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From magma genesis to ore formation; evidence from macro- to nano-scales

Abstracts and field trip guide

Boguszyn, Poland, 16-19 October 2014

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

Quo vadis petrologia?

The last fifty years have seen periods very good for petrological and mineralogical studies. This branch of the Earth sciences have not only had developed very effective investigate methods, which have resulted in great progress, but it has also offered essential stimulation and support to other geosciences. The methods which have led to new interpretations are first of all: precise isotope investigations and considerations of multi-mineral equilibria. As the most important contribution to the general geology I evaluate petrological data as being one of the main foundations of modern plate tectonic theory and of Earth models (present and concerning the geological past), especially in the mantle and crust.

New, well equipped laboratories, built in many countries, have been important in this progress. High-quality analytical data were the factor that stimulated construction of unconventional, but correctly established models in petrology. However, it is sad for me to refer here to the past. Presently, the availability of geochemical data, earlier hardly obtainable and which are more precise, frequently yields elaborations, which are restatement of already published solutions or an application of a well known model to a "new" topic. One or two more fewer after the decimal point may have become the main scientific achievement. Moreover, the chemical or isotope laboratory data frequently overshadow the methodological shortages such as incorrectly taken and insufficiently numerous samples, lack of thoughtful optical microscope analysis of the rock, jargon and the use of imprecise terminology etc.

When reading current petrological publications in "high rank" journals I am amazed commonly at the scarcity of even traces of new ideas or unconventional approach to the investigations. The track which should go more or less, albeit with uncertainties and doubts, forward, appears to me as a circular run around an arena, surrounded by an applauding public. Also it is easy to see that relatively large studies are chopped into pieces and printed as separate articles to have more "published items" per year.

These are the signs of stagnation. Petrology, find the way to go ahead, please.

Andrzej Kozłowski

XXI^st^ Meeting of the Petrology Group of the Mineralogical Society of Poland

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Invited lectures

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POLSKIE TOWARZYSTWO MINERALOGICZNE

Geological cycles and a two-stage history of the continental crust

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The discovery of radioactivity changed our understanding of the thermal evolution of the Earth, and provided ways to determine the age of the Earth and time scales of geological change. The continental crust is the archive of Earth history, and the apparently cyclical nature of geological evolution is a feature of the geological record. The advent of radiometric ages has highlighted that the spatial and temporal distribution of the Earth's record of rock units and events is heterogeneous with distinctive peaks and troughs in the distribution of ages of igneous crystallization, metamorphism, continental margins and mineralization, and in the ages of rocks that reflect new continental crust. The peaks may reflect periods of high magmatic activity, and as such they might be due to magmatism associated with deep-seated mantle plumes. However, the bulk composition of the continental crust is similar to those of magmas generated in subduction-related settings, and the peaks of ages are linked to the timing of supercontinent assembly. It is therefore argued that the peaks of ages reflect the preservation potential of magmatism in different tectonic settings, rather than fundamental pulses of magmatic activity. In contrast there are other signals, such as the Sr isotope ratios of seawater, mantle temperatures, and redox conditions on the Earth, where the records are regarded as primary because they are not sensitive to the numbers of samples of different ages that have been analysed.

Less than 5% of the geological record consists of rocks older than 3 Ga, and there are no known rocks older than 4 Ga. The sedimentary record is biased by preferential sampling of relatively young material in their source terrains. The implication is that there were greater volumes of continental crust in the Archaean than might be inferred from the compositions of detrital zircons and sediments. Recent studies based on the U-Pb, Hf and O isotope ratios of detrital zircons suggest that at least ~60-70% of the present volume of the continental crust had been generated by 3 Ga. The growth of continental crust was a continuous process, but there was a decrease in the rate of crustal growth at ~3 Ga. Before 3 Ga the rates of continental growth were high (~3.0 $km^3 \cdot yr^{-1}$), broadly similar to the rates at which new crust is generated and destroyed at the present time. Since 3 Ga the net growth rate was much lower (~0.8 $km^3 \cdot yr^{-1}$), perhaps because of higher rates of destruction of crustal materials. It is inferred that subduction-driven plate tectonics and discrete subduction zones have been dominant since ~3 Ga.

Because of the poor preservation of rocks and minerals after billions of years of crustal evolution, it remains difficult to establish the composition of new/juvenile continental crust and hence the conditions and the tectonic setting(s) in which it was generated. One approach is to estimate the time-integrated parent/daughter ratios of isotope systems in crustal melts derived from that new crust. ^{87}Rb decays to ^{87}Sr with a long half-life (~48.8 Ga) compared to the age of Earth, and because of the different partitioning characteristics of Rb and Sr within the crust ($D^{Rb} < D^{Sr} << 1$), crustal differentiation processes produce a large range of highly fractionated Rb/Sr ratios. As a consequence there is a strong positive correlation between the Rb/Sr and the SiO_2 content of the crust, and with crustal thickness. The time-integrated $^{87}Rb/^{86}Sr$ ratio can therefore be used as a proxy for the bulk composition of the new continental crust, and even for crustal thickness, back in time. The time-integrated Rb/Sr in crustal material (whole rock samples) with crust formation ages ranging from the Hadean to the Phanerozoic suggest that new continental crust was principally mafic over the first 1.5 Ga of Earth's evolution, and that it became more evolved subsequently. It is concluded that significant volumes of pre-3 Ga crust may have been associated with intraplate magmatism. Since ~3 Ga there has been an increase in Rb/Sr, SiO_2, and the inferred thickness of new crust, consistent with an increase of continental input into the oceans and the onset of plate tectonics. The 60-70% of the present volume of the continental crust estimated to have been present at 3 Ga, contrasts markedly with the volumes of crust of that age apparently still preserved and it requires ongoing destruction (recycling) of early formed crust and subcontinental mantle lithosphere back into the mantle through processes such as subduction and delamination.

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Late Devonian subduction and back-arc extension at the western margin of Brunia: evidence from metavolcanic rocks of the Vrbno Group (Silesicum, north-eastern Bohemian Massif)

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Introduction

Large remnants of pre-Variscan basement, variously deformed and metamorphosed during the Variscan orogeny, occur in Silesicum (Hrubý Jeseník Mts., NE Bohemian Massif). This Cadomian crystalline paraautochton dominated by tonalitic to granitic gneisses of a Brunian affinity (Finger et al. 2000; Kröner et al. 2000; Hanžl et al. 2007) was imbricated with Devonian volcanosedimentary complexes (Schulmann, Gayer 2000 and references therein) within the Variscan cycle. The Devonian to Lower Carboniferous rocks overlying the Cadomian basement provide a complex record of Pragian–Tournaisian extension, Tournaisian–Namurian convergence and flysch sedimentation, Namurian–Westphalian collision and molasse deposition (Kalvoda, Bábek 2010).

Stratigraphy and petrology of the Vrbno Group (VG)

In the studied region of southern Hrubý Jeseník Mts., the Devonian volcanosedimentary sequence of the so-called Vrbno Group starts with clastic sediments (metasandstones and metaconglomerates). The basal quartzites contain Pragian–Emsian fauna (Römer 1870; Chlupáč 1989). The clastics are overlain by phyllites, passing gradually into a thick pile of volcanic products. The top of the sequence is formed by Famennian shales, cherts and graphitic limestones. The low-grade volcanosedimentary complex of the VG occurs in two ~NE–SW trending belts, separated by tectonic slices of the Cadomian metagranitic paraautochton (Oskava Block). The contacts are tectonically reworked and usually SW–NE trending; the metamorphic grade increases from the Chl zone in the SE to the Grt–St zone in the NW.

The **Western Volcanic Belt (WVB)** contains abundant metasedimentary rocks accompanied by mostly basic–intermediate metavolcanites but some rhyolites (banded massive types or agglomerate metatuffs) are also encountered (Fig. 1). At least some basaltic andesites are of subaqueous origin as shown by locally preserved pillow lavas.

The **Eastern Volcanic Belt (EVB)** is almost exclusively metavolcanic and bimodal, with much higher proportion of acid volcanic products. The volcanics are alkaline, ranging from rare subordinate alkali basalt, through trachyandesite–trachyte to prevalent comendite (see also Patočka, Valenta 1996). At least partly, their structures indicate subaeric origin and explosive nature (e.g., acid and basic agglomerate metatuffs, ignimbrites).

Finally, the region was penetrated by numerous massive subalkaline dolerite sheets, up to several dozens of meters wide.

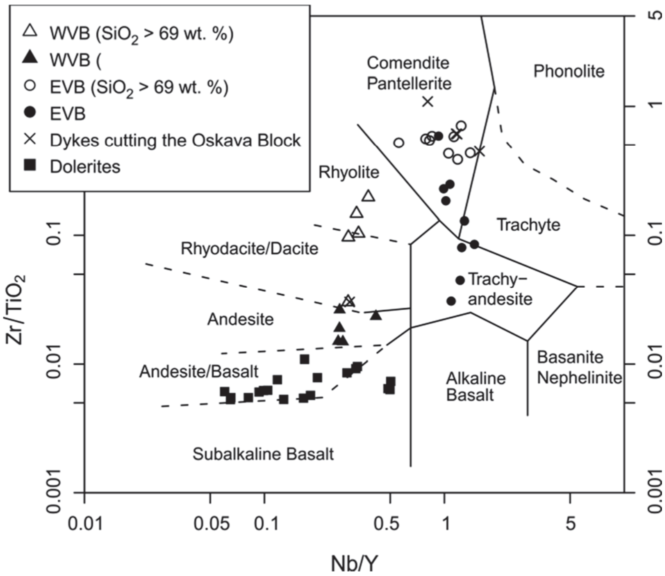

Fig. 1. Classification diagram of Winchester and Floyd (1977) for the studied metavolcanic rocks of the Vrbno Group. The analyses from the Western Volcanic Belt (WVB) and Eastern Volcanic Belt (EVB) are split into two groups at SiO_2 = 69wt%.

Age of the VG volcanism

Zircons from two felsic samples characteristic of both volcanic belts, metarhyolite (Třemešek, WVB) and comendite (Rešov Falls, EVB), were dated by the LA-ICP MS U-Pb method at the University of Frankfurt. The ages indicate that the igneous activity in both volcanic belts was contemporaneous, or at least overlapped significantly in early to mid-Famennian times (~371-374 Ma); (Janoušek et al. 2014).

Whole-rock geochemistry and likely petrogenesis

The metavolcanites of the **Western Volcanic Belt** are variable in major-element composition (SiO_2 55.3-81.7, MgO 4.7-0.04wt%) but all are subalkaline (high-K calc-alkaline) in character. The standard NMORB-normalized spiderplots (Sun, McDonough 1989) are characterized by marked LILE over HFSE enrichments, only part of which can be ascribed to metamorphic mobility (e.g., Cs and Ba). In order to eliminate the metamorphic effects, only relatively immobile components are plotted here, based on selection and order of elements given by Pearce (2014); (Fig. 2). The patterns resemble those of metavolcanic rocks from a continental-arc geotectonic setting (Pearce, Stern 2006 and references therein) as shown also for instance by the diagrams of Wood (1980); (Fig. 3a), Pearce et al. (1984); (Fig. 3b) or Schandl, Gorton (2002); (Fig. 3e).

The basic–intermediate lavas of the calc-alkaline Western Volcanic Belt came from a moderately depleted mantle (ε_{Nd}^{370} ~ +3) strongly modified by an Andean type subduction (Fig. 3c; Pearce 2008, 2014). Rare rhyolites were derived most likely from immature crust or by extensive fractionation of primary basaltic melts. Taken together, the rock association is interpreted as a vestige of a deeply dissected continental arc.

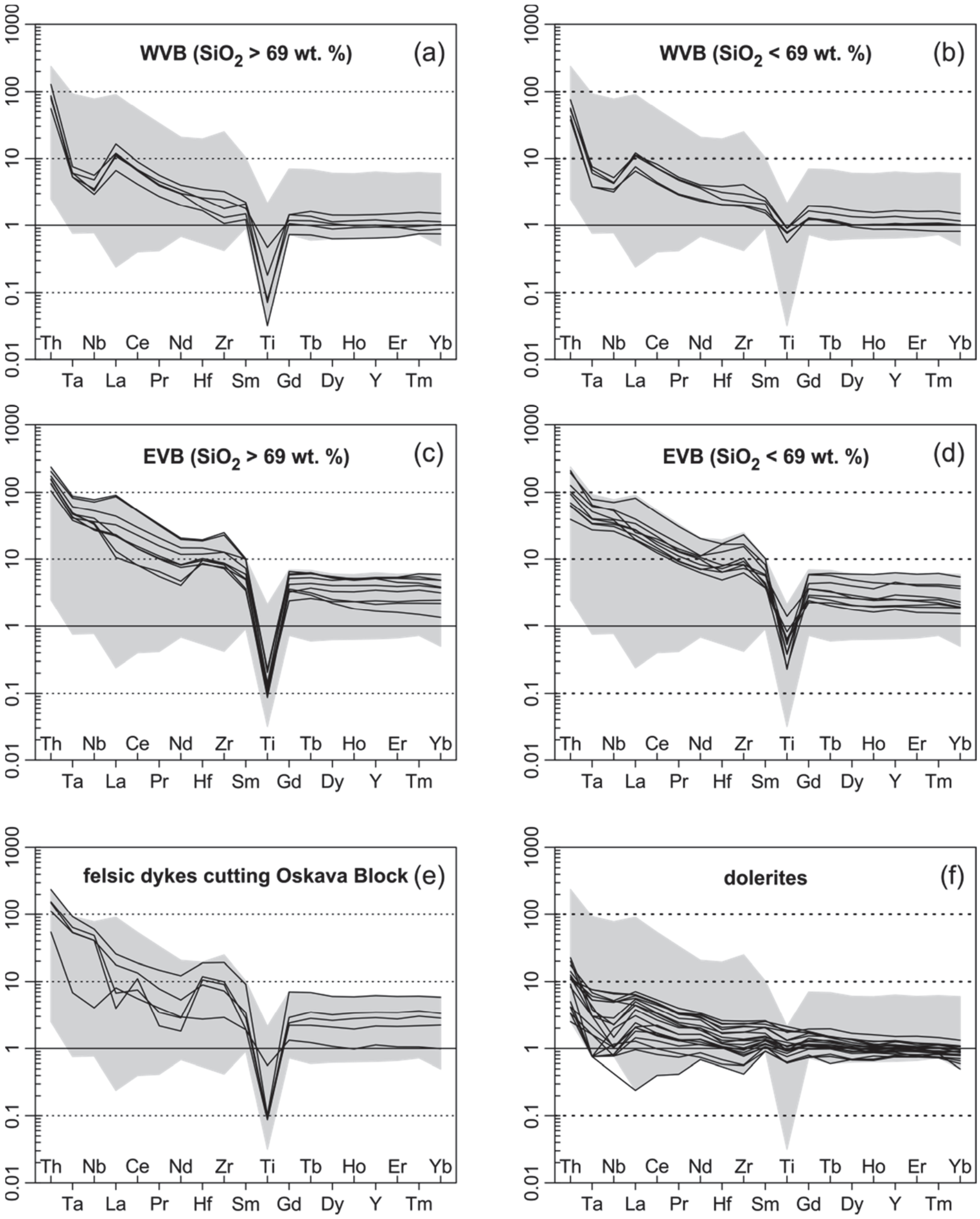

Fig. 2. The NMORB-normalized spiderplots (normalizing values from Sun and McDonough, 1989; order of elements after Pearce, 2014) for the VG metavolcanic rocks.

The **Eastern Volcanic Belt** metavolcanites (SiO_2 52.9-80.7, MgO 2.5-0.03wt%) arecharacterized by high contents of alkalis, REE (except Eu), HFSE (Nb, Ta, Y, Zr and Ga), Zn, as well as elevated Ga/Al and Fe/Mg ratios. This, together with low contents of CaO, trace elements compatible in mafic silicates (Co, Sc, Cr, Ni) and feldspars (Ba, Sr, Eu) is typical of A-type igneous activity (Whalen et al. 1987). Accordingly, they display a distinct within-plate geochemical signature in many geotectonic diagrams (Fig. 3a, b, e). Moreover, diagram Nb/Yb–Th/Yb (Pearce 2008, 2014) shows an OIB-like affinity of the basic EVB suite.

The Nd–Sr isotopic compositions, in combination with petrology and the whole-rock geochemical signature, point to an interaction between basic magmas coming from a strongly LREE-depleted mantle and within-plate volcanites. As shown by experiments, a high-T anatexis of relatively refractory, tonalitic to granitic rocks similar to those of the Cadomian basement would yield A-type like melts analogous to the felsic EVB metavolcanic rocks (Skjerlie, Johnston 1992; Patiňo, Douce 1997). The A-type magmas can originate, *inter alia,* by re-activation of older orogens (typically in rifts, but also former subduction settings – Bonin 2008; Magna et al. 2010). The magmas parental to the EVB thus could have been generated within a significantly thinned lithospheric domain with high heat flow, perhaps further enhanced by the upwelling asthenosphere (Janoušek et al. 2014).

For the geochemically most primitive **dolerite** samples, the trace-element patterns and Nd isotopic compositions (ε_{Nd}^{370} ~ +8) are compatible with direct derivation from a strongly depleted mantle (MORB source). However, the mantle source was influenced by interaction with an OIB component (ascending asthenosphere?) – (Fig. 3c-d, f) and the magmas suffered a variable crustal contamination (ε_{Nd}^{370} dropping down to +5).

Geotectonic significance

The preliminary report of Wilimský, Přichystal (2005) indicated that metavolcanic rocks compositionally equivalent to the VG can be traced further north, as far as to the Polish border. Moreover, the easterly (Nízký Jeseník Mts.) Šternberk–Horní Benešov Volcanic Belt is built mainly by Late Devonian alkaline metavolcanic rocks of the likely intracontinental rift setting (Přichystal 1990) leading to opening of a truly oceanic domain (Kalvoda et al. 2008).

The studied volcanic association seems to reflect a combination of an arc and a back-arc setting, latter having been initiated as an intracontinental rift (Patočka, Valenta 1996; Patočka, Hladil 1997; Janoušek et al. 2014). The current configuration seems to reflect that of the eastward-dipping (in the present coordinates) Late Devonian subduction beneath the Cadomian crust (Brunian Continent). This subduction is taken responsible for generation of the volcanic-arc (WVB) as well as accumulations of arc-derived siliceous detritic sediments (Szczepański 2007). The westward retreat of the subduction and slab roll back (Uyeda 1982) could have caused a significant thinning of the Cadomian lithosphere in the hinterland. The refractory attenuated crust would have melted due to the hot upwelling asthenosphere, leading to generation of voluminous acid alkaline magmas with an 'A-type' geochemical signature. The maximum thinning has been marked by numerous intrusions of relatively late, primitive, mantle-derived dolerites dotting the VG. The subduction presumably passed into felsic crust underthrusting, and the on-going compression led eventually to a gravity-driven extrusion of thermally softened lower plate material in front of the Brunian rigid buttress (Chopin et al. 2012; Mazur et al. 2012).

