proportion between prisms {100} and {110}. Most of crystals can be classified as S16, S18 and S7 types. Evaporation of ten zircons (250-300 μ m) produced 1 σ ages ranging from 280.9±9 Ma to 302.8±8.6 Ma and weighted mean age (WMA) of 291±5.5Ma.

The zircon population of the GGDW sample consists of usually colourless, euhedral crystals with mean elongation above 3. Their morphology is dominated by {110} prism. The most abundant morphological types are: G1, S8 and S3. Many zircons show magmatic oscillatory zoning and rounded cores. Pb-evaporation ages obtained on six individual grains documents strong heterogeneity of the dated material. Ages of 385.2 ± 9.8 Ma, 563.7 ± 11.3 Ma and 592.5 ± 7.6 Ma are interpreted to be mixed ages. Three youngest single-zircon results (288.7 ± 10.3 Ma, 300.9 ± 10.7 and 309.3 ± 8 Ma) are in general similar to those obtained for the GT and GBTDR samples.

CONCLUSIONS

The results of our studies indicate a Late Carboniferous age for the granitoids studied from the Strzelin massif. Combining the Pb-evaporation ages with the interpretation of field data given by Oberc-Dziedzic (1991) suggests that the investigated granitoids were emplaced in a very narrow time interval and documents the youngest and final stage of Variscan plutonism in the Fore-Sudetic Block.

Acknowledgments. This work was supported by 2022/W/ING/05 research project.



Fig.1. $^{207}\text{Pb}/^{206}\text{Pb}$ ages for (a) GT tonalite and (b) GBTDR biotite granite from the Strzelin massif.

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Rafał TYSZKA¹

MICRO-NODULES IN QUATERNARY SEDIMENTS OF THE KACZAWA MOUNTAINS, SUDETES, SW POLAND: FEATURES AND ORIGIN

Abstract: Spherulitic nodules (~0.1-0.5mm in size) commonly occur in sedimentary rocks. Their origin is often ambiguous and involves diagenetic, volcanic, anthropogenic, cosmogenic and biogenic processes. The nodules are characterized by highly variable chemical composition, and two different types are usually distinguished: metallic and silicic. The nodules in the Quaternary sediments of the Kaczawa Mountains represent three varieties: (a) metallic, (b) glassy (silica rich), and (c) silicic (mineral). Based on chemical characteristics, the first two varieties are interpreted to be of anthropogenic origin, whereas the silicic nodules may come from the local basement rocks of the Kaczawa Complex or, in part, from meteoritic sources.

Keywords: Quaternary, nodules, origin, Kaczawa Mountains, Sudetes.

INTRODUCTION

Metallic and silicic nodules (~0.1-0.5 mm in size), occuring in Tertiary and Quaternary soils, have been studied in detail during the last ten years (Uzonyi et al. 1998, Raukas 2000, Dressler & Reimold 2001, Stankowski et al. 2006). The nodules are widely distributed and occur on all continents, in ocean's sediments and on glaciers. The first studies concerning the nodules suggested cosmogenic origin (Brownlee 1981, Smit et al. 1992). However recent studies have proposed a variety of processes leading to their formation such as: diagenetic, biogenetic (Colombetti et al. 1998, Raukas 2000), anthropogenic (industrial and military) (Colombetti et al. 1998), volcanogenic (Martínez Ruíz et al. 1997, Raukas 2000), cosmogenic (including interplanetary dust and products of meteorite destruction) (Darby 1998) and melting due to meteorite impact (Martínez Ruíz et al. 1997, Raukas 2000, Szöőr 2001). The nodules of volcanogenic or industrial origin might be transported over hundreds of kilometres, whereas others (e.g. diagenetic, biogenetic) might be transported only locally. Special attention is paid to nodules of cosmogenic origin. When a meteorite enters the Earth's atmosphere, it rapidly gets heated up to the point of melting. Such a process leads to the formation of tiny particles that fall over large areas of the Earth's surface (Glass et al. 2004). The wide distribution and chemical variability of the nodules can help in lithostratygraphic correlations.

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SAMPLING AND METHODS

Four samples of Quaternary stream sediments were collected in the vicinities of Dziwiszów and Dobków villages (east of Jelenia Góra) in the Kaczawa Mountains The collected material was firstly washed in the bowls and sieved (fraction 0.06-0.25 mm). The nodules were picked manually and described under a binocular and polarizing microscope, and analyzed by means of electron microprobe Cambridge MK9 (EDS system) at Wrocław University.