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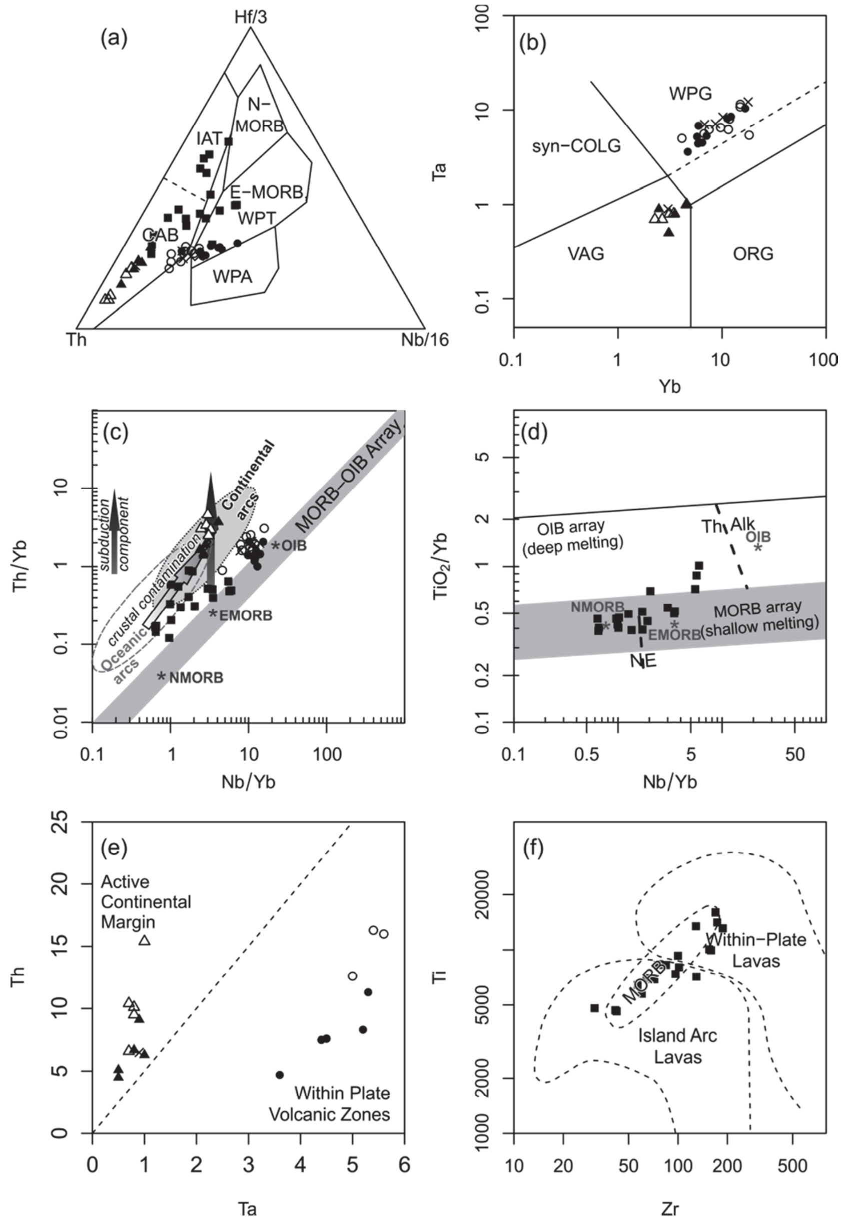

Fig. 3. Selected geotectonic diagrams for the metavolcanic rocks of the VG. (a) Triangular plot Th–Hf/3–Ta (Wood 1980): IAT – Island-Arc Tholeiites, CAB – Calc-Alkaline Basalts, WPT – Within-Plate Tholeiites, WPA – Within-Plate Alkali Basalts. (b) Binary diagram Yb–Ta (Pearce et al. 1984): VAG – Volcanic Arc Granites, WPG – Within-Plate Granites, syn-COLG – Syn-Collisional Granites, ORG – Ocean Ridge Granites. (c) Binary diagram Nb/Yb–Th/Yb (Pearce 2008, 2014). The 'MORB-OIB array' is formed by average NMORB, EMORB and OIB compositions from Sun and McDonough (1989). (d) Binary diagram Nb/Yb–TiO_2/Yb (Pearce 2008, 2014) serving to decipher shallow (MORB array) and deep (OIB array) melting. (e) Binary plot of Ta vs. Th of Schandl, Gorton (2002) used to decipher the geotectonic setting of felsic volcanic suites. (f) Binary plot Zr–Ti (Pearce 1982).

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The volcano-pluton 'interface': a Caledonian perspective

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Calc-alkaline volcanic and plutonic activity in the Caledonian Grampian Terrane started at ~430 Ma, ***after*** subduction of the leading edge of continental Avalonia beneath Laurentia. ID-TIMS U-Pb zircon dating shows that it then persisted for ≥22 million years. I-type, medium- and high-K plutons populate a broad belt that extends ~300 km NE-SW across the Scottish Highlands, on either side of the Great Glen Fault, and, when intrusions of similar age and setting in Shetland and Donegal are included, the belt extends to 750 km. The plutons are the 'Newer Granites' of Read (1961) and are dominated by the compositionally distinct Argyll and Northern Highland Suite (high Ba and Sr, abundant appinites) and the Cairngorm Suite (relatively low Ba and Sr, few appinites; Stephens and Halliday 1984; Halliday et al. 1985; Tarney, Jones 1994; Highton 1999; Fowler et al. 2001). Owing to intrusion by the plutons and to dramatic contemporary uplift and erosion, remnants of coeval (Siluro-Devonian) volcanic rocks in the plutonic belt are few. These include the centred or caldera volcanoes at Glencoe (Kokelaar, Moore 2006), Ben Nevis (Bailey 1960) and Etive (Anderson 1937), a thick and extensive sills-plus-lavas pile in Lorn (Kynaston, Hill 1908), and lavas, tuffs and fossiliferous hydrothermal deposits at Rhynie (Trewin, Thirlwall 2002 and references therein). The volcanics are dominated by basaltic trachyandesite, trachyandesite, trachyte and rhyolite, with sparse basalt, basaltic andesite and dacite; shoshonitic lavas and intrusions also occur. The intrusions and volcanic rocks are not pervasively deformed, but are faulted and tilted; they respectively cut and unconformably overlie metamorphic basement.

The Etive Dyke Swarm, >100 km long by 20 km wide, was mostly emplaced during 418-414 Ma, forming part of the plumbing of a large volcano (≥2000 km^3) that became intruded by the Etive Pluton and was subsequently removed by erosion. Similarly, and throughout the ≥22 million years of magmatism, large volumes (thousands of km^3) of intermediate to silicic magmas were erupted repeatedly, but were mostly removed by contemporaneous uplift and erosion. This very substantial volcanic counterpart to the 'Newer Granite' plutons was fully recognised only recently (Neilson et al. 2009).

The petrogenesis of the Grampian 'Newer Granites', with their associated appinites and lamprophyres, and intermediate to silicic hypabyssal and volcanic rocks, was widely (not universally) considered to have involved hydrous mantle melting above an *active* subduction zone that dipped beneath the Laurentian continental margin (Dewey 1971; Brown 1979; van Breemen, Bluck 1981; Soper 1986; Thirlwall 1988; Fowler et al. 2001; Oliver 2001; Woodcock, Strachan 2002; *cf.* Halliday, Stephens 1984). Despite the distinct paucity of basalts and gabbros, some envisaged an active continental destructive plate margin analogous to the Andean Pacific margin (e.g. Oliver et al. 2008). On the basis that 'Newer Granites' stitched the subduction-suture zone far to the south of the Grampian belt, Pitcher (1982, 1987) and Watson (1984) believed that the ‘Newer Granites’ post-dated plate collision and they advocated a generalised origin involving decompression related to uplift and strike-slip pull-apart. Refinements in age dating, however, show that the southern granites are younger than those to the north, but spatial and temporal reconstructions of the Caledonides (e.g. Stone et al. 1987; Kneller 1991; Kneller et al. 1993; Dewey, Strachan 2003, 2005) do show that the Grampian magmatism was not directly related to active subduction. Neilson et al. (2009) proposed that the post-collision magmatism and uplift resulted from breakoff of subducted oceanic lithosphere (slab) and consequent rise of asthenosphere. They advocated that the intermediate magmas forming both plutons and volcanoes originated mainly by partial melting of heterogeneous mafic-to-intermediate lowermost crust in which high Ba-Sr was derived from previous melting of LILE-enriched mantle, possibly at ~1.8 Ga. This crustal recycling was induced by heat and volatiles from under-plated small-degree melts of LILE- and LREE-enriched lithospheric mantle: the appinite-lamprophyre magmas. It is here proposed that that both the Grampian magmatic belt and the tearing of the continental crust here to produce the Great Glen Fault and nearby parallel faults were a consequence of focussed thermal erosion of the crust, in turn related to asthenospheric heating and partial melting of the lithospheric mantle.

Several authors have suggested that high Ba-Sr ‘Newer Granites’ may derive from the mantle-derived melts primarily by fractional crystallisation with crustal assimilation (e.g. Rock, Hunter 1987; Fowler et al. 2001). That syenite and granite can derive from fractional crystallisation of lamprophyric magma has been demonstrated in a dyke (Macdonald et al. 1986) and interpreted in hybrid appinite-syenite-granite complexes (Fowler 1988; Fowler, Henney 1996). However, the vast volumes of intermediate magmas (trachy-)andesites that have previously been overlooked - the missing volcanoes - renders this direct derivation unlikely to be the fundamental process.

In the region around Glencoe, where a volcano is well preserved owing to tectonically influenced caldera subsidence, it is apparent that the Rannoch, Clach Leathad and Etive plutons constitute parts of a small batholith (the Lochaber Batholith of Neilson et al. 2009). Rannoch and Clach Leathad are both more extensive at depth than at outcrop (Kokelaar, Moore 2006; Kokelaar 2007) and the plutons combine at depth to form a continuous body with a southwesterly age progression. The Etive Dyke Swarm, dominantly of intermediate to silicic compositions, but including lamprophyres, is related to a former centred volcano that was largely obliterated by emplacement of the Etive Pluton and by subsequent erosion. Whereas plutons need not represent magma bodies that were at some time plumbed to the surface to form a volcano (e.g. Annen 2011), several volcanoes in the Grampian belt were cut and partly obliterated by temporally linked plutons. Further, there is direct evidence (1) that plutonic bodies were linked to surface caldera-forming eruptions, (2) that the plutons grew incrementally from successive magma batches in the same style as the associated volcanic piles, and (3) that magma productivity was abnormally high.

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Cooling history of the Lesser Himalaya, Sikkim, India

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We investigated the cooling history of the Lesser Himalaya (LH) in the Sikkim region of NE India by means of apatite fission track (AFT) analyses. The obtained AFT ages range span from 12 to 2 Ma. All dates are the same within analytical uncertainty or much younger than the timing of metamorphism in this area, constrained by previous studies as 17-11 Ma (Catlos et al. 2004, Anczkiewicz et al. 2014). Thus the ages are interpreted as representing primarily cooling related to the uplift and exhumation of the Lesser Himalaya. The ages show a progression from older values in the core of the Teesta dome (TD) towards younger values on the edges of the dome, which are delineated by the Main Central Thrust (MCT). The age progression suggests that formation of the domal structure was responsible for the uplift and exhumation of the LH between 12 and 7 Ma. The essentially similar timing of amphibolite facies metamorphism in the centre of the dome and the AFT ages points to very fast exhumation. This is in accord with the track length estimates which for all analysed samples range from 14.6 to 13.6 µm. Locally much younger ages are obtained, spanning from 5 to 2 Ma, which we relate to the younger activity of the Managan fault and possibly also MCT.

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Timing and duration of regional metamorphism in the inverted Barrovian sequence of the Sikkim Himalaya, NE India

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Sikkim Himalaya in NE India expose a uniquely well preserved and petrologically continuous but inverted (higher grade rocks at structurally shallower level) metasedimentary sequence recording regional metamorphism in response to India-Asia collision. We conducted Lu-Hf garnet dating of petrologically well characterized suite of samples from all major Barrovian zones. Our main goals were to establish timing and duration of metamorphism as well as to provide additional constraints on the origin of the inversion of the sequence.

Lu-Hf ages show remarkable correlation with increasing metamorphic grade and decreasing structural depth. The youngest age is reported for the garnet zone (10.6±0.2 Ma) and then the ages become progressively older in the staurolite (12.8±0.3 Ma), kyanite (13.7±0.2 Ma) and sillimanite (14.6±0.1 Ma) zones. The oldest age of 16.8±0.1 Ma was recorded in the zone marking the onset of muscovite dehydration melting, directly below the Main Central Thrust, which separates the Barrovian sequence from the overlying migmatites. Our geochronological data provide tight constraint on timing and duration of the Barrovian sequence formation, which lasted about 6.2 Ma. Age pattern is clearly inverted similarly to previously reported inversion of pressure and temperature conditions but the age values show "normal" correlation with the metamorphic grade.

Comparison with the prograde metamorphic Sm-Nd garnet age from the classical Barrovian sequence in Scotland reveals some delay before the initiation of garnet growth in progressively lower metamorphic grades in both regions. In Scotland the time difference in crossing the garnet isograd, between garnet and sillimanite zones was established as about 6 Ma (Baxter et al. 2002), which is in a very good agreement with 4 Ma time of the equivalent part of the section in the Sikkim Himalaya.

Despite limited data on metamorphic peak in Sikkim, the age determinations suggest that in both regions thermal peak occurred in all zones within a very short time span. Such similar Tt paths in the inverted and non-inverted sequences indicate that the metamorphic inversion in the Sikkim Himalaya occurred on a retrograde path after metamorphic peak was attained in all grades.

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Andesitic eruptions and magma mixing processes at a Permian tuff ring near Rožmitál (the intra Sudetic basin)

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The andesitic succession at Rožmitál quarries is a part of the Lower Permian Broumov (Słupiec) formation in the central part of the intra Sudetic basin, a late Palaeozoic intermontane trough in the eastern part of the Variscan belt of Europe. The 50-60 m thick Rožmitál succession comprises a bedded volcaniclastic sequence overlain by coherent andesites with andesite breccias and peperites. The volcaniclastic sequence (tuffs, lapilli tuffs and lapillistones) was deposited by pyroclastic fall and surge processes during explosive, phreatomagmatic to transitional, phreatomagmatic or Strombolian eruptions. Palaeo-gullies filled with tuffaceous breccias document episodes of erosion and redeposition of andesitic tephra by mass flows and ephemeral streams. Subsequent effusive activity resulted in the emplacement of andesitic block lavas that capped the volcaniclastic sequence. Some lavas plunged into unconsolidated sediments as invasive flows, and shallow-level subvolcanic intrusions were emplaced in near-vent locations. Overall, the Rožmitál succession is interpreted as a proximal section of tuff ring, several hundred metres in diameter. This tuff ring was, possibly, one of several eruptive centres forming a monogenetic volcanic field on an alluvial plain inside an ignimbrite-related caldera.

Many samples of coherent andesites and, especially, of the volcaniclastic deposits from Rožmitál, show petrographic and geochemical evidence of syn-eruptive incorporation of quartz-rich sediments as well as post-magmatic albitization, kaolinitization, chloritization and cementation by dolomite. However, fresh samples of coherent andesites consist of 5-10% of plagioclase (An30-63) and augite phenocrysts, up to 5 mm long, in a groundmass of: plagioclase, augite, pigeonite, ilmenite, minor quartz, alkali feldspar, biotite, magnesiohornblende with, in some specimens, well-preserved glass. The plagioclase phenocrysts represent a heterogeneous assemblage of euhedral to anhedral, embayed, sieve-textured and variably zoned crystals. Groundmass laths and phenocryst rims (labradorite to andesine) are often enriched in Ca relative to phenocryst cores (andesine to oligoclase). Also, augite groundmass crystals and phenocryst rims are enriched in Mg compared to phenocryst cores. There are corroded xenocrysts of alkali feldspars and quartz. The above evidence suggests that the erupted andesite lava is a hybrid of partly crystallized, variably evolved, intermediate to acidic magmas, mixed with a more primitive melt, possibly in a series of replenishment episodes that affected the magmatic system of the tuff ring.

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Kłodzko-Złoty Stok massif – a new outlook

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The Kłodzko-Złoty Stok intrusion is a small magmatic body, intruded between the Orlica-Śnieżnik dome, the Kłodzko metamorphic unit and the Bardo unit, displays many features pointing to a subduction affinity.

1- Rocks building the intrusion are predominantly composed of hydrous minerals (mainly amphiboles and biotites).
2- Trace elements concentrations are typical of subduction enrichments, namely high abundances of such elements as Rb, Ba, K, U, Th and depletion in Nb, Ta, Ti, P.
3- P-T conditions indicate high pressures, initiation of crystallization of dark minerals; lamprophyric pargasite cores with calculated crystallization conditions up to 22 kbar (60-90 km) where H_2O_{melt} exceeds 10%, but $T < 900°C$.
4- Isotopic signatures show similar trends to those representing typical for subduction related areas (for example the Meissen massif, Saxothuringia).
5- Age of intrusion emplacement 331-341 Ma (Mikulski et al. 2013) is consistent with active subduction.

Despite the name "granitic intrusion", KZS is composed of petrologically different magmatic rocks:

1- From granite (minor) – granodiorite – tonalite – quartz diorite, diorite and monzonite according to the IUGS classification as well as lamprophyres and hypabyssal equivalents.
2- No muscovite was recorded in the whole data set.
3- Amphiboles and biotites are the main dark mineral and occur in almost all kinds of rocks.
4- REE abundances show low concentrations with a small enrichment of LREE and flat spiderdiagrams.
5- Hybridisation and mingling are important differentiation factors that created a huge variety of the investigated rocks.

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Metamorphic evolution of the Planetfjella group, Mosselhalvøya, northern Svalbard

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The Planetfjella group forms the uppermost tectonostratigraphic unit of the Lower Hecla Hoek of northern Ny Friesland and belongs to the Mosselhalvøya nappe (Witt-Nilsson et al. 1998). The Planetfjella group comprises semipelites, psammites, and subordinate marbles and megacryst plagioclase-rich schists (possibly felsic volcano-clastics). Notably, the base of the Mosselhalvøya thrust is underlined by numerous lenses of ultramafic rocks, which suggests that the contact between the Planetfjella group and the underlying Polhem group is a major discontinuity. Previous detrital zircon dating suggests that the Planetfjella metasediments have been deposited after 950 Ma, during the Neoproterozoic or Early Paleozoic (Larionov et al. 1998). A single Ar-Ar date on muscovite gave an intercept (not plateau) at c. 415 Ma (Gee, Page 1994).

Samples for this study have been collected in the vicinity of Mosselbukta, close to the basal thrust. They are represented by garnet-staurolite-mica schists. Peak metamorphic assemblage includes Grt+St+Bt+Ms+Q±Pl. Zircon, monazite, tourmaline, rutile and ilmenite occur in accessory amounts. The content of Alm and Prp in analysed garnets increases towards the rims, while the Grs and Sps decreases. Pressure-temperature (P-T) conditions have been estimated by use of conventional geothermobarometry as well as thermodynamic phase equilibrium modelling. Both methods yield consistent P-T results of c. 8-10 kbar at 580-600°C. Additionally, chemical Th-U-total Pb monazite dating has been performed. Monazite yields generally two groups of ages at c. 450 Ma and 410-400 Ma, respectively. Notably, the latter group is strongly yttrium-depleted and forms either rims on older cores or small homogenous crystals, whereas the former one is characterized by variable content of yttrium and forms cores of the crystals. This in turn leads to the preliminary conclusion that the age of the staurolite-grade amphibolite facies metamorphism has happened late during the Caledonian orogeny at c. 410-400 Ma, contemporaneously or rather just before the emplacement of the Mosselhalvøya nappe. Older monazite is treated as possibly detrital at the current state of the project.

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Diagenetic alteration of Permian glass-rich pyroclastic deposits from Włodowice, intra Sudetic basin, SW Poland

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A 5-km long and ~500m wide, isolated belt of pyroclastic deposits in the vicinity of Włodowice is a small fragment of the Permian volcanic succession in the intra Sudetic basin in the Sudetes, SW Poland. It is a distal, eastern equivalent of the Góry Suche Rhyolitic Tuffs, deposited after a caldera-forming, Plinian-type volcanic eruption approximately 300 Ma ago (Awdankiewicz 1999; Awdankiewicz, Kryza 2010). The alteration of the glass-rich tephra was studied by means of polarizing microscopy, XRD, and EMPA. Altogether, 40 samples were examined.

The pyroclastic deposits (massive, nonwelded ignimbrites) consist of abundant altered glass shards and pumice fragments, scarce feldspar and quartz crystals, angular lithic clasts, and fragments of accretionary lapilli. The lack of volcanic glass and, on the other hand, the uncompacted, well preserved texture of fine vesicular vitroclasts indicate early alteration and rapid cementation. Diagenetic phases that replaced volcanic glass are analcime, quartz, calcite, and, rarely, clay minerals. K-feldspar and albite are the remaining authigenic phases occurring in the rocks.

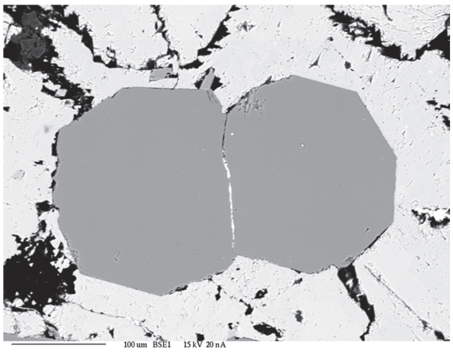

Fig. 1. BSE image of large euhedral crystals of authigenic analcime surrounded by calcite

Analcime shows a high Si/Al ratio equal 2.7 and typical of altered rhyolitic tuffs. It forms psudomorphs after glass fragments, but also conspicuous, large, cubo-octahedral crystals inside spherical concretions (Fig. 1). Analcime and albite, postdating earlier K-feldspar, provide evidence for a saline highly alkaline environment of alteration and a high Na^+/H^+ activity ratio. Since the thickness of the tephra deposits is moderate (40 m), a closed hydrologic system may be inferred.