RESULTS

Three types of nodules were observed: (a) metallic, (b) glassy (silica rich), and (c) silicic (mineral) see Fig. 1.

The metallic nodules (Fig. 2) are isometric, characterized by black or silver surface colour and by metallic lustre. Their surface is either smooth or shows automorphic isometric crystal faces (assemblage of micrometers sized crystals on the surface). The chemical composition does not vary much in individual nodules and between nodules (within EDS detection limit). No zonations or inclusions were observed under the microscope or in BSE images. The main component of the nodules is iron, they contain also heavy metals (mainly Pb, Zn and rarely low amounts of Cr) and sulphur.

The mineral nodules are green, black, grey and red in colour. Their surface is always smooth and their form varies from isometric or ellipsoidal to drop-like (sometimes very elongated). Most of the nodules is transparent to nearly transparent, some, mainly black and grey ones, are translucent. Single gas bubbles or foam-like structure composed of numerous small bubbles often occur in the interior of the mineral nodules. No mineral inclusions were observed. The chemical composition corresponds to that of rock forming minerals, mostly to pyroxene, amphibole and epidote. These nodules, in contrast to metallic and silicic ones, do not contain heavy metals or sulphur.

The glassy nodules are predominately colourless or black. Their surface is always smooth and shows glassy lustre. They are usually spherical in shape or less commonly, drop-like. They contain gas bubbles and foam-like structures and no mineral inclusions were noted. The nodules are composed mainly of silica with addition of Zn, Al and sometimes Pb, Cr and S.

Nickel was not detected in all three types of nodules.

DISCUSSION AND CONCLUSIONS

The origin of nodules is still a matter of discussion. The chemical composition of the nodules is used to discriminate between different hypotheses (Colombetti et al. 1998, Raukas 2000). The nodules from heavy fraction of the studied sediments are characterized by variable chemical composition which is here compared to compositions of nodules derived from various sources and described in the literature (Darby 1998, Kyte & Bohr 1995, Martínez Ruíz et al. 1997, Raukas 2000, Szöőr 2001).



Fig. 1. Nodules from the Bełkotka stream: (a) metallic, (b) silicic (mineral), (c) glassy; scale bar 2 mm.



Fig. 2. EDS spectrum of a metallic nodule from the Bełkotka stream.

A meteorite impact may produce both metallic and glassy nodules: the first ones coming directly from the meteroite, whereas the latter being the product of the impact and melting of the crustal rocks. The nodules that originated by meteorite impact are characterized by high abundances of Ni. The described nodules from the Kaczawa Mountains do not contain this element. However, the lack of Ni might be explained by its removal due to weathering process (Martínez Ruíz et al. 1997, Raukas 2000) or provenance of the material form the outer part of the meteorite body so called 'fusion crust' (Szöőr 2001). On the other hand, the common feature of the metallic and glassy Kaczawa nodules is the presence of Zn and other heavy metals (Pb, Cr). Zinc is too volatile to be a component of the meteroite after its travel through the Earth atmosphere (Darby 1998). Zinc was sometimes observed in meteorite-derived nodules (Queen Elizabeth Islands, Canada) and explained to be due to addition of a crustal material containing significant amounts of Zn during meteorite impact (Darby 1998). However, the presence of elements like Cr and Pb in the Kaczawa nodules (metal and glassy) suggests that they originated due to processes not connected with meteorite impact. Only the Kaczawa silicic (mineral) nodules, especially those of pyroxene composition, may have formed due to a meteorite impact. However, many of oval grains of silicates (e.g. amphibole, epidote) may come from the local basement rocks of the Kaczawa Complex.

Nodules containing heavy metals have also been found in other localities (Caravaca SE Spain) and their origin is thought to be linked with industrial processes (Martínez Ruíz et al. 1997). Typically, such industrial nodules contain also sulfur, the characteristic also shared with the Kaczawa nodules. The common composition of metal and silicic nodules together with their similarity to the nodules described by (Martínez Ruíz et. al. 1997) suggest that they originated due to similar, anthropogenic processes. However, the same process cannot explain the origin of mineral nodules from the Kaczawa Mountains since they do not contain heavy metals and sulphur.