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Heavy minerals in recent sediments of the Bóbr river, West Sudetes, SW Poland

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Recent sediments of the Bóbr river were sampled along the 100-km distance between Jelenia Góra and Szprotawa in order to recognize to what extent the lithological diversity of the Bóbr catchment area is reflected in the composition of its sediments, and to compare the results with the composition of ancient sediments. The Bóbr river and its tributaries drain several contrasting geological units of the West Sudetes: the intra Sudetic synclinorium composed primarily of Upper Palaeozoic and Cretaceous siliciclastic rocks, the East Karkonosze metamorphic unit, the Karkonosze granite pluton, the Izera metamorphic unit, the low-grade metamorphic Kaczawa unit, the North-Sudetic synclinorium with dominant Cretaceous sedimentary rocks, and the Tertiary-Quaternary cover of the fore Sudetic block. Altogether, 40 heavy-mineral concentrates were examined under a polarizing microscope, the opaque phases recognized in three samples by means of XRD, and the chemical compositions of garnet grains analyzed in one sample by microprobe.

The recent sediments of the Bóbr river are rich in heavy minerals, whose contents in the 0.125-0.25 mm fraction vary between 3 and 19wt%. The contents of heavy minerals decrease downstream indicating the increasing input from quartz-rich sediments of the Cretaceous, the Tertiary, and the Quaternary. Twenty-eight various heavy minerals were recognized; the most abundant and characteristic translucent heavy minerals of the Bóbr river sediments are garnet, andalusite, chlorite, and epidote-clinozoisite. Zircon, olivine, and chloritoid occur in higher concentrations in the vicinity of their source rocks – granite, basanite, mica schist. The remaining heavy minerals are clinopyroxene, orthopyroxene, anatase, actinolite, hornblende, apatite, topaz, biotite, tourmaline, staurolite, rutile, monazite, sphene, sillimanite, kyanite. Corundum and glaucophane are characteristic accessory phases. Opaque minerals dominate quantitatively over translucent heavy minerals and are composed of hematite, magnetite, and ilmenite.

Almost half of garnet grains shows chemical compositions typical of garnet of the Izera-Karkonosze massif. The chemical compositions of the remaining half are similar to the compositions of detrital garnet from Carboniferous, Permian, and Cretaceous sandstones. One fifth of the garnet population is composed of high-pyrope high-grossular almandine, recycled from sedimentary rocks of the intra Sudetic synclinorium, and ultimately from high-pressure metamorphic rocks.

Generally, the composition of heavy minerals in recent sediments of the Bóbr river is much more diverse than the composition of these minerals in any ancient sedimentary rocks of the Sudetes. Processes of diagenesis eliminated all but the most resistant heavy minerals. On the other hand, grains from ancient sedimentary rocks are incorporated into recent sediments demonstrating that resistant grains could be of multi-cycle origin.

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Petrologic features and quartz analyses of the Landsberg laccolith at different depths (Halle volcanic complex)

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Central European basin large igneous province (CEB-LIP) extends from the North Sea across northern Germany into Poland and was affected by widespread magmatic activity at the Carboniferous – Permian transition. Halle volcanic complex (HVC) is a small object (approximately 200 km^3) situated at the southern margin of the CEB-LIP and it is dominated by rhyolitic rocks, which were mainly emplaced as large laccoliths (Romer et al. 2001). The laccoliths differ in rock structure, being of two main types: fine grained and coarse grained. In this study we analyze petrographic and mineral-chemical features of the Landsberg laccolith to understand the processes leading to formation of large, but structurally different laccoliths.

The samples come from the borehole material and we chose two samples from the top and from the bottom of the laccolith (16 and 490 meters below the ground level) for the detailed petrological study. Differences in modal composition across the laccolith indicate that the Landsberg laccolith was composed from several magma pulses (Schab et al. this volume) and our aim is to characterize sources of the magmatic pulses by analyzing the composition and microstructures of major and accessory minerals.

The rhyolites are mostly composed of strongly altered phases: K-feldspar, plagioclase and biotite. The only unaltered phase is quartz and we used CL quartz characteristic to define differences between uppermost and lowermost sections of the laccolith. CL images of quartz grain show that the uppermost section contains two types of quartz, whereas the lowermost one only one. All grains are cracked and resorbed, but the timing of the resorption seem to be different between the laccolith sections. The general implication is that detailed CL studies characterize different pulses of magma forming laccolith units. The CL analyses should be combined with chemical characteristic of quartz grains in order to gain information on chemical nature of the pulses.

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Metamorphic processes recorded in chromitites from the Gogołów – Jordanów serpentinite massif

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The Gogołów-Jordanów serpentinite massif (GJSM) is a peridotitic member of the Variscan Ślęża ophiolite (SW Poland). Chromitite veinlets and pockets occur in the Czernica Hill within strongly serpentinized rocks of harzburgitic-dunitic protolith.

Chromitites consist of rounded chromite grains up to 3 cm and chlorite filling the interstices. The veins are embedded in serpentine-olivine-chlorite aggregates. Chromite grains are heterogeneous, they consist of chromite I $(Mg_{0.678}Fe^{2+}_{0.317}Mn_{0.003}Ni_{0.03})(Cr_{0.98}Al_{0.957}Fe^{3+}_{0.059}Ti_{0.002})O_4$ and chromite II $(Fe^{2+}_{0.493}Mg_{0.491}Mn_{0.008}Ni_{0.006})(Cr_{1.219}Al_{0.494}Fe^{3+}_{0.284}Ti_{0.002})O_4$. The grains are strongly fractured and chromite II occurs mainly in fractures and on grain margins. Marginal parts of grains display spongy texture. The chromite II could have variable composition, and it forms zones differing in Cr^{3+}, Al^{3+}, Mg^{2+}, Fe^{2+} and Fe^{3+} contents (see Fig. 1). No silicate or platinum group minerals inclusions occur within chromite grains.

The chromitites from the GJSM are similar in terms of composition and mode of occurrence to those from the Dobromirtsi massif and Golyamo Kamenyane, Rhodope Mountains, Bulgaria (Satsukawa et al. 2014). Absence of inclusions and changes in contents of Cr, Al, Mg and Fe in both chromite I and II are caused by recrystallization during metamorphism of the host serpentinites.

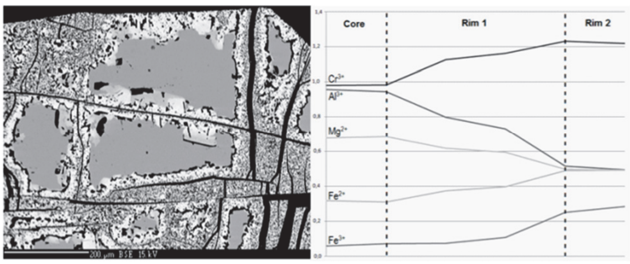

Fig. 1. Zonation of chromite grain from chromitites from the GJSM.

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Composition of water located in the coal waste dumps in Lower Silesia, Poland

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Stagnant water collected at the top and at the foot of the burning coal waste dumps indicates which elements can be quickly and easily washed out from the deposited wastes. This is the aim of our investigations. Six water samples were collected in the vicinity of four coal waste dumps in Lower Silesia. Two samples were collected from puddles filled mainly with rain water located at the top and 15 m below the top of the "6/4 Pole Piast" dump in Nowa Ruda. One sample comes from a pond located next to the dump in Nowa Ruda – Słupiec, were water can be composed of rain- and groundwater. The dumps are still thermally active although their extinction in the past. Other three water samples were collected at the foot of dumps in Przygórze and Wałbrzych ("Piast" mine), which were thermally active in the past, and where coal-wastes are overburned but cool at present.

Water pH is near neutral and ranges from 7.09 to 7.58 with the average of 7.26 and its conductivity is from 221 to 400 µS/cm with the exception for pond water collected at the foot of the Wałbrzych dump which conductivity equals 1019 µS/cm. Following components were analysed by atomic emission spectrometer with inductively coupled plasma (ICP-AES) and ion chromatography (IC): Al, B, Ba, Ca, Cd, Cr, Cu, Fe, K, Li, Mg, Mn, Na, P, Pb, Si, Sr, Zn, NH_4^+, HCO_3^-, F^-, Cl^-, NO_2^-, Br^-, SO_4^{2-} and NO_3^-.

There are no or negligible amounts of bromine, cadmium, chromium, copper, lead, zinc and manganese in investigated water samples. It means that harmful elements are neither washed out nor concentrated in stagnant water at the dumps. Water collected from ponds is enriched in Si, Na^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Cl^-, HCO_3^-, SO_4^{2-} and ammonium compounds. Aluminum, potassium and fluorine contents remains the same. There is no difference between water composition collected at the dumps of present or past thermal activity.

Water which stays longer, forming ponds at base of coal-waste dumps, concentrates anions represented by Cl^-, HCO_3^-, SO_4^{2-}, NO_2^-, and NO_3^-, and cations represented by Ca^{2+}, Mg^{2+}, and Na^+. This water may yield evaporate minerals. They can be similar to the set of efflorescences blooming at the fissure openings, composed of gypsum, mohrite -boussingaultite solid solution, halotrichite-group minerals, tschermigite, alum-(K), mascagnite and rozenite, identified at the burning dump in Nowa Ruda – Słupiec.

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Geochemical evolution of lithospheric mantle – Pilchowice xenoliths case study

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Intrasudetic fault is one of the major tectonic lines in northern part of the Bohemian Massif in Central Europe. It originated during the formation of Variscan orogen and marks the contact between two different crustal domains. The Cenozoic Pilchowice basanite is located at the fault. The basanite contains abundant, small (< 10 cm) peridotite xenoliths (clinopyroxene-bearing spinel harzburgites and spinel dunites).

Based on the Fo content in olivine, three groups of xenoliths were distinguished: group A (Fo 90-91.4%), group B (Fo 88.6-89.9%), group C (Fo 83.2-86.6%; one xenolith only). Olivine in all the groups is characterized by high NiO content (0.31-0.45wt%). Orthopyroxene has the composition of Al-Cr-Fe enstatite (mg# 0.86-0.92), whereas the clinopyroxene is Al-Ti-Cr diopside (mg# 0.80-0.95). Spinel is mainly chromite with wide variation of cr# (0.40-0.80). Clinopyroxene occurring in all the groups is LREE-enriched with convex downward pattern at the most incompatible elements. Only clinopyroxene from the xenolith M3314a shows constant LREE enrichment. All the clinopyroxenes show distinct Ti and Zr-Hf negative anomalies. Orthopyroxene is either LREE-depleted or shows U-shaped REE pattern.

Low Al_2O_3 content in orthopyroxene suggests that Pilchowice peridotites are restites after extensive (16-35%) partial melting (Faccini et al. 2013, *J. Petrol.*). As trace element composition of clinopyroxene shows features typical of the reaction with alkaline silicate melt (negative inflection at the most incompatible trace elements) and carbonatite (Ti, Zr, Hf anomalies), we suggest that group A and B xenoliths were metasomatized by the an agent being an immiscible mixture of carbonatite and silicate melt. Xenolith M3314a represents a part of mantle affected mostly by the carbonatitic metasomatism. Xenolith "C" is probably cumulate of mafic silicate melt similar to the host basanite.

Evolution of upper mantle recorded by Pilchowice xenoliths was first recognized in xenoliths from Krzeniów (Matusiak-Małek et al. 2014, *J. Petrol.*). However, significant variations recorded by xenoliths from other sites in Lower Silesia (e.g. Księginki, Puziewicz et al. 2011, *J. Petrol*; Wilcza Góra) suggests that this only one of the types of upper mantle underlying northern margin of the Bohemian Massif.

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High-Al chromitites from the Braszowice-Brzeźnica massif, the Central Sudetic ophiolite – geochemical features and origin

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The Braszowice-Brzeźnica massif (BBM), being a part of the Central Sudetic ophiolite, is a small ultramafic-mafic body localized southwardly to the Góry Sowie block. Its ultramafic rocks, mostly serpentinized, comprise harzburgites, lherzolites and dunites which correspond to the upper mantle tectonite unit as well as the transitional zone of the ophiolitic sequence. The later is also supported by the presence of the podiform chromitites (Delura 2012).

The BBM chromitites form small elongated bodies, hosted by olivine-tremolite rocks. The chromitites display three main textural varieties: massive, nodular and disseminated. The particular varieties show a wide spectrum of Cr-spinel to chlorite matrix ratios as well as the grain sizes. Rarely, analyzed samples are brecciated or display a centimeter-scale indistinct layering. The single Cr-spinel grains are usually deformed, with irregular cracks filled with chlorite.

The Cr-spinels are usually slightly altered that is evidenced by a narrow alteration rim composed of "ferrichromite" developed on the primary Cr-spinel. The primary Cr-spinel does not display any compositional changes inside individual grain. The chemical analyses, however, revealed two clearly distinct compositional groups of the Cr-spinel, that cannot be ascribed to the specific textural variety. They vary clearly in the Al, Cr, Fe, Mg and Ti content. The first group is extremely Al-rich (*cr#* from 38.38 to 42.10) whereas the second is Al-poorer (*cr#* from 43.63 to 45.97). The *mg#* varies from 80.71 to 87.31 in the first group and from 66.24 to 78.17 in the second one. The TiO_2 is usually up to 0.22wt% and up to 0.40wt%, respectively.

According to the high Al-content, the Braszowice-Brzeźnica chromitites can be treated as the high-Al ones (*cr#* <70). The chemical composition of primary Cr-spinel, the presence of two compositional types of chromitite as well as petrological observations indicate that the Braszowice-Brzeźnica chromitites precipitated within mantle rocks, very close to the Moho zone, inside the small magma conduits. The process took place at the early stages of the subduction due to the mixing of evolved and primitive basaltic melt inside the magma conduit (González-Jiménez et al. 2011).

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Secondary evaporite minerals from the historic Bochnia Salt Mine

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The Bochnia Salt Mine is situated in S Poland, at S margin of the Carpathian Foredeep, ca. 40 km E of Cracow and ca. 25 km E of its more famous 'sister' in Wieliczka. In both historic mines exploitation of the Badenian rock salt commenced in the thirteenth century and continued for over 700 years. The salt-bearing series (Wieliczka beds) consist of strongly deformed and disturbed, intercalating layers of anhydrite, marly clays, clays with anhydrite or dispersed halite crystals (so-called *zuber*), as well as rock salt. The entire complex of the 'folded Miocene' is still subjected to tectonic movements, in particular, to the pressure exerted by the Carpathians. Hence, primary layers are densely cut by a network of fissures, filled with crystalline halite (predominating), fibrous gypsum, occasionally also with calcite or iron (hydro)oxides.

The last, recent generation of secondary minerals is directly connected with 700 years of the salt mining. The most common halite, precipitating from NaCl saturated waters, may be observed on the top and walls of mining excavations, as well as on wooden casings or even old, abandoned miner's tools. Recent halite crystals occur in the form of stalactites, crusts, cauliflowers, skeletal crystals or fibrous aggregates, the latter known as 'St. Kinga's hair'. Euhedral, cubic crystals also form in small water pools in the mine galleries and chambers. Secondary anhydrite and gypsum are less common, the latter may occur in the marginal and top parts of the deposit, formed as a result of hydration of the primary anhydrite.

Detailed inspection of the stalactites, recently formed at the top of a gallery in the first, oldest level of the mine (Danielowiec, 70 m below the surface), close to the Sutoris shaft, revealed presence of another mineral phase. Its physical properties (whitish to colourless, relatively soft, bitter, prismatic and fibrous crystals), together with results of heating to 160°C, point to hydrous sodium sulphate – mirabilite ($Na_2SO_4 \cdot 10H_2O$), theoretically 44.1wt% Na_2SO_4 and 55.9wt% H_2O. Loss on weight of the analysed, somewhat humid samples amounted to 57.4wt%. Mirabilite was also recognized in the X-ray powder diffraction patterns (peaks at 5.50, 3.26, 3.21, 3.11 Å) and in the FTIR spectra. However, in the higher-angle part of the X-ray pattern the mirabilite peaks were weaker than expected, whereas some peaks characteristic for thenardite, anhydrous Na_2SO_4, appeared. Mirabilite turned out to be so vulnerable for heating, that dehydrated during the X-ray analysis.

Recent halite crystallizes from saturated salt waters, omnipresent in the mine. Mirabilite was detected in the vicinity of the Sutoris shafts, in very well ventilated part of the mine. It could crystallize from sodium sulphate solutions in high-humidity and relatively low, but stable temperature (13-15°C) mine environment.

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Organic compounds in water collected in burning coal-mining waste dumps in Lower Silesia, Poland

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Coal-mining waste dumps located in Lower Silesia have undergone the processes of self-heating and self-ignition triggering emission of organic compounds from the deposited wastes and their migration and deposition in surrounding water, soil and plants. The aim of the work was to find the relationship between coal waste fire and water composition.

Dissolved organic compounds present in water samples were isolated by solid phase extraction on C18 PolarPlus columns (BAKERBOND). Prior to separation water samples were filtrated. GC-MS of extracts involved an Agilent 7890A gas chromatograph with a DB-35 column coupled to a 5975C XL MDS mass spectrometer. Conditions were as follows: carrier gas He; temperature programs: 50°C (2 min) to 175°C at 10°C/min, to 225°C at 6°C/min and to 300^{oo}C (held 20 min) at 4°C/min. The spectrometer was operated in the electron ionisation (EI) mode (70 eV, full scan) and scanned from m/z 50-650. Compounds were identified by means of the mass spectra and by comparison with the standard retention times.

Organic compounds comprised fossil fuel biomarkers: *n*-alkanes (n-C_{13} to n-C_{31}, but mostly n-C_{16} to n-C_{29}), pristane (Pr), phytane (Ph), polycyclic aromatic hydrocarbons (PAHs), mostly with 3-4 rings and their alkyl derivatives. In Słupiec water (W3) sampled at a fire vent, a series of benzothiophene and benzenethiol alkyl derivatives were found. Phenol derivatives occurred in only low concentrations as well as very light compounds, common in pyrolysates, e.g. alkylnaphthalenes. Methylphenanthrene Index (MPI-1) is 0.94-1.55 indicating advanced maturity with calculated vitrinite reflectance Rc 0.93-1.33%. The Pr/Ph values correspond to those of humic coals. Heavier compounds, from fossil fuels (hopanes and steranes) were absent due to their low water solubility. Extracts are poor in compounds from recent plants (only a series of alkyl-methyl ketones). There was no evidence of mixing of fossil fuels n-alkanes with plant-wax compounds as testified by CPI values close to 1.25.

It can be assumed that two processes influenced composition of water extracts:

1) self-heating which produced phenols and light sulphur compounds such as benzenethiols and benzothiophenes due to cracking of organic matter macromolecule and gave a narrow range of n-alkanes and PAHs. By boiling temperatures of these compounds it can be estimated that temperatures of self-heating did not exceed 350-400^{o}C in the history of these coal waste dumps. However, temperatures were sufficiently high to remove light organic compounds completely, among them alkyl naphthalenes, i.e. were higher than 240°C when the process was at its peak activity.

2) water solubility of compounds now present is surface coal wastes. Many polar compounds, products of coal waste pyrolysis are well soluble when heavier aliphatics are nor so readily transported to water what led to absence of most typical biomarkers.

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Mineralogical study of Baroque stuccoes from the Church of the Assumption of the Virgin Mary (The Lubiąż Abbey, SW Poland)

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Mortars and plasters from historic buildings are a legacy of the building techniques. The study of such materials allows a better understanding of the civilization development. They need to be well known and preserved. Detailed studies of these materials allow to assess their characteristics and finally design compatible repair mortars. Thus, the mineralogical characterization of historic stuccoe mortars from the Church of the Assumption of the Virgin Mary (The Lubiąż Abbey) has been carried out by means of optical microscopy, X-ray diffractometry, simultaneous thermal analysis, scanning electron microscopy with energy dispersive X-ray spectroscopy and Fourier transform infrared spectroscopy.

Two areas were selected for sampling: decorated domes of St. Benedict chapel and St.Bernard chapel and the Monument of Eight Bishops, located behind the presbytery. Their decoration was created in the fall of the seventeenth century.

The stucco covering domes is composed of two-layers. Both layers differ in function, composition of their binder and grain size of a filler. The filler is dominated with quartz, whereas feldspars and lithic grains are less common in both layers. The lowermost layer serves as a priming coat, it has coarser grained filler, its heterogenous binder is composed of microcrystalline calcite, rich in lime-lumps. The outermost layer contains finer grained filler, the binder is mostly composed of calcium carbonate, with small amount of gypsum disseminated in the micritic mass. Such a mixture was used intentionally, since lime reduces setting time, whereas gypsum prevents from cracking of fresh mortar during drying. Additionally, the outermost layer contains brick dust, which serves as a coloring agent and as a latent hydraulic additive.

The stuccoes from the Monument of Eight Bishops are three layered. The two lowermost coats are composed of a siliceous aggregate (mostly quartz) and a binder consisting of calcite, but comprising noticeable amounts of gypsum. These two layers are covered with a lime coat, with a red or black vein decoration. The red marbleizing is a lime stucco, consisting of very fine grained quartz as a filler, colored with strongly dispersed hematite as a dye. The binder is microcrystalline calcite mass, rich in lime lumps. The black decoration contains gypsum as an additive, whereas soot plays a role of a dye.

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First data on organic compounds of "chocolate" flint from Holy Cross Mountains Mesozoic margin

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One of the important problems related to studies of the Stone Age is identification of the sources of siliceous rocks used by prehistoric communities. Several kinds of flint were widely used in prehistoric times is "chocolate flint" which occurs in the Holy Cross Mountains Mesozoic margin. At present we know about 30 exploitation points and many outcrops of this flint, forming the most numerous complex of prehistoric mining fields in Poland (Budziszewski 2008). Yet, though research of the occurrence and geological nature of this raw material is over ninety years old, there are still many gaps in our knowledge.

In archaeology to distinguish origin of this flint, a macroscopic identification is in common use (Schild 1971). This method is fallible.

Results of our investigations present the possibility of use of the organic compound (geochemical identification methods) as a solution to this problem.

The analyzed organic matter (OM) extracts from flints were dominated by the polar and aliphatic fraction over the aromatic one. The aliphatic fraction was predominated by *n*-alkenes over tri-, penthacyclictriterpenoids and steranes with diasterans.

In aromatic fraction fluoranthene or pyrene were the compounds with the highest relative concentration. Phenanthrene and its methyl derivatives concentration was relatively low like other polycyclic aromatic compounds (there were found chryzens, fluorantens and benzopyrens, trace amounts of naphtalen and its methyl derivatives. Trace amounts of compounds with sulphur (dibenzothiophene and derivatives) were also recognized.

Environmental interpretations based on different molecular parameters with a group of aliphatic hydrocarbons were ambiguous (e.g. Pr/Ph <1 indicates the anaerobic conditions of sedimentation, $CPI_{(25\text{-}31)}$ indicates once marine environment of OM deposition and once OM derived from terrestrial plants; e.g. Killops, Killops 2005; Peters at al. 2005). This is interesting if consider homogeneity of the analyzed flints and surrounding limstones.

The analysis of maturity parameters gives less divergences. Here, the data indicate immature organic matter in flints.

Further analysis will allow to resolve inconsistencies in the above interpretations and may give rise to specific identifiable conditions of formation of the dark flint within the light and homogeneous Upper Jurassic limestones.

The obtained preliminary data on chemical composition of OM could be used as a tool to recognize prehistoric points of exploitation of "chocolate" flint.

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Metabasites from the NW part of the Zábřeh unit – first insights into geochemical features

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The metamorphosed volcano-sedimentary succession of the Zábřeh unit which mantle the Orlica-Śnieżnik dome from the south, comprises the intercalations of amphibolite-facies metabasites in its north-western part. These rocks are fine- to medium-grained, sometimes porphyroblastic and strongly foliated or banded. They have chemical composition of basalts with variable degree of fractionation (mg# 45-68, Cr 80-400 ppm). The metabasites show chemical characteristics ranging from mildly alkaline to strongly tholeiitic (Nb/Y 0.04-0.71, Ti/V 30-58). The chondrite-normalized REE diagrams reveal gradual change of slope of the diagram profiles from negative to flat or slightly positive one and thus variable enrichment in LREE ($[La/Sm]_{CN}$ 0.80-2.15, $[La/Yb]_{CN}$ 1.08-6.14). Also a weak HREE fractionation is observed as evidenced by $[Tb/Yb]_{CN}$ values 1.16-1.81. On N-MORB normalized diagrams the profiles of the studied rocks mostly resemble that of E-MORB or are intermediate between E-MORB and OIB. The diagram lines also show variable yet distinct negative Nb anomaly. Several geochemical features (e.g. Nb/Y vs. Zr/Y, Th/Yb vs. Nb/Yb, Zr/Nb, Hf/Sm) indicate that magma was generated from a depleted asthenospheric mantle source at shallow levels (spinel ± garnet facies). Furthermore, the source was presumably heterogeneously modified by components derived from an active supra-subduction zone and also affected by within-plate–enrichment type.

A minor group of the metabasites found in the Zábřeh unit is conspicuous by its contrasting geochemical features, which include high mg# (69-75), elevated ratios of Zr/Nb (22-68), La/Nb (2.80-4.67) and Th/Nb (0.30-0.54), and low Ti content (TiO_2 0.20-0.61wt%, Ti/V 6-19) or CaO/Al_2O_3 ratio (0.64-0.70). Their REE patterns and N-MORB-normalized profiles are slightly concave and reveal low abundances of HREE (0.1-0.7 × N-MORB). The geochemical characteristics of these rocks is akin to either low-Ti island arc tholeiites or low-Ca boninites generated from strongly depleted, refractory mantle source.

The association of dominant tholeiites with subordinate low-Ti basalts or boninites suggests the tectonic setting of back-arc basin which might have been related to the Cadomian volcanic arc recognized in the south-eastern part of the Teplá–Barrandian domain.

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Extension related alkaline magmatism in the Outer Western Carpathians – mantle source and magma differentiation

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Teschenite association rocks (TAR) in the Outer Western Carpathians at the Czech-Polish border form a suite of melano- to mesocratic dykes and sills. Their emplacement is commonly related to Early Cretaceous rifting (Narębski 1990). In this study we focus on further constraints of TAR petrogenesis utilizing Sr, Nd and Hf isotopes. Additionally, we aim at constraining rates of magma differentiation applying high precision Lu-Hf apatite dating as well as U-Pb sphene geochronology.

Form of occurrence and composition of TAR is typical for alkaline basic and ultrabasic lamprophyres. Normative TAR composition show strong silica undersaturation. The observed trends in major oxides are consistent with those produced by progressive crystallisation of mineral assemblages found in TAR samples (clinopyroxenes, amphiboles, biotites, apatites, Fe-Ti-oxides, olivins, feldspars, and opaque minerals, altered glass and secondary analcime). A main difference between ultrabasic and basic varieties is greater abundance of feldspar in basic verities. TAR were subjected, to a different extent, to secondary alterations (e.g. serpentinization, chloritization, carbonatization, saussuritization, zeolitization).

Minor and trace elements composition show within-plate, alkaline basalts characteristics. All TAR samples show very narrow range of εNd – (CHUR) from +5.0 to +5.7, supported by εHf values – from +7.9 (CHUR) to +10.2. These suggest homogenous HIMU mantle source, confirmed also by trace elements ratios e.g. Zr/Nb (2.0-4.2), K/Nb (<179), and little crustal contamination. Variation in $^{87}Sr/^{86}Sr$ ratio reflects secondary alteration of rocks (confirmed by Th/La<0,14). Probably both partial melting and fractional crystallization processes influenced on the magma composition.

Previous geochronological studies results based on the $^{40}Ar/^{39}Ar$ kaersutite dating of lamprophyres from the Polish side suggest that more evolved lamprophyres were emplaced c. 2 Ma later than more primitive magma (Lucińska-Anczkiewicz 2000). However, age precision achieved in the latter study does not allow to fully resolve the age difference. We applied Lu-Hf dating of apatite, a mineral commonly present in nearly all sample types. Strong Lu/Hf fractionation by this mineral makes it suitable for high precision geochronology. Our preliminary 121.34±0.66 Ma age obtained for the mesocratic teschenite is in a very good agreement with previously published 122±1.5 Ma $^{40}Ar/^{39}Ar$ date. The achieved precision allows to fully resolve potential time difference in emplacement of evolved to various degree teschenites and to determine rates of magma differentiation.

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The origin and position in space and time of the Kłodzko-Złoty Stok intrusion – a reinterpretation

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The Kłodzko-Złoty Stok intrusion (KZSI) and surrounding geological units have been studied for a few decades by many researchers often having different points of view and aims (Bagiński et al. this volume). In most regional publications the KZSI is shown in cross-sections as a "balloon" intrusion with steep walls continuing to some unknown depth (probably to the mantle). Such a view does not fit the KZSI (if indeed to any granitoid intrusion), as the KZSI is not well mixed and is in fact strongly heterogeneous.

After a thorough survey of publications of the KZSI and regional geology we have concluded that it is a composite intrusion tilted from its original position toward the NW; the basis of the following evidence:

Using spatially-enabled data from Wierzchołowski (1976) we have observed that pegmatites are found on the NW side and ultramafic rocks, interpreted by us as cumulates, are situated only on the SE side of the intrusion.

The lit-par-lit character of intrusion observed in some S, SE localities of the intrusion and the layering orientated parallel to the elongation of the intrusion. The "cupola" structures identified by Wojciechowska (1975) and huge blocks of hornfelses (often called "roof pendants") are orientated as intrusion.

Bardo hornfelses have andalusite but no sillimanite, SE hornfelses and hornfelses of Snieżnik Massif have sillimanite (Bagiński 2002)

Sedimentary rocks with a marine fauna and inter-layered bentonites (same age as intrusion, Kryza et al. 2008) from the Paprotnia beds of the Bardo sedimentary unit, a few km away from intrusion to NW

Jawornickie granitoids with pressures calculated at 6-4 kbar and a very similar Ar-Ar age (Białek, 2001)

generally, metamorphic facies indicate higher pressures in the Śnieżnik massif to the SE of the KZSI (amphibolite → granulite → eclogite) where the maximum degree of metamorphism is of similar age to the KZSI intrusion (Chopin et al. 2012).

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The apophyses and "apophyses" of the Kłodzko-Złoty Stok intrusion – amphibole and 2 pyroxene thermobarometry

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"Apophysis – an irregular or sheet-like vein or dyke which originates from a larger igneous rock body" (Allaby, Allaby 2003). Based on our recent study not all dykes emplaced in the Bardzkie Mountains, NW of the Kłodzko-Złoty Stok intrusion (KZI) should be called apophyses, though commonly are.

Magmatic dyke-like bodies emplaced in the Bardzkie Mountains can be divided into 3 types based on mineral paragenesis and location (Tab. 1). A dyke outcropping by the Kłodzko-Laskówka road is an example of a dyke which should not be called an apophysis as the magma was not derived directly from KZI – on the basis of different mineralogies and calculated depths of Opx-Cpx (Putirka, 2008) or Ca-Amp (Ridolfi, Renzulli, 2013) crystallization. Nonetheless, similar zircon ages (Mikulski, Williams, 2013) of intrusion and our geochemical data show that the KZI and dyke are related by the same magma source. Other dykes could be apophyses as the P-T zone is similar or partly overlapping; still the term should be used cautiously as Bardo town "apophysis" could be simply a prolongation of the KZI which outcrops at the bottom of the valley. A dyke from the "Ostra Góra" peak is similar to the other dykes (with similar P-T) cutting KZI, and calling it an apophysis of KZI is also questionable.

Table 1. most important similarities and differences of P-T between Bardzkie Mts. dykes and KZI

Locality	Classification	Temperature (°C)	Pressure (kbar)
Few hundred m S of Bardo town	Bt-Hbl tonalite	≤850 (Amp)	~1.8(core); ~1(rim)
By the road Kłodzko–Laskówka	Opx-Cpx andesite	1030+/-80 (2Px)	4 ±1
"Ostra Góra" peak	Cpx-Bt-Hbl andesite	900-820; 850 (Amp)	2.6-2.1(core);≤1.8(rim)
KZI granitoids (for comparison)	Bt-Hbl granitoids	≤ 850 (Amp)	≤ 1.8

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The origin of lamprophyres and related dykes in the Kłodzko-Złoty Stok pluton – insights from isotope chemistry and thermobarometry

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The Kłodzko-Złoty Stok (KZS) Variscan granitoid intrusion (c. 341-330 Ma, Mikulski, Williams 2013) in the NE part of the Bohemian Massif (Bagiński et al, this volume) is cut by dykes of lamprophyre and related mafic-intermediate rocks. We have found correlations between whole-rock Nd-Sr isotopic compositions, calculated P-T crystallization conditions of amphibole phenocrysts and calculated H_2O content of melts from which the amphiboles crystallized (Tab. 1, Fig. 1; calculations according to Ridolfi, Renzulli 2012). Another group of andesitic-tonalitic dykes in country rocks of the pluton near Bardo is described in another abstract (Jokubauskas et al, this volume).

Based on the isotopic and thermobarochemometric data two end-member magma types which contributed to the formation of the KZS intrusion can be defined. These are: (1) Bardo two-pyroxene andesites and tonalites (2) Mąkolno spessartites. Mixing, mingling and further differentiation of such subduction and post-subduction derived magmas led to the formation of the heterogeneous KZS granitoids. The Chwalisław andesite-dacite and vogesite, based on field observations and calculated P-T values, could be younger than Mąkolno spessartite. All the dyke rocks cutting the KZS intrusion could have originated during uplift-induced melting of subduction-modified mantle.

Table 1. Isotopic compositions, amphibole chemistry and calculated water contents of the melts for KZS granitoids and dyke rocks.

	KZS granitoids	**Mąkolno spessartite**	**Chwalisław andesite-dacite**	**Chwalisław vogesite**
$\varepsilon Nd_{(335Ma)}$	-1.0 ÷ -3.6	-6.2	-3.4	-2.9
$^{87}Sr/^{86}Sr_{(335Ma)}$	0.7063-0.7072	0.7088	0.7073	0.7060
Amphibole core-rim zonation	no zonation	↑mg#, Fe^{3+}/Fe^{2+} ↓K,Na,Al,Ti	↓mg# ↓K,Na,Al,Ti	↓mg#, Fe^{3+}/Fe^{2+} ↓Na,Al
max H_2O_{melt}	6wt%	>12wt%	9wt%	7wt%

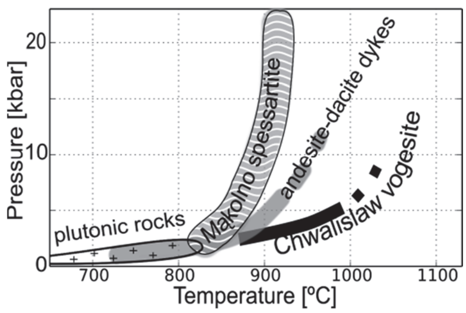

Fig. 1. Simplified P-T trends of amphibole crystallization from KZS granitoids and dyke rocks.

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Sorption properties of minerals from the iron arsenates group (scorodite, kaňkite, zýkaite, bukovsýite, jarosite, schwertmannite)

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Minerals from iron arsenates group (scorodite, kaňkite, zýkaite, bukovskýite) and also common with them the iron sulphates (jarosite, schwertmannite) have different sorption characteristics. Depending on the use of chemical reagents - methylene blue (an example of inert compound), azotetrazolate (an the example of an anion) or copper cations, tested adsorption characteristics can be very different. These results are preliminary stage of research for complete characterization of the sorption properties of minerals from the arsenates group occurring in the hypergenic zones, especially in the environment of acid mine drainage (AMD) in old mines of polymetallic deposits.

Freundlich and Langmuir adsorption isotherms seem to be relatively suitable to characterize the process at low concentrations equilibrium. Experiments have clearly demonstrated that the minerals used in the study can be characterized by a relatively large amount of oxonium ions in the exchange complex, which may determine significant anion adsorption In this study we have demonstrated a strong adsorption of azotetrazolate ions in contrast to very low adsorption of methylene blue. The results suggest a small specific surface area of the minerals, but because of the substantial protonate of the mineral surface, tested materials may have significant sorption of anions. This process is probably controlled by mechanism of the exchangeable sorption and physisorption. An important factor influencing the amount of sorption is the crystallographic system of studied minerals, and secondly their exact chemical composition. A perfect example are scorodite ($FeAsO_4 \cdot 2H_2O$) and kaňkite ($FeAsO_4 \cdot 3.5H_2O$) – two minerals, which have very similar chemical formula differing only 1.5 molecules of water per crystallochemical formula. But they have different crystallographic systems – scorodite is orthorhombic and kaňkite monoclinic. It results in the sorption of methylene blue by these two minerals – kaňkite did not adsorbe the methylene blue (within detection limit), and scorodite shows significant adsorption (compared to the other studied minerals). In addition, methylene blue was only adsorbed by two minerals – scorodite and bukovskýite, and the rest of the ivestigated minerals showed no sorption properties. In case of azotetrazolate, the sorption was present in all the minerals, but in a different stage. This suppurts our hypothesis of a strong protonation of minerals surface. Again we see the same difference in the sorption degree depending on the crystallographic system, otherwise a sulfate ion affinity is clearly matters – arsenate minerals with a sulfate ion show a much higher sorption than minerals without this ion.

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Fe-Ti-V magmatic mineralization of the Strzegomiany – Kunów zone, the Ślęża ophiolite (SW Poland)

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The Strzegomiany – Kunów zone is a continuous Fe-Ti mineralisation area located within subvolcanic and volcanic members of the Ślęża ophiolite. The host subvolcanic and volcanic units are a single well evolved co-magmatic suite with a high content of incompatible elements and flat to slightly depleted LREE patterns (Floyd et al. 2002). High content of Fe and Ti (up to >12% FeO and >2.5% TiO_2) connects the above described complex with modern oceanic ferrobasalts (Kryza et al. 2010, Natland 1980) Both host rocks and magmatic Fe-Ti-V mineralisation are altered by submarine hydrothermal processes and subsequent regional metamorphism (Floyd et al. 2002).

Ore mineralisation consists of predominantly disseminated xenomorphic grains of ilmenite and laths of ilmenite relicts after dissolved vanadiferous titanomagnetite (>1.5% V_2O_5). The variously altered relics of vanadiferous titanomagnetite are also present. The relics of magnetite usually occupy the inner parts of titanomagnetite grains, that is in places where it was shielded by more resistant ilmenite laths. Magnetite is commonly replaced by hematite (martite) and locally by lepidocrocite. Well preserved to unaltered, mostly xenomorphic titanomagnetite grains are rare and they are present only in the less altered samples. Ilmenite grains and laths are locally overgrown and replaced by titanite. Titanite is subsequently replaced by pseudomorphic anatase. Altered Fe-Ti oxides are locally intergrown with sulphides (pyrite and minor chalcopyrite).

The alteration processes that affected the magmatic Fe-Ti-V oxides of Strzegomiany - Kunów zone gives an insight into the evolution of mid-ocean ridge hydrothermal system and elemental fluxes resulting from it. The alteration of ilmenite is evidence of at least micrometer scale Ti (HFS group element) mobilisation and dilution during oceanic hydrothermal alteration.

The described dissolution of magnetite should be kept in mind as an important factor in terms of the economic value of a potential Fe-Ti-V deposit.

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Reconstruction of seasonal mammoth mobility from spatially – resolved trace elements and Sr isotopic records in molar enamel

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Elemental and isotopic composition of animal skeletal elements, especially dental tissue, can be used to investigate mammal mobility, diet and palaeoenvironment. In this study trace elements concentration and Sr isotopic ratios were measured in-situ by laser ablation (multi collector) inductively coupled plasma mass spectroscopy (LA MC ICP MS). This method offers possibility of obtaining high resolution data with minimal sample use and archieving tissue incremental features.

Our study material – single mammoth (*Mammuthus primigenius* Blum.) upper molar (M^3) – was excavated at the Upper Palaeolithic (Gravettian) site Kraków Spadzista located in southern Poland. This short-term camp was frequently revisited in period 20-24 000 yrs BP and was related to mammoth hunting (Wilczyński et al. 2012). The studied specimen was cut longitudinally and the exposed section of the dental plates was polished prior to analysis. Analysis was performed along continuous profile from occlusal surface (crown) towards the root in inner enamel layer (3D enamel) near enamel dentine junction (EDJ). Sr isotopic ratios and trace elements concentrations were measured along the same path to extract time-resolved signals from continuously mineralizing tooth constituent.