Acknowledgements. I would like to thank Aberra Mogessie for inviting me to the Graz University and for valuable discussions and help. The visit in Graz was supported by the CEEPUS fellowship.

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SHRIMP ZIRCON AGES AND SOURCE AREAS OF METASEDIMENTARY ROCKS IN THE CENTRAL EUROPEAN VARISCIDES: THE RADZIMOWICE SLATES, KACZAWA COMPLEX (SUDETES, SW POLAND)

Abstract: SHRIMP zircon dating from two samples of the Radzimowice Slates of the Kaczawa Mountains reveals that the main populations of detrital zircon are dispersed within the "Cadomian range", between 550 and 650 Ma. One sample also contains zircons of 493-512 Ma age corresponding to Early Palaeozoic magmatism. Younger ages are scarce and need verification. The new data support possible genetic links between this part of the Bohemian Massif and the Northern Gondwana.

Keywords: SHRIMP zircon dating, slates, Kaczawa Complex, Sudetes, Variscides, Gondwana.

INTRODUCTION

Many sedimentary sequences in the Variscan basement of Central Europe have poor age constraints which implicates their problematic stratigraphic position and, consequently, tangle palaeogeographic and tectonic reconstructions. Among the well-known examples are the Radzimowice Slates (RS) of the Kaczawa Complex in the West Sudetes, the age of which remains debatable. In this report we outline our new results of SHRIMP dating of detrital zircons in two samples of the RS and preliminarily discuss their possible stratigraphic and palaeogeografic implications.

GEOLOGICAL SETTING

The Radzimowice Slates form an aligned outcrop, c. 1-3 km wide and 20 km long, in the middle part of the southern area of the Kaczawa Mountains. Formerly, based on regional lithological correlations, they were assigned to the Uppermost Proterozoic and considered as the lowermost part of the Bolków Unit, thrust over the (para)autochthonous Świerzawa Unit. More recently their age was revised to not older than Ordovician, based on conodont findings and they were re-interpreted as a separate tectonic unit, the Radzimowice Unit. The RS comprise gray slates, metasandstones, minor dark and siliceous slates, and, in places large (up to a few hundered meters across) bodies of greenstones and crystalline limestones (olistoliths?), all inter-

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preted to have been deposited in an oceanic trench environment (Kryza & Muszyński 2003, and refs. therein).

METHODS

Two samples were selected for SHRIMP zircon dating:

- sample CHR22 is a dark gray, fine-grained slate, composed of quartz, white K-mica, and minor albite, K-feldspar and black carbon-rich matrix; it comes from a small gorge, 300 m NW of the church at Chrośnica, in the W part of the RS outcrop;

– sample RDZ214 is a pale gray to greenish gray, fine-grained slate, composed of quartz, white K-mica, and subordinate K-feldspar and chlorite (altered biotite?); it was collected in a small exposure, 1.5 km east of Wojcieszów Górny (eastern part of the RS outcrop).

The samples, each c. 3 kg in weight, were crushed, and heavy minerals separated by conventional heavy liquid (sodium polytungstate, d 3.0 g cm⁻¹) method. Hand-picked zircon grains were studied under the optical microscope, and selected representative grains mounted in resin, ground and polished for CL imaging and SHRIMP analysis. The analyses were performed on the SHRIMP II in VSEGEI, St. Petersburg. The analytical conditions and data treatment procedures were those as described in Larionov et al. (2004).

RESULTS

Sample CHR22

The zircons in this sample have very diversified morphology and internal features, most of the grains being prismatic to subrounded (Fig. 1). Distinct cores are fairly common and many grains display simple or complex and regular ("magmatic") zoning. They differ also in their brightness in CL, from very bright to dark.

The ²⁰⁶Pb/²³⁸U age spectrum is widely dispersed between 279 and 2427 Ma. The three youngest ages, 279 ± 6 , 411 ± 11 , and 442 ± 5 Ma, were obtained from grains with high common Pb, so they should be treated with caution. The remaining ages are all Precambrian, and older than 558±7 Ma. Rather indistinct age clusters are around 560, 580-600, 610-620, 630-656, 734-780 Ma. The two oldest grains are 1889±21 and 2427±31 Ma.