Low U and REE content indicate excellent preservation of the studied specimen. Trace elements concentrations profiles show that mineralization proceeds in the same pattern in proximal and distal side of the dental plate. Uniform Sr/Ca and Ba/Ca values are consistent with plant-based diet. The $^{87}Sr/^{86}Sr$ profiles along a molar plate show considerable regular variation with the values ranging between 0.7108 and 0.7127. Observed Sr isotope peaks are spaced c. 5 (basal area) to c. 10 mm (occlusal and central part of the plate). Estimated time of studied dental plate formation (based on values obtained by Dirks et al. 2012 for *Mammuthus columbi*) suggests that this variation can be related to seasonal life history changes. Obtained $^{87}Sr/^{86}Sr$ values do not correlate with the local Kraków Spadzista biological characteristic obtained from teeth of small rodents characterized by less radiogenic isotopic ratios. Trace element concentrations and Sr isotopic ratios can be used to track sequential enamel mineralization as well-corresponding peaks were found in following profiles.

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Chemical and petrological heterogeneity of lithospheric mantle beneath N Patagonia (Argentina) evidenced by Cerro Chenque xenoliths

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Back arc mantle xenolith bearing Pliocene – Quaternary alkali basalts occur along Patagonia, in Argentina in Rio Negro province (Bjerg et al. 2005, *J. S. Am. Earth.Sci.*). The Cerro Chenque in Rio Negro province trachybasaltic lavas carry small (up to 10 cm in diameter) xenoliths of anhydrous spinel bearing lherzolites, dunites, wehrlites, websterites, as well clino- and orthopyroxenites and norites. Chemical composition of the studied rocks is given in Table 1.

Table.1. Composition of peridotite-forming phases from Cerro Chenque xenoliths.

rock	dunite	lherzolites	wehrlite	websterite	clinopyroxenite	norite
Ol Fo [%]	~90.5	~91-92	93-93.5	-	-	-
Opx mg#	0.91	0.91-0.93	0.94	0.91-0.92	0.90-.092	0.71-0.77
Cpx mg#	~0.92	0.92-0.95	0.94-0.95	0.93-0.95	0.91-0.93	0.72-0.77
Spl cr#	0.60-0.62	0.60-0.70	0.65	0.69-0.81	0.82-0.84	Up to 0.08
Pl An [%]	-	-	-	-	-	71-81

Primitive mantle-normalized rare earths elements (REE) patterns of clinopyroxene vary from xenolith to xenolith, but three main types may be distinguished: (1) U-shaped (lherzolites, pyroxenites; La 0.5-40 × primitive mantle value (PM), Lu 0.5-30×PM), (2) Light REE (LREE) enriched (dunites; La 3-20, Lu 2-7×PM), and (3) LREE enriched concave at Nd; La=7×PM, Lu=7×PM). The REE patterns of orthopyroxene either (1) mimic the U-shaped pattern of coexisting clinopyroxene or (2) show constant depletion from HREE to LREE in xenoliths where clinopyroxene is LREE enriched

High cr# of spinel occurring in the lithospheric-mantle-derived Cerro Chenque xenoliths suggests intensive melting. This is also indicated by depleted REE patterns of orthopyroxene and the low Yb_N, La_N of clinopyroxene. High mg# in clinopyroxene is rather a result of equilibration in low temperatures typical of sub-arc environments (Brey, Köhler, 1989, *J. Petrol*.). The LREE enriched composition of clinopyroxene indicates metasomatic enrichment. The high $(La/Yb)_N$ and Ti/Eu ratios suggest enrichment by anhydrous silicate melt (Coltorti et al. 1999, *J. Petrol.*). Chemical characteristic of clinopyroxenites, wehrlite and websterite suggests their provenance from mantle depths, while norite could have its origin in the MOHO.

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Chemical composition of glasses and associating mineral species in various pyrometamorphic rocks from coal-mining dumps of the Lower Silesia

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Various types of pyrometamorphic rocks, mainly buchites, metapelites and minor parabasalts (*scoria*), occurring in the surface zone of burnt coal-mining dumps in Przygórze, Nowa Ruda ("6/4 Pole Piast") and Ludwikowice Kłodzkie, were microprobed. Although some of the rocks resemble smelter materials (so-called slags or sinter), they are often intercalated with macroscopically unchanged coal shales and porcellanites (i.e., white metapelites), that are common in coal-mining dumps of other basins (e.g., in the Upper Silesian coal basin). The more, at Ludwikowice, a dark elongated zone surrounded by red zone was found. Such dark zones are typical of the burning/burnt dumps and are known as "black blocks". In the black block an assemblage typical of the reductive-conditions metapelites were found, with celsian as one of its constituents, of the following formula: $(Ba_{0.97}K_{0.03}Mg_{0.03}Na_{0.01})_{\Sigma 1.04}(Al_{1.81}Fe_{0.06})_{\Sigma 1.87}Si_{2.10}O_{8.03}$. The "black block" glass contains [wt.%]: 50.5-67.68 (mean 53.04) SiO_2, 23.47-44.48 (mean 40.05) Al_2O_3, 0.28-0.70 (mean 0.49) FeO, 0-1.18 (mean 0.43) MgO, 0.07-2.03 (mean 0.54) CaO, 2.79-4.55 (mean 3.64) K_2O, 0-0.48 (mean 0.24) Na_2O, with no Mn and, usually, Ti, Ba, P and S. Black buchite-like glassy vesicular rock within the "black block" contains minor, often two-phase, iron silicide or sulphide globules. Analyses correspond to $(Fe_{5.92}Ni_{0.06}Co_{0.02}Cu_{0.01})_{\Sigma 6.01}(Si_{0.93}P_{0.04})_{\Sigma 0.97}$($Fe_6Si$), pyrrhotite or troilite ($Fe_{1.02}S_{0.98}$) and a Fe_7S_6 phase. Dark, greenish buchite from Nowa Ruda contains suessite or gupeiite-schreibersite solid solution, stoichiometric and non-stoichiometric, $(Fe_{2.92}Ni_{0.05}Co_{0.02}Cr_{0.01})_{\Sigma 3.00}(Si_{0.75}P_{0.25})_{\Sigma 1.00}$ (n=6), and $(Fe_{2.96}Ni_{0.05}Co_{0.02}Cr_{0.01}Cu_{0.01})_{\Sigma 3.05}(Si_{0.85}P_{0.12})_{\Sigma 0.97}$ (n=14), respectively. This solid solution associates with native iron, $Fe_{0.97}Si_{0.01}Cu_{0.01}$ (n=17). Two phosphide analyses correspond to $Fe_7(P,Si)_3$ and $Fe_5(P,Si)_3$ phases. Composition of an interstitial pyrite-surrounded carbonate within the buchite is given as $(Fe_{0.78}Mg_{0.11}Ca_{0.11})_{\Sigma 1.00}(CO_3)_{1.02}$. Composition of glass of grayish-green buchite covering an undifferentiated gray metapelite (UGM), both constituting a breccia, was tracked from its contact with UGM, through a central zone up to its further, Fe-rich zone, and is, respectively (in wt%, mean): 46.46, 26.64 and 55.86 SiO_2; 0.83, 1.50 and 1.30 TiO_2; 46.35, 41.09 and 19.09 Al_2O_3; 3.26, 3.7 and 17.00 Fe_2O_3; 0.24, 0.00 and 0.25 Cr_2O_3; 2.25, 1.65 and 3.27 MgO; 0.06, 0.16 and 1.21 CaO; 0.64, 1.74 and 3.02 K_2O; 0.38, 0.36 and 0.20 Na_2O. V and Zn are found occasionally. The corresponding values for the UGM are: 50.11, 0.97, 38.75, 3.77, 0.25, 2.17, 0.14, 0.67 and 0.37, occasionally with Co and Ni. Spinel at the buchite/UGM border is $Hc_{55}Sp_{42}$ with mean 0.5% chromite and minor other members, thus its chemistry being $(Al_{1.95}Cr_{0.02}Fe^{3+}_{0.01}Ti_{0.01}V_{0.01})_{\Sigma 2.01}(Fe^{2+}_{0.57}Mg_{0.43})_{\Sigma 1.00}O_{4.01}$

(n=5). It slightly contrasts with hercynite from two parabasalt inclusions from the same breccia, 1 – $(Al_{1.74}Fe^{3+}_{0.22}Cr_{0.02}Ti_{0.01}Si_{0.01})_{\Sigma 2.00}(Fe^{2+}_{0.80}Mg_{0.19})_{\Sigma 0.99}O_{4.01}$, i.e. $Hc_{70}Sp_{16}Mag_{9}Mfr_{2}Chr_{1}$, and 2 – $(Al_{1.71}Fe^{3+}_{0.26}Cr_{0.02}Si_{0.01})_{\Sigma 2.00}(Fe^{2+}_{0.60}Mg_{0.37}Mn_{0.01})_{\Sigma 0.99}O_{4.01}$, i.e. $Hc_{58}Sp_{32}Mag_{5}Mfr_{3}Chr_{1}Gal_{1}$. Parabasalt hematite is $(Fe_{1.76}Al_{0.18}Mg_{0.03}Ti_{0.01}Si_{0.01})_{\Sigma 2.99}O_{3.99}$.

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U-Pb clock and $\delta^{18}O$ mantle tracer - identifying zircon isotope composition on SHRIMPIIe/MC ion microprobe – an example from Mława and Ełk alkaline intrusions

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Introduction

Nonmetamict zircon can preserve the original U, Th, Pb and oxygen isotope composition of melt from which it precipitated. Enhanced version of SHRIMP IIe/MC ion microprobe equipped with two replaceable sources of the primary ions (O^{2-} vs Cs^{+}) permit measurement of U/Pb and oxygen isotopic ratios at the microscale in the same mineral zones. The aim of this contribution is to report new aspects the timing and petrogenesis of the two prominent alkaline intrusions of Mława and Ełk syenite, known from drilling survey of unexposed basement in NE Poland.

Isotopic single grain investigation

The several alkaline and mafic bodies of variable dimensions (up to 400 km^2) are distributed within a consolidated basement of NE Poland in limited area near the Teisseyre-Tornquist zone, but most extensive are the Mława and Ełk intrusions. These rocks are generally undeformed, show no sign of metamorphism, and display intrusive links to the Late Paleoproterozoic arc related supracrustal rocks of the Mazowsze domain. The U-Th-Pb investigation were made on the SHRIMP II of the RSES, ANU in Canberra but the oxygen isotope analyses were conducted on the new SHRIMP IIe/MC of PGI-NRI in Warsaw in the same zircon samples analyzed for U-Pb datings.

CL images of the zircon grains from two samples of Mława syenite show typical magmatic simple structure with sharp oscillatory or rhythmically banded zoning. The $^{206}Pb/^{238}U$ age values of 338.1 ± 3.3 and 344.2 ± 2.4 Ma are consistent with crystallisation age previously measured on zircon from alkaline rocks in this area, including Ełk syenite emplacement time at 348 ± 8 Ma and indicate a peak of alkaline activity at about 345 ± 4 Ma.

The zircon from Mława samples has oxygen isotope $\delta^{18}O_{zrn}$ ratio between 5.22‰ ± 0.09‰ and 7.63‰ ± 0.08‰. In contrast, the average oxygen isotope composition of zircon from Elk foid syenite is lighter 2.56‰, with number values in range 3.15-5.17‰. Frequency of typical mantle-like zircon $\delta^{18}O$ values (i.e. +5.3‰ to +5.6‰) in Early Carboniferous (Visean) syenite bodies suggests a derivation of the melt from mantle source, with limited role of hydrothermally or metasomaticaly-altered material in the alkaline melt. The parent magma of Mława syenite should arise from the interaction with higher $\delta^{18}O$ materials by source mixing or by slightly crustal contamination. Besides a low-$\delta^{18}O$ zircon values detected in Ełk indicate a rift zones interacted with meteoric waters at high-temperature.

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Mantle xenoliths from the Feldstein basalt (Thuringia, Germany)

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The Feldstein alkali basalt (ca. 16.3 Ma) occurs nearby Themar, 60 km south-west of Erfurt (Thuringia, Germany). The Feldstein basalt belongs to the Heldburger Gangschar subset of the Central European volcanic province (Abratis et al. 2007, *Chem. Erde*) and contains abundant peridotite xenoliths, commonly 4-6 cm in size, some up to 12 cm.

The Feldstein xenoliths consist of olivine, orthopyroxene, clinopyroxene and spinel. Rare earth elements (REE) patterns of clinopyroxene classify the Feldstein xenoliths into two groups: ***group A*** – containing clinopyroxene with depleted light REE (LREE) abundances (2 xenoliths); ***group B*** – containing clinopyroxene with enriched LREE abundances (10 xenoliths). Xenoliths from the both groups are characterized by protogranular texture with typical grain size of 2-3 mm. Chemical compositions of olivine (88.95-91.36 %Fo) and orthopyroxene (mg# 0.90-0.93) in the two groups are similar. The group A clinopyroxene is characterized by significantly higher mg# (0.93-0.95) than that of group B (mg# 0.90-0.93). The ortho- and clinopyroxene occurring in group A xenoliths are not in chemical equilibrium. Those occurring in the group B yield equilibration temperatures (Brey, Köhler 1990, J. Petrol.) from 850°C to 1010°C. Samples with the highest temperature have the lowest mg# in silicates.

The primitive mantle normalized (McDonough, Sun 1995, *Chem. Geol.*) clinopyroxene REE patterns of ***group A*** indicate that this is a residue after significant degrees of partial melting. One of the xenoliths seems not to be affected by metasomatic overprint, whereas the other one contains clinopyroxene which is Al- and REE-enriched and supposedly was slightly modified by metasomatism. However, partial melting does not fully explain the very high mg# in clinopyroxene. The spinel peridotites from the ***group B*** have been variably affected by percolating CO_2-rich silicate or unmixed silicate-carbonatite melts. Variable REE and trace element patterns as well as differences in mineral chemistry show that the kinds of metasomatism were different depending on the sample.

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Clinopyroxene megacrysts from alkaline lavas from the Polish part of Central European volcanic province

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Megacrysts of clinopyroxene, usually few centimetres in size, occur in SW Poland in Cenozoic alkaline lavas of the Central European volcanic province (Księginki, Lutynia, Ostrzyca Proboszczowicka). The megacrysts from Księginki have the composition of augite and diopside (mg# 0.79-0.86). They are hosted by 27-32 Ma nephelinite which contains abundant xenoliths of mantle peridotites and pyroxenites. The Księginki megacrysts probably come from crystal mushes formed during the passage of host lava through the lithospheric mantle (Puziewicz et al. 2011). The Lutynia megacrysts occur in the 5.5-3.8 Ma basanite containing also mantle peridotite xenoliths. The megacrysts have the broadly varying composition of augite and diopside (mg# 0.77-0.97, Na ≤ 0.12 atoms pfu, Ca 0.65-090 atoms pfu).

The Miocene basanite from the Ostrzyca Proboszczowicka near Złotoryja contains clinopyroxene megacrysts but no mantle xenoliths. The Ostrzyca megacrysts have the composition of Fe-rich diopside (mg# 0.61-0.71), contain significant sodium (Na up to 0.12 atoms pfu) and are calcium rich (0.89-0.92 atoms of Ca pfu). The basanite itself has mg# 0.65. The megacrysts contain millimetric intergrowths of euhedral apatite. The clinopyroxene is enriched in REE relative to primitive mantle, and the REE patterns are strongly enriched in LREE relative to HREE. The TE PM normalized patterns are characterized by slight negative Sr and Y anomalies and strong Pb anomaly, slight negative Ti and strong positive Ta, Zr and Hf anomalies. This is different from the Księginki and Lutynia clinopyroxene patterns, which have positive Ta and negative Zr, Hf and no Ti one. The megacrysts from Lutynia are chemically similar to the "type 2" of megacrysts described by Woodland, Jugo (2007) from basanites of Mont Briançon and Marais de Limagne in French Massif Central. They come from coarse-grained cumulate which formed at mid-crustal levels from the evolved alkaline melt, which composition was different from that of their host.

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Influence of microbial activity on biotransformation of arsenopyrite under aerobic conditions

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The Radzimowice deposit is located in Sudetes, in south-east part of Kaczawskie Mountains. It is a polimetalic deposit, which contains mainly ores of arsenic and gold. The mining activity ended there in 1957. In an abandoned adit microbiological mats, which overgrew whole walls, were obsereved. Microbial activity marks its presence by occurrence of sec
ondary minerals such as pitticite, jarosite, schwertmannite, zykaite, scorodite, which can be products of arsenopyrite biotransformation.

The purpose of research was to state the influence of microbial activity on the oxidation of arsenopyrite and changes of the enviroment conditions caused by microorganism. Hence, it was attemped to determine which of secondary minerals were the products of the biotransformation process. Laboratory experiment was based on cultivation of bacteria, gathered at the Radzimowice adit, under aerobic conditions. Culture media used in experiment contain arsenopyrite; the experiments were conducted under different pH conditions. Growth of bacteria was controlled by measuring concentration of sulphate and iron (II) ions.

Results of the experiment were different from the observations from Radzimowice adit. Biotransformation of arsenopyrite was observed in which microbial activity had dominant influence. This activity caused rapid expulsion of sulphate and iron (II) ions to the solution. Secondary minerals, which were products of microbial process of oxidation, crystallized according to sequence: pitticite – scorodite – tooleite. Zonation in a distribution of secondary minerals formed from arsenopyrite was also observed. Changes of the secondary minerals are preconditioned by fluctuations of pH and chemical composition of solution, caused by microbial activity. The main difference between the natural environment and laboratory experiment is precipitation of tooleite instead of schwertmannite, which might have been caused by influence of accumulation of ions on solid phase in closed system.

There is possibility of applying biotransformation in hydrometallurgy – to process metal ore, and in environmental protection due to retention of toxic elements and compounds in precipitated secondary minerals.

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Phase equilibrium modelling of blueschists from the Lasocki Ridge, Bohemian Massif

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The presence of blueschists in the Lasocki Ridge has been known for decades. However, the significance of these rocks has increased since then because the blueschist occurrences mark out tectonic sutures and help to reveal a complex structure of the Variscan belt and timing of its accretion.

The studied rocks from the Kopina Mt. consist mainly of garnet, glaucophane, clinozoisite-epidote, chlorite-I, titanite, hematite and quartz. The original high-pressure assemblage is overprinted by later, lower-pressure assemblage, which comprises mostly Ca-amphiboles, chlorite-II, albite and K-feldspar. The latter occurs in polymineral inclusions in other phases together with albite and chlorite that are interpreted as phengite breakdown products. Garnet forms euhedral to subhedral poikiloblasts. Inclusions usually form snowball structures in the oval centre of crystals, whereas rims are inclusion-free and have euhedral shapes in thin sections. Garnets show chemical compositional variation from $Alm_{54}Prp_{3}Grs_{30}Sps_{13}$ in the cores to $Alm_{66}Prp_{4}Grs_{29}Sps_{1}$ in the rims. The almandine zoning is bowl-shaped, whereas spessartine profiles show bell-shaped trends. The grossular and pyrope contents are generally constant throughout the grain. Rather gradual changes in the chemical zoning suggest a progressive, one-step garnet growth pattern. Glaucophane, although commonly well preserved, in some cases disintegrates to the albite-chlorite assemblage. Sometimes, it is rimmed by the secondary Ca-amphibole.

The pressure-temperature (P-T) conditions were estimated using the phase equilibrium modelling in the NCKFMMnASHTO system using the Perple_X software. The compositional isopleths cross cut in the stability field of Grt+Gln+Ep+Chl +Pheng+Ttn+Hem+Q. The P-T estimations indicate that the peak conditions could occur at c. 14-17 kbar and 470-500°C, which corresponds to quite a low geothermal gradient in the range of 8-10°C/km.

The result obtained is practically identical to that published by Faryad and Kachlík (2013) for samples from the southern and eastern cover of the Karkonosze granite. Our data provide further support for the presence of an exhumed tectonic suture in the metamorphic envelope of the Karkonosze granite. The P-T conditions estimated lie on a low temperature geotherm that is typical for a relatively cool subduction of the oceanic crust. Therefore, the origin of the studied rocks dates back to the time preceding accretion of the Sudetes and defines one of the key tectonic boundaries in the Bohemian Massif.

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Petrologic and geochemical features of mafic xenolithic cumulates from Polish part of Central European volcanic province – preliminary results

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Xenoliths of Earth's upper mantle from Polish part of Central European volcanic province have been studied since '80 of 20th century. However, mafic xenoliths coexisting with the peridotitic ones have been scarcely examined. Gabbroic and pyroxenitic xenoliths have been described from Księginiki nephelinite (Puziewicz et al. 2011, *J. Petrol*), Krzeniów basanite (Bakun-Czubarow and Białowolska, 2003, *Miner. Soc. Poland-Spec. Pap.* and references therein) and Winna Góra (Matusiak, 2006, *Miner. Polon.-Spec. Pap.*). In this study we present new results on mafic xenolithic rocks from the Wilcza Góra, Winna Góra, Góra Świątek, Mnisia Górka and Grodziec volcanic rocks in the Złotoryja-Jawor volcanic complex.

Mafic xenoliths have composition of clinopyroxenite, websterite and scarcely gabbro or olivine-bearing gabbro. They are typically smaller than peridotitc ones, blackish and show clear cumulative, coarse grained (clinopyroxene 2-8 mm, olivine 0.5-5.0 mm) texture. Beside the rock-forming phases, the mafic xenoliths may contain spinel, sulfides and amphibole. Usually clinopyroxene grains occurring in gabbros are strongly corroded or disintegrated, while other phases are well-preserved. The Contact xenolith-host volcanic rock is usually sharp with subhedral crystals of clinopyroxene growing at the xenolith surface.

The mineral grains are usually zoned and chemical equilibrium between phases are rare case. Clinopyroxene has the composition of Al (±Ti, ±Cr) diopside or augite. Its mg# is variable: 0.68-0.81 in gabbros, 0.81-0.87 in websterites and 0.72-0.91 in clinopyroxenites. Clinopyroxene is always enriched in LREE, the patterns of clinopyroxene forming some of the gabbros and plagioclase-bearing clinopyroxenites show negative Eu-anomaly. Orthopyroxene occurring in websterites has composition of Al-enstatite with mg# 0.75-0.80. It is strongly LREE-depleted. Olivine occurring in websterites is more magnesium rich than that from gabbro (Fo_{70-80} vs. Fo_{64-70}). Anorthite content in plagioclase forming gabbro varies from 0 to 56%, but enrichment in Na may be due to strong alteration of plagioclase.

Modelling based on the trace element composition of clinopyroxene suggests that all the studied xenoliths are precipitates from alkaline silicate magmas, usually similar to the host volcanic-rock. Relatively high content of iron in silicates suggests crystallization at crustal depths or at crust-mantle boundary. Origin of xenoliths from Złotoryja-Jawor volcanic complex is different than that of clinopyroxene-rich mafic rocks from Lutynia basanite

(Lądek Zdrój volcanic complex) which were interpreted as solidified CO_2-rich melt, causing modal metasomatism of upper mantle (Ackerman et al. 2012, *J. Geosci.*).

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Multi stage peridotite-melt reaction evidenced by xenolith suite from Wilcza Góra basanite (SW Poland)

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Hydrous phases in Earth's lithospheric mantle are manifestation of modal metasomatism. Mantle xenoliths occurring in northern margin of the Bohemian Massif usually contain no hydrous phases. The latter, if present, are typically small and scarce crystals of pargasitic amphibole (e.g. Nowak et al. 2010, _Geophys. Res. Abstr._; Matusiak-Małek et al. 2010, _Lithos_). However, the xenoliths from Wilcza Góra basanite are exceptional in this context. They have composition of dunite, harzburgite and wehrlite; pyroxenitic xenoliths of cumulative texture occur as well. Pargasitic amphibole occurs in all the types of these xenoliths. Amphibole forms: 1) large (up to 1 cm) subhedral crystals, 2) exsolution lamellae in pyroxenes, and 3) cores of secondary clinopyroxenes in integranular aggregates. Composition of amphibole varies in wide ranges between xenoliths (e.g. mg# 0.73-0.95). The mineral is in equilibrium with coexisting clinopyroxene (mg# 0.79-0.93) in terms of major and trace elements. Composition of spinel is strongly variable (mg# 0.44-0.68; cr# 0.26-0.63); spinel occurring in group B and C is enriched in TiO_2 0.20-1.69wt%.

Variations in composition of olivine (Fo 77-92) and orthopyroxene (mg# 0.85-0.92) suggest continuous reaction of primary depleted peridotite with fractionating mafic silicate melt which led to enrichment of the peridotite-phases in Fe (Matusiak-Małek et al. 2014, _J. Petrol._). As clinopyroxene and spinel records no melting (lack of cr#-mg# negative correlation), they cannot be a primary phase and must have been introduced into peridotite by metasomatic reaction and thus record modal "stealth" metasomatism (O'Reilly Griffin 2013, _Springer-Verlag_). Trace element composition of clinopyroxene and amphibole and their equilibrium suggest their crystallization from the fractionating mafic silicate melt, possibly the same which caused enrichment of peridotite-phases in Fe. The melt must have been 1) hydrous (crystallization of amphibole) and 2) relatively "cold" (crystallization of clinopyroxene; Baltitude and Green 1971, _J. Petrol._). Composition of the final product of the melt fractionation was very similar to the host Wilcza Góra basanite. Modelled composition of Wilcza Góra amphibole and clinopyroxene in equilibrium with alkaline silicate melt suggests that the two minerals occurring in part of the peridotites and in cumulative xenoliths are simple precipitates from host basanite.

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The metallogenic evolution of the Kłodzko-Złoty Stok intrusion in the light of geochemical and isotopic geochronologic data

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The changeable ways of magma fractionation, degree of compositional evolution and further tectonic processes may have produced different types of ore mineralization that reflected transition from magmatic to hydrothermal environments. Emplacement of the Kłodzko-Złoty Stok intrusion (KZSI) took place in Early Carboniferous Middle Mississippian (Viséan) during early-plate collisional setting of the thickened Variscan crust. The main zircon population from the KZSI magmatic rocks represents the various degrees of mixing or mingling of the felsic and mafic magmas in the hypabyssal magmatic events of the different composition granitoids and lamprophyre (spessartite) crystallization from ca. 343 to 329 Ma (Mikulski et al. 2013; Mikulski, Williams 2014). The KZS massif consists mainly of metaluminous and minor weakly peraluminous, highly potassic I-type granitoids containing abundant mafic enclaves. Its metallogenic evolution indicates that granitic magmas mixed with more basic components derived from the whole area of the KZSI yielded during post-magmatic activities variable types of ore mineralization (skarns, breccias, dissemination, replacements and veins) with enrichments in gold of economic and indicatives values. Ore mineralization depends also on the composition of the country rocks and different distance to contact with granitoids. Around the core of KZSI the following zones of ore mineralization may be distinguished: W, Ti, As, Fe → Pb, Cu, Zn and outward from the core → Fe, Au, Bi, Ag → Au, As, Sb → Ca. In the area of the Ptasznik prospect, inclusively with metasomatic-type of scheelite-titanite mineralization, granitoids have a high trace element (REE) contents and are enriched in incompatible elements, indicating advanced granitoids fractionation (REE enrichment. This W-Ti mineralization is younger (ca. 331 Ma; U-Pb zircon determination) if compare with polymetallic auriferous ore mineralization of metasomatic type found in intimate contact with the Graniec-Bardo and Myszak apophyses that represent the earliest stage of the pluton emplacement with rocks originating from hybrid magmas (ca. 343 Ma).

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Mineralogic and textural relationships among Pb-Sb sulphosalts from the Dębowina mine, Bardzkie Mountains, Sudetes

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The Dębowina mine (abandoned „Reiche Silber Glück" adit) is the only known place in Poland, where the antimony ores were mined (Dziekoński 1972; Mączka, Stysz 2008). The adit was excavated in the Upper Devonian through Lower Carboniferous highly pyritized greywackes of the Bardo-Młynów unit at the Bardzkie Mts. Genesis of the mineralization is related to hydrothermal processes within greywackes of the Bardo-Młynów unit at their contact with the Kłodzko-Złoty Stok granitoid intrusion (KZSGI). The hydrothermal processes are probably related to crystallization of the granitic dykes of the KZSGI that intruded the highly pyritized graywackes of Bardo-Młynów unit. The ore vein system represent medium to low temperature zone (below 300-250^{o}C), distal in relation to the high temperature As-Au ore zone known from the Złoty Stok area.

The antimony ores occur in the form of veins from 0.5 to 8 cm in thick (Nejbert et al. 2013). Three vein types were recognized: (I) quartz veins, containing sphalerite, jamesonite, bournonite, Ag-rich tetrahedrite, chalcopyrite, galena, stibnite, and gersdorfite; (II) massive stibnite veins, containing numerous minute intergrowths of sphalerite, jamesonite, galena, chalcopyrite, covellite, pyrite, and arsenopyrite; and (III) carbonate veins, containing sphalerite, jamesonite, stibnite, and galena.

The Pb-Sb sulphosalts occur in small amounts in quartz and carbonate veins where they associate with Cu-Fe-Sb sulphosalts, e.g. tetrahedrite, bournonite and jamesonite. Taking into account their chemical composition (EPMA data) boulangerite $Pb_5Sb_4S_{11}$, fülöppite $Pb_3Sb_8S_{15}$, plagionite $Pb_5Sb_8S_{17}$, heteromorphite $Pb_7Sb_8S_{19}$, and twinnite $Pb(Sb_{1.63}As_{0.37})_{\Sigma 2}S_4$ were identified. The examined Pb-Sb sulphosalts grains have Sb content ranging from 25.04 to 46.18wt%, Pb from 29.95 to 55.55wt%, S from 18.38 to 22.70, and As from 0.24wt% to 0.56wt%. The Cu, Zn, Fe, and Se contents reach up to 0.45wt%, 0.24wt%, 0.1wt%, and 0.21wt%, respectively. The Sb/S mole ratios fill the range from 0.36 to 0.54 while Pb/Sb vary from 0.37 to 1.29.

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Geochemical and isotopic study of zircon from the Izera metabasites, West Sudetes, Poland

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The Izera metabasites represent rift-related alkali basalts and form a swarm of the WNW-trending subvertical basic veins in the northern part of the Izera-Karkonosze massif. They cut c. 500 Ma Izera granites and then were jointly deformed and metamorphosed. Two types of zircon crystals, named I and II, differ in colour, size, habit, variable zoning and U-Pb ages were identified in the metabasites. Colourless, transparent and euhedral, 300 µm sized, CL-bright zircon of the type I displayed inherited cores as well as c. 500 Ma oscillatory zoned rims. Their U-Pb ages are almost identical with the previously determined intrusion age of a protolith for the Izera metagranites (U-Pb, zircon, 515-480 Ma). Zircon of the type II forms brown, turbid, subhedral crystals up to 600 µm size and dark in CL. Their large (c. 2/3 of the grain size), almost homogeneous and often microinclusion-rich inner parts are surrounded by thinner oscillatory zoned rims. They yield age of c. 370 Ma.

In situ REE, Ti, $\delta^{18}O$ and εHf_i analyses were performed for zircon crystals from the Izera metabasites and granites in order to determine the origin of the two types of zircons from the metabasites.

Zircon of the type I shows the $\delta^{18}O$ (6.2-9.1‰) values and the Ti-zircon temperatures (600-780°C) typical the felsic magmatic melt which are similar to the data from the Izera gneiss zircon grains. Their REE spider diagrams exhibit the same narrow range of values. Such coincidence indicates that the zircon of the type I is probably inherited a xenocrysts incorporated into the basic magma by assimilation of material of the local granitic crust. Their εHf_i values (-10.8 to +2.7) akin to gneiss zircon εHf_i data (-14.4 to +3.2) confirm the origin of the type I zircon from granitic magma which was formed by partial melting of crustal, probably metasedimentary material.

Zircon of the type II displays a wide range of Ti-zircon temperatures (630-800°C), variable REE contents and varied $\delta^{18}O$ (4.5-8.9‰) and εHf_i (+7.6 to +18.4) values. They can be divided into two groups. 1) Grains showing $\delta^{18}O$ from 5.1-5.5‰ present coherent magmatic-style REE patterns with positive Ce and negative Eu anomalies, which indicate their magmatic origin. Positive εHf_i (+7.9 to +11.9) values coupled with $\delta^{18}O$ (5.1-5.5‰) data of the homogeneous inner cores and oscillatory zoned rims of type II grains indicate that this zircon crystallized from a mantle-derived magma. 2) Dark and inclusion-rich centres of some type II grains with low $\delta^{18}O$ (4.5-5.0‰) show a wide range of εHf_i (+7.6 to +18.4) values, incoherent REE patterns, LREE enrichment and often a lack of Ce anomaly that suggest their precipitation from hydrothermal fluids. Results of the two groups are consistent with the type II zircon crystallizing from a fluid-saturated residual melt or more likely representing magmatic mantle-derived crystals hydrothermally altered by fluids coming from the surrounding metagranites.

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Oborniki (Wargowo) 2012 – best documented space debris fall in Poland

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The fall of a small object took place during night between 27 and 28 April 2012 in Wargowo village near Oborniki, about 25 km NW from Poznań (Nowak, Muszyński 2012). The object was identified as a space debris fall (Nowak et al. 2013). Space debris are completely man-made objects, including their fragments and parts, whether their source can be identified or not, in Earth orbit or re-entering the dense layers of the atmosphere that are non-functional with no reasonable expectation of their being able to assume or resume their intended functions or any other functions for which they are or can be authorized [definition proposed by The Scientific and Technical Subcommittee of the United Nations Committee on the Peaceful uses of the Outer Space].

The fragment of the object passed for future studies is mostly rounded, with a predominant gray colour, metallic luster and weight of about 18 g. Based on microscopic observation and preliminary chemical data three different chemical phases were recognized (Nowak, Muszyński 2012). Analyses in thin-section revealed that the dominant phase is internally inhomogeneous and three sub-phases were additionally distinguished (Nowak et al. 2013). According to the chemical data we can say that sample was recrystallised in cooling or supercooling conditions, causing change both in its chemical composition and internal structure.

Identification of the origin of the Wargowo fall was performed in the Institute Astronomical Observatory of the Adam Mickiewicz University in Poznań (IAO AMU). According to astronomical data two objects re-entered the Earth's atmosphere on 27 April 2012 (based on the Satellite Situation Report): the 37877 (SOYUZ-TMA 22) and the 35127 (FENGYUN 1C DEB). Available data from the Norad TLE Catalog and ephemeris software (EFEM) developed in the IAO AMU allowed determination of ground tracks of these two objects on the date of the fall. The first object 37877 (SOYUZ-TMA 22) did not pass over Wargowo, at the same time the second object could pass over that area 3 times. The 35127 (FENGYUN 1C DEB) are remains of meteoritic Chinese satellite Fengyun 1C "Wind Cloud" (FY-1C) which was launched into orbit on May 10, 1999. On January 11, 2007 satellite was destroyed during Chinese anti-satellite missile test, producing great amount of space debris, estimated 3378 pieces (Johnson et al. 2008).

In recent times we are close to increased solar activity related with Solar Cycle 24. It increases density of the thermosphere and creates a higher drag on satellites and space debris. Therefore in the near future we could observe a large number of debris falls, similar to that of Wargowo.

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Dynamic evolution of the volcanic body from the Wołek hill (Sudetes, SW Poland) – part II. New fluid inclusions data from mantle xenoliths

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The current contribution presents data collected during three scientific trips (July 2013, May/June 2014, July 2014) to University of Federico II in Naples (Italy). The investigations (micro-thermometric measurements), were dedicated to fluid inclusions (FI) from Wołek hill mantle xenoliths. The first data set, from July 2013 – was already presented (Nowak et al. 2013).

Fluid inclusions (FI) as well as melt inclusions (MI) were recognized in all three types of Wołek Hill mantle xenolits (with modal metasomatism – I type, cryptic metasomatism – II type and without any signs of any metasomatism – III type). The inclusions occur as fluid inclusions assemblages (FIA) and isolated inclusions (I). The size of single FI vary from >1μm to <10μm, the shape of inclusions is also very variable (circle, oval, dendritic etc.). The FIA are mostly located along lines but also occurs in planes.

Measurements were performed in several individual crystals of OlI (Fo 90-91) and OlII (Fo 86-89), OpxI (En, mg# 90-92) and CpxII (Di, mg# 85-91), all experiments were focused only on almost pure CO_2-FI, based on first melting temperature (-56.6ºC). Data from 138 FI from 17 crystals in 3 samples (xenoliths – I and II type) were collected; measurements in other 11 crystals did not show presence of CO_2-FI (mostly in III type of xenoliths).

Studied CO_2-bearing FI show homogenization to liquid at temperature (T_h) ranging between -29.7ºC to 15.4ºC. The lowest (T_h) occurs in OpxI from II-type of xenoliths (mostly in range -29.7ºC to -20ºC, with single FIs homogenized below -20ºC). The FI in OlI from II-type xenoliths display (T_h) between -19.6ºC and -2.03ºC; in OlII from I-type xenoliths (T_h) was estimated in the range from -29.8ºC to +9.7ºC. The highest (T_h) were measured in Cpx from II type xenoliths, and vary from -11.5 ºC to 15.4ºC. At the same time (T_h) measurements in Cpx from modal metasomatised sample (I type) shown values between -27.26ºC and 0.8ºC.

Estimated densities show a range from 1.075 to 0.818 g/cm^3, corresponding to pressures between 0.944 and 0.504 GPa, based on the equation of state and assuming temperature of entrapment of 1100ºC, and from 0.811 to 0.422 GPa for temperature of entrapment of 900ºC (calculation were made in spreadsheet proposed by Hansteen and Klügel, 2008).

The calculated pressures correspond to depths ranging from 20 to 35 km, assuming an average crustal density of 2.8 g/cm^3 (Ladenberger et al. 2009). The obtained results are in agreement with data previously found in mantle xenoliths from Wilcza Góra (Ladenberger et al. 2009) and Wołek hill (Nowak et. al 2013). CO_2 inclusions in Wołek hill xenoliths show and entrapment related to depths deeper than the lower crust – no data corresponding with middle and lower crust until now have been found.

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A new isotopic dating of alkaline basalts from the Lublin basin

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The volcanic rocks, which were described as diabases or tufo-lavas, occur within the lowermost part of Carboniferous succession in the northeastern part of Lublin basin. The first radiometric investigation of volcanic rocks from this area, were conducted by Depciuch (1974). The whole-rock K-Ar age (319 and 333 Ma) pointed to the late Visean and even Serpukhovian age. Thus, the main aim of this study is to precisely define the age of the volcanic activity within the Lublin basin.

The selected boreholes Parczew IG 7 and Parczew IG 9 comprise the sequence of massive basaltic lava flows within lower and middle part and amygdaloidal, sometimes brecciated, strongly altered lavas within uppermost part of profile of volcanic rocks. Generally, the alkaline basalts are characterised by fine-grained structure and massive texture. The slightly altered groundmass consists of plagioclase laths of labradorite-andesine composition, fine grained clinopyroxene, olivine and analcime crystals, which occure in different proportion. The accessory minerals include magnetite (euhedral and skeletal), titanomagnetite, ilmenite and apatite.

The whole-rock samples for the $^{40}Ar/^{39}Ar$ geochronological analyses have been carried out at the Lund University Geochronology Laboratory (Sweden). The new isotopic data constrain the age of volcanic activity and emplacement of alkaline basalts to the Late Tournaisian and Middle Visean. Additionally, the new data caused to correlate the volcanic processes occurring within the Lublin basin with alkaline and carbonatite provinence discovered in NE Poland in southern Fennoscandia dated by Demaiffe et al. (2013).

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Nickel, chromium and cobalt distribution and extractability in silicified serpentinite from the Szklary massif

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Silicified serpentinite known as birbirite – a ferruginous and siliceous rock displaying evidence for pseudomorphic replacement of the primary minerals by silica (Lacinska, Styles 2013). Silicified serpentinite occurs in Poland only in Lower Silesia (Mikulski 2014). The aim of our study was to compare the EDTA extractability of Ni, Cr and Co in birbirite and serpentinised peridotite from the northern part of the Szklary massif.