Sample RDZ214

The zircons in this sample also vary widely, from idiomorphic to rounded grains, some contain more or less distinct cores, and most crystals display zoning. In CL they range from predominating rather dark, to more rare bright grains (Fig. 1).

The youngest calculated 206 Pb/ 238 U age of 358 ± 7 Ma, again, needs verification, considering that this grain is also high in common Pb. The main zircon populations are older than c. 490 Ma, and they cluster around 493-512, 524-592, and 630 Ma. Four analyses yielded considerably older ages of 1024 ± 13 , 2169 ± 28 , 2626 ± 24 , and 327.



Fig. 1. CL images of selected zircons of sample CHR22 (a) and RDZ214(b). Analytical points indicated by brighter ovals.

CONCLUSIONS

1. The zircon ages younger than c. 490 Ma are rather scarce in the studied samples of the Radzimowice Slates, and in all cases these grains are rich in common Pb which indicates possible disturbance in the U-Pb isotopic system. These ages, if positively confirmed, could indicate the possible age limit of the deposition of the RS.

2. Sample RDZ214 shows a clearly defined cluster of zircon ages between 493 and 512 Ma that corresponds with the Early Palaeozoic magmatism well documented in the Kaczawa Complex and elsewhere in the region.

3. Both the samples studied have the major populations of zircons with ages dispersed within the "Cadomian range", roughly between 550 and 650 Ma. Characteristically, the ages are evenly distributed within that long period, suggesting that the source rocks comprised most likely magmatic protholiths of fairly diversified ages.

4. Sample CHR22 contains three grains dated at around 734 to 779 Ma, whereas both the samples have inherited components, up to 3271±41 Ma. Similar zircon ages have been reported e.g. from North Africa, which formed a part of Gondwana. The North Gondwana and the Bohemian Massif (with the Radzimowice Slates) shared a range of common events, e.g. intense Cadomian magmatism between 700 and 540 Ma, orogenic igneous activity and sedimentation in extensional basins (540-520 Ma), and continental breakup with associated rift magmatism at c. 520-510 Ma (Pereira et al. 2006 and refs. therein). The new data point to a close similarity in zircon ages and, consequently, possible genetic links between this part of the Bohemian Massif and the North Gondwana.

The study was supported by the KBN research project 2P04D 015 27, and internal Wrocław University grants 1017/S/ING, and 2022/W/ING.

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HELLAS PLANITIA AS A POTENTIAL SITE OF SEDIMENTARY MINERALS

Abstract: Hellas Planitia is a circular impact crater which could have been a water basin in the past, so it is suspected to find rock sediments and sedimentary minerals there. The Planetary Fourier Spectrometer (PFS) passing over Hellas and the surrounding terrain such as valleys recorded some spectra with characteristic band. We see the band around 1160 cm⁻¹ in emissivity, which could be assigned to sulphates or shocked basalt. Other band that appear in around 350 cm⁻¹ may belong to hematite spectrum.

Keywords: Mars, Hellas Planitia, Mars Express, PFS-Planetary Fourier Spectrometer, emissivity, sulphates, hematite.

INTRODUCTION

Hellas Planitia is a roughly circular impact crater about 3000 km long by 1500 km wide located in the southern hemisphere of the planet Mars. The basin was formed when a large asteroid impacted Mars during the heavy bombardment period of the Solar System about 3.9 billion years ago.

The topography of this broad crater slopes down from an average highland altitude of about 2 km above the Martian reference radius (3394.2 km) to an average depth of about 6 km. It reaches a minimum of -7.5 km in its NW corner, which is the lowest point on the entire surface of Mars (Richardson, no publication date).

The bottom of the basin is relatively smooth, filled with dust and numerous small impact craters. Many dendritic channels lead to the basin, the most noticable of them emerge from the eastern side of Hellas (Ruell Vallis and others). Narrow gullies on the upper surface of a large debris apron complex south of Ruell Vallis show fluvial erosion (Crown et al. 2002). Their origin is interpreted in three ways, as channels leading water into the basin, lava channels of late volcanism (Lahtela et al. 2003) or tectonic fracture eroded after impact.