The Ni and Cr concentrations in studied silicified rock reaches 1450 and 1990 $mg \cdot kg^{-1}$ respectively. Birbirite contain also important concentrations of Co (up to 143 $mg \cdot kg^{-1}$). Mineralogically, the rock is composed of silica, Cr-bearing magnetite and clinochlore. The highest concentrations of Ni, Cr and Co are observed in magnetite (average 0.54wt% of Ni, 16.5wt% of Cr and 0.7wt% of Co). Clinochlore constitutes also an important source of Ni and Cr and contains up to 0.19 and 1.25wt% respectively. Silica does not contain important concentrations of Ni, Cr and Co. However, an interesting feature of studied birbirite is presence of numerous pseudomorphs after olivine. They are composed of silica and some microinclusions of secondary Fe oxides which might be Cr, Ni and Co carriers. Fractionation of Ni, Cr and Co, estimated using 0.05 M EDTA, aimed to determine the easily removable part of these elements. Nickel is mobile in similar way in both birbirite and serpentinised peridotite and Ni-EDTA extractable fraction reaches 5% of the total Ni concentration in rock. Chromium is the least mobile element and its proportions of EDTA-extractable fraction reaches similar values in birbirite and serpentinised peridotite (0.02 and 0.05% of the total Cr respectively). Proportion of Co present in the EDTA-extractable fraction ranges from 3% in serpentinised peridotite to 12% in birbirite.

Our results show similar extractability of Ni and Cr in birbirite and serpentinised peridotite. It may indicate that minerals in both rocks are dissolved in the same extent. Only mobility of Co is higher in birbirite than in serpentinised peridotite. It may be due to fact that pseudomorphoses after olivine (composed of silica and secondary Fe oxides) in birbirite might realase important Co concentrations during extraction.

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The Central European basin large igneous province – is it a typical SLIP?

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Silicic large igneous provinces are formed in various extensional geotectonic settings such as intra-continental rifting, post-orogenic collapse or back arc. They are characterized by large volumes of silicic magma that are produced within relatively short period (Bryan, Ferrari 2013). Volcanic products are dominated by rhyolites and rhyodacites and their chemical and isotope composition may vary between different provinces and within the province. Both mantle and continental crust are important sources of heat and material for formation of SLIPs, but their relative input is not well understood.

The Central European basin – large igneous province (CEB-LIP) was formed at Carboniferous/Permian boundary during the final stage of the Variscan orogen. CEB-LIP is similar to other silicic province in that it comprises large volume of magma produced within 10-15 Ma. However, important differences are revealed when CEB-LIP is compared to other SLIPs. The valuable information can be, for example, obtained from isotope and chemical analyses of zircon, as is illustrated by comparing our data from CEB-LIP to the zircon data from the Snake River Plain (Pietranik et al. 2013). Differences in O isotope composition shows that vastly different crustal sources occur in both provinces, however their remelting produced similar final product: large volume of rhyolite. Also, the zircon analyses from different parts of the CEB-LIP show that different sources may be involved in the rhyolite formation, even though magmatic processes controlling the rhyolite magma evolution are similar. Especially interesting is the contribution from the mantle that seems to be important e.g. in the NE German basin and the Polish Lowland, but is probably negligible in the Halle Volcanic Complex. Altogether, the general picture emerges that suggests important differences in magma sources between SLIPs and suggests more extensive analyses of different SLIPs in order to estimate the quantitative proportions between sources and their impact on the volumes of the volcanic rocks.

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Zircon in magmatic rocks from the Niemcza zone: what do we expect to learn?

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Intrusive rocks occur in several places in the Niemcza zone and they belong to two groups: dioritic and granodioritic. Dioritic magmas composition change from normal calc-alkaline to ultrapotassic, but precise times of involved in this process, as well as full chemical characteristic of different magmas occurring in the Niemcza zone are not fully constrained (Pietranik et al. 2013). In this study we analysed major and trace element composition of 20 samples from different localities in the Niemcza zone. We also characterized zircon separates and thin sections from 8 different types of dioritic rocks. Our aim was to link zircon variability to geochemical characteristic of diorites in order to estimate the potential of future zircon analyses. Zircon may provide important information on time and processes of magma evolution, but only if its timing of crystallization within magma is well recognised.

At the first approximation the dioritic rocks from the Niemcza zone could be divided into three chemically distinct groups: (1) medium-K including two types of diorites from Przedborowa (also with characteristic low Rb and U concentrations), (2) high-K including one type from Przedborowa and diorites from Koźmice and Brodziszów (with moderate Rb cocnetrations) and (3) ultrapotassic represented by syenite from Wilków Wielki (characterized also by extremely high Rb and low concentrations of other trace elements). Despite similar Zr contents (whole rock) in all the medium and high-K rocks, zircon varies in the form from one rock type to the other and is small and elongated, included in mafic phases (e.g. in two of the Przedborowa types), to large and stubby occurring mostly at the grains borders (in one type from Przedborowa and one from Koźmice). It is interesting to see such large variations in zircon occurrence in rocks of generally similar geochemical composition. It seems that zircon saturation in any given magmatic rock is not always linked to the chemical composition of the rock (Zr and major elements concentrations, which should define the temperature of zircon saturation in magma). The implication is that the interpretation of zircon age and composition may be strongly affected by local saturation/dissolution processes occurring in the magma. Alternatively, it may mean that zircon cargo is dominated by antecrystic grains.

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Weathering crust on building sandstone in urban environment – examples from the city of Wrocław

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Sandstones are main building stones in historical and modern architectural object in the city of Wrocław. The dominant variety is a light yellowish-gray, fine- to medium-grained quartz arenites from the local Lower Silesian Upper Cretaceous deposits. Their petrographic features influence their physical and mechanical parameters and, consequently, their resistance to weathering and deterioration, *i.e.* processes that are particularly intense in the polluted urban environment.

In this report, we present results of petrographic investigations on the weathering of sandstone architectural elements from façades of two selected historical buildings in the centre of Wrocław: the National Museum and the Architecture Museum. The stone elements at these sites were partly covered by moss (*Tortula muralis* Hedw) and lichen (*Lecanora saxicola*). The samples analysed were drill cores, 15 mm in diameter and c. 5 cm long. Comparative petrographic observations were made in sections at different depth: (a) the surface weathering crust, (b) subsurface weathered zone (usually at depth of 0-10 mm), and (c) deeper interior of the stone (at c. 40-50 depth). The focus was put on identification of the mineral and textural changes, including the formation of new weathering products and substance alteration in the sandstone matrix within the weathering zone. The methods used comprised polarizing microscope, electron microprobe EMP-EDS, SEM and XRD.

The sandstones from the two sites are petrographically similar: fine- to medium-grained quartz arenites, with the grain framework composed of quartz (+quartzite) 68-87vol.%, feldspars 3-10% and micas 0.9-1.5%. The grains vary from well-rounded to angular. The porosity measured in thin section is between 12.5 and 21.6vol.%, but the pores may be, in part, artefacts resulting from thin section polishing procedure. The cement, 10-15vol.%, is siliceous-clayey, with admixture of iron hydroxides.

The surface weathering crust contains blackish, opaque matter, apparently with carbonaceous substance, not detectable in EDS and XRD. EDS spectra reveal the presence, in various proportions, of sulphur and phosphorus, which are not observed in deeper interior of samples. Phosphorus occurs locally, down to c. 4 mm below the surface. Sulphur is observed down to c. 8 mm, often together with calcium, thus reflecting the presence of secondary gypsum. However, in the external crust, within c. 2 mm depth, the EDS Ca peak is much higher than that of sulphur, being evidence of the presence of an additional Ca-rich phase, possibly calcite.

Within the subsurface zone, 0-10 mm deep, the original cement is partially removed and replaced by secondary blackish substance. However, the original siliceous-cleyey cement is partly preserved, often mixed with iron hydroxides, gypsum and calcite. EDS spectra collected in interstitial spaces often show high amounts of Al and Si, reflecting, most likely, kaolinite, as well as lower Al/Si with addition of K (± Fe), corresponding to illite. The common presence of secondary gypsum and calcite in the weathering crust has been confirmed by XRD data from the study samples.

The source of calcium for the secondary phases seems to be the binder in the wall of the building (taking into account the low amount of carbonate in the original cement of the sandstones), as well as precipitation water. The source of sulphur can be sulphur oxides contained in the polluted urban atmosphere, whereas the phosphorus, most likely, comes from birds' excrements (*c.f.* Přikryl 2007, Wilczyńska-Michalik 2004).

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Relics of depleted peridotites in lithospheric mantle beneath SW Poland

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The Phanerozoic subcontinental lithospheric mantle (SCLM) is hotter, thinner and more fertile than the Archean or Proterozoic one. Recently, the increasing number of studies shows that the Phanerozoic SCLM lithologies considered to be the residues after partial melting are affected by metasomatic events, which are difficult to recognise because of lack of textural record (O'Reilly, Griffin 2013). The lithological features of Phanerozoic SCLM is known in large part due to xenoliths in alkali basalts. These xenoliths commonly come from SCLM domains affected by extensive metasomatism by the alkaline melts, shortly preceding their entrapment into the erupting lavas. The xenoliths which come from mantle parts not affected by this kind of metasomatism or refertilized are rare.

Our recent studies of mantle xenolith suites from Lower Silesia in SW Poland and adjoining part of Upper Lusatia (SE Germany) revealed the group of xenoliths (we call them "group "A") which were not affected to strong alkaline melt metasomatism and thus preserved much of the "primary" characteristics (Matusiak-Małek et al. 2014, Puziewicz et al. 2014). They are characterised by forsterite content in olivine of 90.5-92.0 and corresponding mg# of orthopyroxene. The latter is poor in Al (typically <0.10 atoms pfu). These xenoliths contain no or little clinopyroxene and have harzburgitic compositions. The clinopyroxene is strongly magnesian (mg# 0.92-0.95) and commonly rich in Ca, suggesting low equilibration temperatures, and poor in Al. Spinel is absent in most samples; if it occurs we interpret it to be a metasomatic phase. Clinopyroxene trace element compositions possibly record metasomatic events which happened after major depletion and before the last, volcanism-related alkaline melt metasomatism.

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Ore minerals assemblages in serpentinized ultramafic rocks from the southern part of the Szklary massif (Bobolice)

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Mafic and ultramafic massifs surrounding Góry Sowie block are known as dismembered parts of ophiolite suite. The Szklary massif is situated at the eastern border of the Góry Sowie Block, in the southern part of Niemcza dislocation zone. The Szklary massif is composed of ultramafic rocks serpentinized to various degree. These rocks are regarded as mantle peridotites of Sudetic ophiolite complex (Dubińska, Gunia 1997). Ultramafic massif is covered by Cenozoic laterite weathering cover. Within the weathering cover there are three saprolitic nickel deposites.

Detail microscopic examination in reflected and transmitted light reveals ore minerals assemblages. Investigation was carried out on samples from drill cores situated in the southern part of the Szklary massif and collected in the field. Chemical composition was determined using CAMECA SX 100 electron microprobe. Serpentinites host oxide and sulfide ore minerals. EPMA analyses show that the most aboundant ore minerals are oxides like chromite, Fe-Cr spinel and magnetite. Documented sulfides are the following: Fe-Ni sulfides like pentlandite $(Fe,Ni)_9S_8$, pyrrhotite $Fe_{(1-x)}S$ pyrite FeS_2, chalcopyrite $CuFeS_2$, millerite NiS, heazlewoodite Ni_3S_2, cobaltite CoAsS and single native metal inclusions (such as: native iron, native copper, silver and silver-gold solid solution). Primary ore minerals like chromite, pentlandite, pyrrhotite and chalcopyrite were affected by fluids, which results in precipitation of secondary mineral phases: Fe-Cr spinel, Cr-magnetite, magnetite, Fe-Ni sulfides. Sulfides form dispersed, anhedral grains which vary in size from several μm up to several dozen of μm. Pentlandite is frequently enriched with Co up to 15wt%. Ni sulfides are enriched with Fe. During processes of serpentinization Cr, Al, Mg in chromite structure were replaced by Fe. Results of these are Fe-Cr spinel and magnetite. Magnetite also crystalized in pseudomorphs after olivines and pyroxenes. Frequent intergrowths of sulfides with magnetite or Cr-magnetite indicate simultaneous precipitationduring serpentinization process. Ore minerals assemblages identified in the Szklary massif are typical of weathering zone of a serpentinized ultramafic rocks of Sudetic ophiolite complex (Sadłowska 2011; Delura 2012).

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Isotopic composition measurements of natural and isotopically enriched materials by MC-ICP-MS

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The aim of this work was to establish mass spectrometry protocols for routine Te isotopic composition determination by a Multicollector-Inductively Coupled Plasma Mass Spectrometer (Thermo Finnigan NEPTUNE). We prepared tellurium standard solution from a TeO powder produced by Johnson and Matthey Chemicals, USA. Concentrated Te solution was prepared by dissolving TeO in 5% HNO_3 on a hot plate. Prior to analyses, standard was diluted to concentrations suitable for the MC-ICP-MS analyses with 2% HNO_3. Solution was introduced into the mass spectrometer with the use of dessolvating nebulizer Aridus II™ by CETAC. This introduction allows reducing oxide production level $^{140}CeO^+/^{140}Ce<0.1\%$ and enhances sensitivity about 4 times in comparison to wet plasma conditions on our instrument.

Mass spectrometry measurements were carried out in the static mode with internal normalization to $^{124}Te/^{128}Te = 0.148530$ (Lee, Holliday, 1995). Initial results of the isotopic composition of the Te standard show very good agreement with the results presented by Lee and Holliday (1995) and Fehr et al. (2004) measured by MC-ICP-MS.

We will present the results of isotopic composition measurements of isotopically enriched materials used in nuclear reaction studies.

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Variations in the modal composition of the Landsberg laccolith (Halle volcanic complex) – detailed analyses of the 0.5 km deep borehole material

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The Halle volcanic complex (HVC) is located within the transtensional Saale Basin. It is dominated by rhyolites. Rhyolites differ in structure (coarse grained and fine grained types). Each rock type form a separate laccolith units. The whole rock composition of rhyolites is uniform (Romer et al. 2001), but they contain chemically diverse zircon grains (Słodczyk et al. sub.). The project, started by a student group, aims at better understanding of processes leading to formation of such structurally diverse, but chemically similar rhyolites. The project involves analyses of the borehole material from the Landsberg laccolith (coarse grained type) and the Petersberg laccolith (fine grained type). The samples were taken every 25 meters, what offers possibility to analyse very detailed sections through the laccoliths. As such the project will also provide detailed information on amalgamation of laccolith units.

The first stage of the project involved analyses of modal composition and its variations with depth through the Landsberg laccolith. Altogether 80 samples from 20 depth intervals were analysed. The analyses were done by means of free software MicroVision®. The modal proportions of plagioclase, K-feldspar, biotite, quartz and glass were constrained. The glass is the major constituent (over 60%) and major mineral phases are plagioclase and feldspar (10-15%). The proportions between plagioclase and K-feldspar vary consistently through the borehole, i.e. similar proportions are observed over 100 meter intervals and at least 3 such intervals were identified. The first interval is characterized by predominance of plagioclase over K-feldspar, whereas K-feldspar dominates in the second interval, the third one shows similar proportions between the two phases. The implication is that the Landsberg laccolith was formed by several pulses of magma formed under diverse conditions, but each pulse consisted of similar magma volume. The differences in proportions between the main phases may reflect the differences in initial magma composition, pressure or water content. Chemical analyses of different phases should provide further information on magma origin and processes of the laccolith formation.

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Secondary arsenic minerals from old adits in the Złoty Stok area (Sudetes, Poland)

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Mining of Au and As ores in Złoty Stok area has very long and interesting history. Several old shafts, adits and relicts of gold and arsenic smelters are present in this area. Weathering zone of Złoty Stok deposit is relatively poorly recognized. Only several secondary minerals were described in 19th and 20th century from old dumps and iron cap of deposit (arsenolite, asbolane – now not recognized as a mineral, azurite, erythrite, goethite, covelline, hydronium jarosite, malachite, scorodite and wavellite). Based on the of PXRD and SEM-EDS analysis six supergene minerals unknown from Złoty Stok area were identified. Those minerals crystallized recently in old adits and underground workings.

Pharmacosiderite occur in the Masters adit (Sztolnia Mistrzów in Polish). It formed thin, yellow to green crystalline crusts and coatings in fissures in barren rock. Pharmacosiderite agregates are composed of pseudocubic crystals up to 0.5 mm. It usually coexists with brown scorodite and goethite.

Aggregates of arseniosiderite was recognized in Fox adit (sztolnia Lisia in Polish). Thin brown crust of it are build by thin crystals up tu 0.1 mm long. Arseniosiderite occurs in association with goethite and scorodite.

The most interesting supergene minerals were identified in Gertruda adit. This adit was build in the beginning of 20^{th} century. In one part of the adit, a small pocket of arsenopyrite-löllingite ore (about 30 cm in diameter) is exposed. Ore minerals are in the calc-silicate rocks. Weathering processes of ore minerals led to crystalization of secondary minerals and the main of them is scorodite. It occurs in two generations. First form of scorodite – grey earthy aggregates occur in the central part of oxidized ore pocket. Relics of arsenopyrite and löllingite are present in this type of scorodite. In the marginal parts of the first form there appears the second generation of this mineral. The second form of scorodite is created by spherolitic aggregates up to 30 µm. With this type coexists pitticite. This phase is composed of brown or honey-yellow botryoidal aggregates which usually are cut by fissures connected with dehydratation of pitticite. Sometimes pitticite overgrow small crystals of gypsum. Zone dominated by second generation of scorodite and pitticite change gradually to kaňkite's zone. Kaňkite occurs as yellow-green crystalline coatings which are composed of small ball-like agregates up to 100 µm in diameter. In the marginal parts of weathered ore pocket, on the border between kaňkite zone and barren rock the Ca and Mg arsenates crystallized, where the main mineral is picropharmacolite. It occurs as white acicular to hair-thin crystals grouped in radiating aggregates and spheres up to 0.5 cm in diameter. Picropharmacolite coexists with hörnesite. It occurs as radiating spherical aggregates composed of acicular crystals up to 0.2 cm long. Individual crystals are colorless or white. Marginal parts of zone is dominated by Ca-Mg arsenates. The present Mg arsenate is closely related to microbial colonies.

In other parts of the Gertruda adit, yellow, dusty masses of jarosite, rusty accumulations of schwertmannite and goethite were found. These minerals occurs mainly in tectonic zones where pyrite oxidation takes place.

Very similar assembles of secondary minerals, like in Gertruda adit, occurs in medieval Emanuel adit. Additionally presence of yellow sulphide of arsenic was recognize. It occurs as earthy coatings on old wooden mining constructions. The same phase was identifies from relicts of wooden pillar in Gertruda, Black (Czarna Sztolnia in Polish) and Masters adits.

Crystallization of the described above supergene minerals is connected with oxidation processes of ore minerals (arsenopyrite, pyrite and löllingite) and interactions between products of those reactions and barren rocks.

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Different magma sources recorded across the Polish Lowland based on δ^{18}O in zircon

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Isotope and chemical analyses of zircon from the Polish Lowland provide information on magma sources and processes of magma evolution during the period of intense magmatism that affected Central Europe at the Carboniferous/Permian boundary. Since zircon reflects ^{18}O/^{16}O of the magma from which it crystallized, we have measured the ^{18}O/^{16}O in zircon to establish the fraction of the rhyolite precursors that was derived from juvenile magmas and also to reconstruct magma evolution during the zircon crystallization. Zircon isotope ratio determinations were conducted at the GFZ-Potsdam using the Cameca 1280-HR SIMS instrument. The reference zircon 91500 (Wiedenbeck et al. 2004) was analyzed 39 times as part of this project, yielding a repeatability of ± 0.2‰ (1SD).

We studied zircon grains from four localities Pniewy, Wysoka, Daszewo and Chrzypsko. Altogether more than 100 magmatic grains were measured. The highest δ^{18}O values were measured in Daszewo and the lowest in Wysoka suggesting that magmas from different localities represent different sources. Each locality have zircon with the range of δ^{18}O values exceeding the error, which is consistent with zircon crystallizing in an evolving magma or in separate magma batches. The latter seems to be more probable as zircon is not zoned in δ^{18}O from the core to the rim. As the whole, zircons from the Polish Lowland have the greatest variability in δ^{18}O observed so far amongst all of the localities studied from the Central European basin large igneous province (Pietranik et al. 2013). The results extend from low values typical for derivation of the magmas from the sources altered by hydrothermal activity up to results consistent with a important sedimentary input into the system. So far the localities from the Polish Lowland are the first ones studied within the CEB-LIP, which show δ^{18}O lower than the mantle values (δ^{18}O <5.3‰).