The material which fills Hellas is layered, eroded in some places that show rock bedding with ripplemarks on the top. Accumulation of this material may have proceeded during river sedimentation or lake sedimentation as well as during eolian processes in the late Hesperian (3.8 to 1.8 billion years ago) and Amazonian eras (1.8 to today). The deposits are estimated to be 100-200 m thick (Tanaka, Leonard 1995).

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Hellas could have been a water basin in the past so we suspect to find there rock sediments and minerals, like carbonates, sulphates and ferrite oxides that have been formed undoubtedly in the presence of liquid water along with basic materials, which Hellas consists of, like pyroxenes, plagioclases and sheet silicates. Chemical weathering of these minerals is also taken into consideration. These minerals could be components of atmospheric dust in the Hellas basin and could be identified in the atmospheric part of the PFS spectrum.

PFS-PLANETARY FOURIER SPECTROMETER

The PFS-Planetary Fourier Spectrometer aboard Mars Express provides spectra in the range 200-8000 cm⁻¹ with spectral resolution equal to 2 cm⁻¹. Such resolution improves earlier attempts of fitting the spectra of mineral mixtures to those measured.

RESULTS

Each spectrum recorded by PFS over Hellas, apart from the deep CO_2 band with a minimum at 667 cm⁻¹, revealed a dust spectral shape at 1075 cm⁻¹. We see band at around 1160 cm⁻¹ which can identify with sulphate spectra (Fig 1).

The band around 1160 cm⁻¹ may indicate a deep band of gypsum (Fig 2). Sulfates could appear as products of evaporation when the Hellas basin was supposedly filled with water. Sulfates may also form at depth in the presence of sulfur-rich fluids in hydrothermal conditions. Layered deposits could have originated as volcanic ash or eolian deposits and later possibly altered to sulfates by acidic groundwater circulation. Finally, sulfates could result from alteration of mafic minerals by rain or frost acidified through volcanic outgassing. The second idea is to compare the band ~1160 cm⁻¹ to the spectrum of shocked basalt which depends on the degree of shock metamorphism caused by impact meteorites.



Fig. 1 PFS spectrum of Hellas Planitia with band around 1160 cm⁻¹ which is interpreted as sulphates or shocked plagioclases



Fig. 2 Laboratory gypsum spectrum with around 1160 cm⁻¹ characteristic band. (ASU Thermal Emission Spectral Library)

The Martian surface was bombarded by meteorites in the past hence should contain shock material. All Martian meteorites, shergottites, contain maskelynite-(plagioclase glass) and other shock features that influence their spectra. Plagioclase and orthopyroxene experimentally shocked to various pressures between 17 and 56 GPa show similar spectral features. (Wright et al. 2006, Wright, Newsom. www.marscraterconsortium.nau.edu/WrightMCC7).



Fig. 3 PFS spectrum of Hallas Planitia with band around 350 cm⁻¹ which is interpreted as a hematite or carbonates.



Fig. 4 Laboratory spectra of calcite, magnesite and hematite with around 350 cm⁻¹ characteristic band. (ASU Thermal Emission Spectral Library)

Another characteristic band recorded by PFS is found around 350 cm⁻¹ (Fig. 3) It can assign this band to the hematite spectrum (Fig. 4)

Hematite is an important mineral component of the Martian surface. The preferred formation mechanism for gray hematite implies precipitation from large basins of Ferich water. Hellas could have been a water basin in the past. Other previously proposed explanations for hematite assumy that the mineral precipitated in large lakes or in hot springs when Mars' ancient volcanoes were active or that hematite remained after water leached away other minerals, or that it formed when volcanic ash deposits were altered chemically (Kirkland et al. 2003).

Carbonates are other characteristic minerals, that have a band near 350 cm⁻¹. We compare this band to the spectrum of calcite and another carbonate-magnesite (Fig. 4). It is possible that carbonates could exist on Mars but only under specific conditions, i.e. if we assume that Hellas was a water reservoir or that Mars' atmospheric pressure at the bottom of the Hellas basin allows water to remain in a liquid state.

CONCLUSIONS

The interpretation of PFS spectra is confirmed by the Mars Express spectrometer OMEGA which discovered sulfates like kieserite, gypsum, bassanite and epsomite on its shortwave channel SWIR-C 0.93-2.73 μ m on Martian terrains of Vallis Marineris and Terra Meridiani (Gendrin et al. 2005). Hematite and other ferrite oxides were discovered in the form of small 1 cm spherules by Martian Rovers Spirit and Opportu-

nity on the Gusev Crater and Terra Meridiani by Mossbauer Spectrometer and Mini-TES equipment (Christensen et al. 2004, Morris et al. 2004). Hematite and silicates were confirmed by OMEGA but the existence of carbonates is not yet certain.

The problems with correct interpretation of the bands recorded by PFS is spectral calibration and noise affecting the short waves above 1200 cm⁻¹. Therefore, their interpretation is confined to 200-1200 cm⁻¹. However, sulfates and hematite have characteristic deep bands and are very noticeable in this range, excluding the band of CO_2 (667 cm⁻¹). We believe that this interpretation could be valid since the Hellas basin could have been filled with water in the past and gullies could have led water into the basin. It is conceivable that atmospheric pressure of Mars at the bottom of the Hellas basin might presently allow water to persist in a liquid state.

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MINERALOGIA POLONICA – SPECIAL PAPERS Volume 29, 2006

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AN APPLICATION OF THE WATER-TO-ROCK MOLAR RATIO FOR CALCULATING THE AMOUNT AND COMPOSITION OF METAMORPHIC FLUIDS WITH REGARD TO RAYLEIGH DISTILLATION

Abstract: A new approach to evaluation of the water-to-rock molar ratio (WR) is presented for isotopic fractionation processes described by the Rayleigh distillation model. In contrast to methods previously applied, newly defined formulas are capable to reproduce the full range of the WR values from infinity to zero. The accurate evaluation of the WR is essential to estimate the amount of metamorphic fluids in reactions undergoing Rayleigh distillation. **Keywords**: stable isotopes, serpentinite, water-to-rock ratio

INTRODUCTION

The water-to-rock molar ratio (WR) is essential for the evaluation of isotope mass balance calculated for metamorphic fluids, notably for serpentinization solutions. Hitherto existing methods of the WR estimation (Taylor 1974, 1977) are largely unsuccessful while applied to processes described by Rayleigh distillation. In this paper the plausible estimation of the WR for reactions of isotopic exchange consistent with the Rayleigh distillation model is presented.

QUANTIFICATION OF WATER-TO-ROCK MOLAR RATIO

The water-to-rock molar ratio (WR) allows estimation of the intensity of isotope exchange between a rock and metamorphic fluids e.g. fluids circulating during the serpentinization of ultramafic rocks. The WR is defined as:

$$\begin{split} \frac{W}{R} &= \frac{(\delta_{w}^{r} - \delta_{v}^{r})}{(\delta_{w}^{i} - \delta_{w}^{f})} \quad (1) \\ \text{for a closed isotope system (Taylor 1974, 1977) or:} \\ \frac{W}{R} &= \ln \left[1 + \frac{(\delta_{v}^{f} - \delta_{v}^{i})}{(\delta_{w}^{i} - \delta_{w}^{f})}\right] \quad (2) \end{split}$$

for an open system (Taylor 1977) where

 $\delta^i_r, \delta^f_r~$ – represent initial and final rock isotope composition, respectively

 δ_w^i, δ_w^f – represent initial and final fluid isotope composition, respectively

If the initial and final rock isotope compositions given in equations (1) or (2) were attributed to the isotope composition of a rock before and after the serpentinization, estimated using the Rayleigh distillation model, the difference between δ_r^i i δ_r^f would

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depend exclusively on the reaction temperature. The isotopic fractionation of a rock and fluid undergoing Rayleigh distillation can be described by following equations:

$$\delta_{w}^{t} = (\delta_{w}^{i} + 1000) * F^{\alpha - 1} - 1000 \text{ for fluid (Rayleigh 1896)} (3)$$

$$\delta_{r exp}^{t} = \frac{\delta_{w}^{i} (\delta_{w}^{t} - \delta_{w}^{i}) + \delta_{r exp}^{i} (\delta_{w}^{t} - \delta_{w}^{t})}{(\delta_{w}^{i} - \delta_{w}^{t})} + 2\delta_{w}^{t} \text{ for rock (4)}$$

where: δ_w^i - fluid isotope composition before initiation of reaction δ_w^t - temporal fluid isotope composition during reaction δ_w^f - fluid isotope composition after reaction $\delta_r^t \exp$ - expected rock isotope composition before reaction $\delta_r^t \exp$ - expected temporal rock isotope composition during reaction α - isotope fractionation coefficient during reaction F - amount of fluid remaining in a system

Before the initiation of the serpentinization process (exchange of hydrogen molecules between an ultramafic rock and fluid) the WR molar ratio should approach infinity, since all hydrogen still remains in the fluid. On the other hand, after the completion of this reaction the same ratio should be close to zero if all the hydrogen particles reacted with the rock. Surprisingly, equations (1) and (2) directly applied to the Rayleigh distillation model are unable to reproduce the full range of WR values from infinity to zero.

water-to-rock molar ratio and RAYLEIGH Distillation

The WR at the commencement of isotope exchange reaction can be derived from the newly formulated equation:

$$\frac{W}{R} = \frac{\left(\delta_{r real}^{f} - \delta_{r real}^{i}\right)}{\left(\delta_{w}^{i} - \delta_{r real}^{f}\right)} \quad (5)$$

where:

 $\delta_{r real}^{i}$, $\delta_{r real}^{f}$ – represent values of initial and final rock isotope composition, respectively, as they are measured in specimens

 δ_w^i – represents initial isotope composition of fluid equal to expected final isotope rock composition ensuing from the Rayleigh distillation model.

Equation (5) employs actually measured values of initial and final rock isotope composition instead of those estimated using the Rayleigh distillation model as in equation (1). Consequently, the application of equation (5) allows reproducing the full range of WR values.

The incremental WR molar ratio during isotope fractionation can be described by the equation (Fig. 1):

$$\frac{W^{t}}{R} = \frac{\left(\delta_{r \text{ real}}^{i} - \delta_{r \text{ real}}^{t}\right)}{\left(\delta_{r \text{ real}}^{t} - \delta_{r \text{ exp}}^{t}\right)} (6)$$

where: W/R^u - transient WR molar ratio

 δ_{rexp}^{t} – transient expected isotope rock composition corresponding to isotope rock composition ensuing from the Rayleigh distillation model

 $\delta_{r \, real}^{t}$ – transient real isotope rock composition as it is measured in a specimen $\delta_{r \, real}^{t}$ – initial real isotope rock composition as it is measured in a specimen



Fig. 1: Variability of isotope composition for serpentine and fluid at 240°C depending on different WR. Expected values of δD and $\delta^{18}O$ result directly from the Rayleigh distillation model for the WR molar ratio approaching infinity. The variability of δD and $\delta^{18}O$ derived from measurements is shown by curves whose shape depends on the water-to-rock molar ratio.

The relationship between actually measured values of δD and $\delta^{18}O$ and the initial water-to-rock molar ratio is shown on WR_H vs. WR_O diagram (Fig. 1). With the current progress of isotope fractionation, the transient WR molar ratio (6) come up to zero whereas the δD and $\delta^{18}O$ composition follows a path whose shape depends on the initial WR molar ratio (Fig. 1). The expected hydrogen and oxygen isotope rock composition ensuing from the Rayleigh distillation model approaches values of δD and $\delta^{18}O$ for the initial isotope composition of fluid before the start of reaction (Fig. 1).

Basing on the equations (3), (4) and (6), the current progress of isotope fractionation can be assessed as well as the amount of fluid remaining in a system:

$$\frac{W}{R} = \frac{W}{R} * (1 - F) (7)$$

where: W/R^{u} - incremental WR molar ratio

W/R: initial water-to-rock molar ratio

F – amount of fluid remained in a system

The equation above allows calculation of the amount of fluid remaining in system (F), that has not yet reacted with a rock and, in addition, to estimate the initial mass of fluid.

CONCLUSIONS

The reliable estimation of the WR molar ratio is feasible for isotopic fractionation undergoing Rayleigh distillation and allows for:

1. Calculation of the actual amount of fluid reacting with a rock.

2. Assessment of the initial isotope composition of metamorphic fluids.

The initial amount of fluid (F) can be derived from the Rayleigh equation (3) if the proportion between rock and fluid is known before the commencement of isotope exchange. To estimate the above mentioned proportion the WR molar ratio is essential. The original isotope composition of penetrating fluids controls the measured δD and $\delta^{18}O$ in the analysed rock. The magnitude of this relationship is dependent on the WR molar ratio and can be accurately quantified using equation (5).

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