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Conditions of formation and crystallization of the Ostrzyca Hill basanite (Lower Silesia) – preliminary constrains from geothermobarometry

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The understanding of the evolution of volcanic systems requires data on the formation depths of magma and its possible subsequent storage and crystallization during the rise towards the surface. The course of these pre-eruptive processes affects magma supply to shallow levels of volcanic systems, and eventually influences the eruptive behaviour of volcanoes. We have studied these problems for the couse of the Miocene(?) Ostrzyca Proboszczowicka basanite from Lower Silesia, in the eastern part of the Central European volcanic province, as an example. The Ostrzyca basanite occurs as a neck and its form, bulk-rock composition and petrographic features are representative of the mafic intraplate monogenetic volcanism that affected the region in the Cenozoic times. The Ostrzyca basanite consists of olivine (Fo 0.87-0.75) and diopside (En 0.32-0.40, Wo 0.48-0.53) phenocrysts in groundmass of clinopyroxene, olivine, plagioclase (labradorite An 50-60), nepheline, spinel (aluminian titanomagnetite) and apatite. There are also Fe-rich diopside megacrysts, rare olivine aggregates and quartz xenocrysts.

The formation and crystallization conditions of the Ostrzyca basanite magma were evaluated by use of the following geothermometers and geobarometers (Putirka, 2008 and references therein): the silica activity barometer, the olivine-melt thermometer, the clinopyroxene barometer and the glass (liquid) thermometer. The barometers are T-dependent and the thermometers P-dependent, so the calculations were carried out for assumed T or P, respectively. Bulk-rock chemical composition of the basanite (assumed to represent melt composition) and representative olivine and diopside phenocryst compositions were used. For calculation of the liquidus temperatures were also calculated using the MELTS software was also used (Ghiorso and Sack, 1995; Asimov and Ghiorso, 1998). The results of P-T calculations were compared with the regional geological data such as the depths of Moho and of the lithosphere-asthenosphere boundary.

The results suggest that the Ostrzyca basanite magma was generated under pressures above 2,5-3 GPa at temperatures above 1380°C, possibly close to the lithosphere-asthenosphere boundary (depths of c. 90-100 km) or in the upper part of asthenosphere. Olivine phenocrysts began to crystallize at temperatures above 1400°C, soon after magma segregation from the source. Diopside megacrysts are out of equilibrium with the host basanite and are xenocrysts possibly picked up by the magma from the lithospheric mantle. Diopside phenocrysts crystallized at lithospheric mantle depths or at crustal depths, or both. Distinctive depth zones of the Ostrzyca basanite magma storage and crystallization, corresponding to possible magma reservoirs, cannot be easily defined at this preliminary stage of our study, partly due to relatively large errors of the geothermobarometers used (e.g., ±0,31 GPa for the Cpx barometer).

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Secondary phases from the Zn-Pb smelting slags from Katowice – Piekary Śląskie area, Upper Silesia, Poland: a SEM – XRD overview

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Slag dumps are common in Upper Silesia landscape. Studied wastes from Katowice – Piekary Śląskie sites are a result of continuous ore smelting, waste storage and weathering for about 150 years. As a result we observe large variety of secondary phases, mostly in specific localization within slag dump, related to fresh exposure of material, but sheltered from direct external factors that may cause extensive rinsing and thus leaching of secondary phases. In this study we follow Brils et al. (2008) definition of secondary phases i.e. formed after primary ones crystallized from melt initially in the slag, on textural basis. As a result, among the secondary assemblage we can find also relatively high-temperature phases effected in deuteric and hydrothermal alteration. According to the XRD data (PANalytical X'PERT PRO; Co Kα1 radiation, 45kV voltage, 30mA intensity) and SEM-EDS (FET Philips XL30) investigations the secondary phases are represented by: carbonates (calcite – aragonite), hydrated carbonates (pyroaurite, lansfordite – hydromagnesite), sulfates and hydrated sulfates (anhydrite – gypsum), hydrated sulfate-carbonates (rapidcreekite) and oxides (hematite and zincite) and some other secondary phases.

Gypsum in the studied slags forms anhedral or needle-shaped aggregates up to 5mm; barite with cerium and strontium enrichment is present as anhedral laths up to 50 µm; beudantite-like ($PbFe_3[AsO_4][SO_4][OH]_6$) sulfate-arsenate is present as anhedral grains up to 100 µm, with K and Ca substituting Pb; Ca-Al rich sulfate close to ye'elimite ($Ca_4Al_6[SO_4]O_{12}$) or ettringite ($Ca_6Al_2[SO_4]_3[OH]_{12}\cdot 26H_2O$) forms lath aggregates up to 70 µm; rapidcreekite is present as needle aggregates up to 3mm, or separate subhedral crystals up to 200 µm. Cerussite is locally fill the interstices in sulfides; phosphates with compositions close to harrisonite ($Ca[Fe^{2+},Mg]_6[PO_4]_2[SiO_4]_2$) or perhamite ($Ca_3Al_{7.7}Si_3P_4O_{23.5}[OH]_{14.1}\cdot 8H_2O$) showing enrichments in As and Zn form laths and columns up to 250 µm. Arsenate with nealite-like composition ($Pb_4Fe^{3+}[As^{3+}O_3]_2Cl_4\cdot 2H_2O$) and Zn concentrations present as needle-aggregates up to 20 µm; anhedral AsFe component occurs with exsolved Fe droplets. Zincite forms pipe-like aggregates of lath crystals on slag surface. Since the secondary phases could be easily dissolved, they could be treated as the couse of potential environmental contamination.

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Mantle-crust transition zone in the Ślęża ophiolite (SW Poland) and in other European Variscan ophiolites from Rheic Ocean

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The Variscan Ślęża ophiolite in SW Poland is a remnant of the ancient Rheic Ocean. The stratigraphically lower part of the massif consists of serpentinites with harzburgitic affinity, serpentinites with non-serpentine phases, ultramafic cumulates, layered and isotropic gabbros. The non-serpentine phases form: (1) olivine-clinopyroxene aggregates, (2) microcrystalline olivine-clinopyroxene aggregates ("brownish aggregates"), (3) clinopyroxene-spinel symplectites, (4) coarse-grained olivine aggregates, (5) olivine grains with magnetite inclusions (with or without cleavage), (6) olivine-chromite aggregates and (7) chromite veinlets. Olivine occurs in three main varieties of different forsterite, NiO and MnO content. Clinopyroxene occurs in four varieties differing by mg#, Al_2O_3 and Cr_2O_3 content and is generally depleted in Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu relative to chondrite and primitive mantle. Chemical composition of chromite defines two groups with various cr#, MgO and FeO content.

The non-serpentine phases recorded various processes associated with serpentinite formation: [1] depletion processes of peridotite, [2] Ca-rich melt migration, [3] alteration of peridotite during ocean floor metamorphism and [4] greenschists facies metamorphism. The Ca-melt migration phases originated due to impregnation of peridotite, what is typical of peridotites occurring in the Moho transition zone. The impregnated peridotites occur above mantle harzburgites and below ultramafic cumulates in the Ślęża ophiolite, thus fitting the model ophiolitic stratigraphy. In other Variscan ophiolitic massifs in Europe, like the Careón or Lizard, this succession is not so clearly visible although the paleo-Moho could be also defined (cf. García et al., 1999, Power et al. 1996). The Ślęża ophiolite preserves very good MTZ section compared to other Variscan ophiolites.

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The new occurrence of the „hyperite" (olivine metagabros) in the Góry Sowie block (SW Poland)

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The "hyperite" is the old name of gabbros (norite) consisting of orthopyroxene (hyperstene-enstatite), plagioclase and augite. The name "hyperite" was later redefined i.a. to noritic rocks with hypersthene coronas around olivine (Le Maitre, 2002). We present new petrological and geochemical data about "hyperites" – olivine metagabros found near Owiesno (SW, Poland).

Owiesno is located about 32 km SE from Wałbrzych, about 5 km SW from Piława Górna and belongs to the Góry Sowie block (Sudetes Mts.). Although some rocks near Owiesno were previously defined as "hyperite" (Trepka, Gawroński 1957), we describe samples which were found in NW part of the village, in the area originally described as amphibolite surrounded by gneiss and migmatite (Trepka, Gawroński 1957). The outcrop is located on the top of hill (365,8 m a.s.l.), in the agriculture area. Two types of metagabros were recognized. They are cross-cut by a thin leucocratic pegmatite veins (Łobos, 2007; Wośkowiak, 2011). Unique mineralization of gem quality amphiboles could be found in that occurrence (Łobos, 2007), on the border between metagabros and leucocratic rocks (Wośkowiak, 2011).

For future studies two samples were collected – coarse (AM-1) and fine grained one (AM-2). In the AM-1 sample three types of structures were recognized. Structure I (SI) is characterized by coronas around olivine (Ol), structure II (SII) displays coronas around zones with epidote and structure III (SIII) contain Cpx and Ol. The SI structure is dominant in this sample; the main minerals are Ol (0.5-2 mm in diameter; with rather constant chemical composition Fo 78 - decreasing near to the cracks to 68) surrounded by coronas with: 1) chlorite (mg# 85-89); 2) amphibole (Prg, mg# 75-84; Act-Tr, mg# 85-90), 3) orthopyroxene (En, mg# 79-80) and 4) garnet (Py 60). The coronas around olivine are about 0.2-0.7 mm in diameter. Structure II is focused around epidote zones (1.8 to 4.6 mm), the single epidote crystals do not exceed 600 μm. Epidotes display spongy structure and variable chemical composition (Al content decreases from core to rim). Minor feldspars, amphiboles and barite occur between them. Coronas around the epidote zone contain also chlorite, amphibole, orthopyroxene and garnet – similar like in the SI structure. Structure III is 2.5 - 7 mm in diameter, and displays subpoikilitic texture with pyroxenes enclosing olivine crystals. Chemically Ol from the SIII structure do not differ from those from the SI structure. Clinopyroxene is diopside (mg# 88).

The sample AM-II differs from the AM-I sample. The coronas are around Ol (Fo, 71-74) surrounded by Opx (En, mg# 77-78), Amp (Prg, mg# 79-90), and Spl (Pleonaste, mg# 31-38). In the AM-II sample micas, garnets and apatites were also recognized.

The "hyperite" i.e. two pyroxenite metagabbro was recognized in several occurrences in the Sudetes (Kryza, Pin 2002). Samples found around Owiesno slightly differ, mineralogical and chemically from those described in previous publications (Kryza, Pin 2002; Kryza, Pin 2010) – future studies are still needed.

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Petrologic features of gabbroic veins from the Braszowice-Brzeźnica massif (SW Poland) – evidence for the processes within the Moho transition zone (preliminary data)

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The Braszowice-Brzeźnica massif (BBM) is located in the south end of the Niemcza dislocation zone in SW Poland (NE part of the Variscan Bohemian Massif in Central Europe) and consists of gabbros and serpentinites.

The rodingitic, pyroxenitic and gabbroic veins occur mostly in the western part of the BBM in the Mnich Hill (Gunia, 1992). The contact between gabbroic veins and serpentinites is sharp, the gabbros are: (1) isotropic fine- to medium-grained, (2) pegmatitic and (3) layered. The surrounding serpentinites consist of olivine-clinopyroxene aggregates or single clinopyroxene grains embedded in antigorite groundmass. Clinopyroxene has structural formula $(Ca_{0.91}Mg_{0.95}Fe^{2+}{}_{0.08})(Si_{1.90}Al_{0.10})O_6$ and is Ti- and Na-free, olivine $(Fo_{0.90-0.93})$ contains 0.35-0.45wt% NiO. The gabbros consist of clinopyroxene and saussuritized plagioclase. The clinopyroxene has composition of diopside-augite and structural formula $(Ca_{0.93}Mg_{0.85}\,Fe^{2+}{}_{0.10}Ti_{0.01}Na_{0.03})(Si_{1.89}\,Al_{0.11})O_6$.

The chemical composition of clinopyroxene from aggregates is similar to that occurring in serpentinites from the Gogołów-Jordanów serpentinite massif, which have been interpreted to be the melt-percolation phase (Wojtulek et al. 2013). The occurrence of gabbroic veins associated with melt phases in serpentinites supposed to be a result percolation is typical of transitional serpentinites from the Moho transition zone (Boudier and Nicolas, 1995). Thus, we speculate that the MTZ section is exposed in the BBM.

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Rare metals content in cassiterite from Bangka (Indonesia)

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The Southeast Asian tin belt is an important metallogenic province with significant deposits of minerals such as cassiterite, wolframite, columbite-tantalite series, as well as monazite, xenotime and zircon. In Indonesia, the belt comprises of Bangka and Belitung islands, which are extremely rich in Sn and locally W mineralization associated with primary deposits of the greisen type later redeposited within paleoplacers that are presently major source of tin and accompanying metals in the region.

During field works on Bangka and Belitung islands since December 2012 till March 2013 over 400 samples were taken from diversified mining sites as well as processing plants. The samples represent cassiterite sands, preliminary concentrate of heavy minerals, final cassiterite concentrate and tailing containing mixed heavy minerals. Additionally slags formed after tin smelting were sampled. Chemical and mineralogical analyses has been carried out on representative samples of all subdivided types.

The study of individual grains of cassiterite, the major component constituting the input to the furnace, show up to 1.12wt% of Ta_2O_5 and 0.25wt% Nb_2O_5. No columbite-tantalite was detected. Analyses of slag fragments consisting of distinct layers of different chemical composition revealed significant concentration of rare earths (particularly cerium, lanthanum, neodymium and yttrium) as well as niobium, tantalum, zirconium and titanium.

Literature data indicate that within the Southeast Asian tin belt concentration of niobium and tantalum in cassiterite concentrates decreases to the south of the considered region and is relatively low for Bangka and Belitung ores (Schwartz et al. 1995). However, due to the significant enrichment in tantalum and niobium in the examined slag further systematic characterization of material constituting furnace input is justified. Cassiterite and tailings from mining and processing of the cassiterite ores are important and yet poorly developed source of many critical and deficit elements, including rare earths, niobium and tantalum (Szamałek et al. 2013).

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From magma genesis to ore formation; evidence from macro- to nano-scales

Appendix

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Petrographic and mineralogical features of an ancient pottery from Niemczańska street, Wrocław

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Ceramic petrography is an important issue in the field of archaeometry. Simplicity and amount of information on technological features obtained as a result, make possible to examine ancient pottery on more advanced level. Presented poster is going to be first comprehensive report on the results of the research conducted on the Bronze Age ceramic material from Niemczańska street during last academic year.

The material for study comes from the archaeological excavations held in 2003 and 2005 in Wrocław, The site is situated at Niemczańska street and it has presented settlement type of objects and artifacts with numerous fragments of ceramic vessels. During macroscopic observations material has been divided into two main groups – "thin" and "thick" wall pottery but as diversity in forms and an admixture have been noticeable, it led to selection of representative groups of each kind of pottery in number of 15. This material has been prepared in form of thin sections with thickness of the sample ranging between 20μm and 30μm and it was then observed under polarizing microscopes in transmitted and reflected light. The goal of petrological analyses was recognition of mineralogical type of an admixture, granulometric shape, size and amount of grains, as well as possible suggestion of clay provenance and intentionality of an admixture preparation. Laboratory observations were conducted in the Institute of Geology, Wroclaw University.

Microscopic observations enabled to distinguish more detailed types of pottery with appearance of: 1) thicker [e.g NIEM/05/154/a] and 2) smaller [NIEM/05/180/a] grains of an intentionally prepared admixture, 3) naturally formed grains of fine river sand [NIEM/05/158/a], and at least 3 types that differed in type of clay plasticity: type with 4) more [e.g. NIEM/05/111/a] and 5) less [NIEM/05/161/a] numerous grains of matrix as well as 6) clay containing or composed nearly entirely of clay minerals [NIEM/05/182/a].

In general the mineral composition of admixture in the whole set has been rather homogeneous. It suggested similar origin of the source of the admixture, presumably as a local one. Most commonly quartz (40-65%) and feldspar (15-30%) appeared, often with some muscovite (1-5%), vermiculite (1-5%), opaque minerals (0,5-3%), limestone (0,5-1,5%) and ferruginous (0-10%) or clay aggregates (0-8%). As most of those phases are present in soil, it is hard to point whether it has already been a natural admixture or if it has been added (and if so, what is an exact source of those phases). Presumably it can be established that grains originate from both sedimentary and igneous rocks that have been transformed by weathering. Nevertheless few important mineralogical variation can be observed. Most important are connected with intentionally made, or prepared, elements.

Some of samples have shown unusually high amount of old pottery fragments [NIEM/05/160/a (10%), NIEM/05/161/a (32%)], other contained small rock pieces, mostly granitoids [NIEM/05/158/a (9,5%), NIEM/05/160/a (9%), NIEM/05/161/a (7%)] and some presented numerous organic fragments [NIEM/05/182/a (12%), NIEM/05/154/a (9%)]. Analysis have also shown that mineralogical composition of "thin" and "thick" wall pottery differed – "thin" wall pottery has been prepared with more careful selection of an admixture and noticeably smaller amount of pottery and rock pieces.

It was also possible to distinguish oxidation conditions of firing the vessels. Firing in majority was performed in an inaccurate oxidizing conditions [e.g. NIEM/05/199/a, NIEM/05/183/a] but few samples presented a type of reducing firing as well [NIEM/05/92/a, NIEM/05/154/a, NIEM/05/180/a] and these are going to be analyzed with an electron microprobe for the presence of an organic pigment in clay that would be responsible for the unusually dark color.

Presented observations allowed to recognize many technological details of vessels production. It has been possible to distinguish granulometric types of used grains and appoximate applied temperature of firing that has been rather low, around 500-700^{0}C.

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Very low-grade metasedimentary rocks of the Kaczawa Mountains (SW Poland) – preliminary mineralogical and geochemical data

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Here we present a new data on mineralogical composition and geochemical characteristics of metasedimentary rocks (mélange, metamudstones, metasandstones and phyllites) from various structural units of the Kaczawa Mountains (Sudetes, SW Poland).

The chemical characteristics of minerals (white mica, chlorite and feldspar) have been determined using Cameca SX100 electron microprobe (WDS system and BSE imaging). Based on the microprobe analysis white mica can be classiffied as illite/phengite. White mica and chlorite usually occur as small plates (few to several µm in size) filling in the pore space between larger grains of quartz and feldspar. Chlorite occasionally forms larger crystals (up to 100 µm) or intergrowths with white mica. Such intergrowths (chlorite-mica stacks) are more frequent in turbiditic sediments. Mg-Fe^{2+} type chlorite is dominant over more Fe-rich species. Feldpar in most of samples has composition of albite, with an exception of one type of the Radzimowice slate, which contains K-feldspar.

The whole-rock chemical analysis (59 elements per sample) of 20 samples allowed us to define more precisely the provenance of the metasedimentary rocks of Kaczawa unit, which based on smaller amount of samples in previous study (Kostylew et al. 2013) indicated an old continental crust as the likely main source for the sediments, with minor recycled sedimentary and trench-derived components.

The results of investigations support interpretations that the Kaczawa unit forms part of the Variscan accretionary prism, and as such is one the key areas for understanding the formation and evolution of the Variscan Belt in Central Europe.

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Kostylew, J., Kryza, R., & Zalasiewicz, J. (2013). Provenance and metamorphic conditions of very low-grade metasedimentary rocks of the Variscan accretionary prism of the Kaczawa Mts (SW Poland): geochemical and mineralogical evidence. *Mineralogical Magazine, Goldschmidt Conference Abstracts 2013, 77*, 1502.

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Fluid mediated alteration of REE-bearing phases in the Grängesberg apatite-iron oxide deposit, central Sweden

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The Kiruna-type apatite-iron oxide deposits of Bergslagen in central Sweden not only represent the biggest iron ore resource in central and southern Sweden, but also they are substantial occurrences of REE and P. Data from mineralogical, textural and mineral chemistry studies of the major REE-bearing assemblages in the Grängesberg deposit, comprising REE-fluorapatite, allanite-(Ce), monazite-(Ce) and xenotime-(Y), are presented here. Primary REE-enriched fluorapatite of orthomagmatic origin has been subjected to intensive fluid-mediated alteration. The first phase of, presumably acidic, fluid influx resulted in formation of inclusion swarms comprising monazite-(Ce) and xenotime-(Y) in the interior of fluorapatite grains. Inclusions formed by dissolution of parent fluorapatite and reprecipitation of (REE,Y)-phosphates, whereas additional elements (e.g. Ca, F) have been incorporated and transported away. Later stage of fluid activity caused leaching of both flourapatite inner parts and rims. This process resulted in mass transfer of REE, Y and P from fluorapatite and other elements from the silicate enriched groundmass and promoted the growth of mainly secondary allanite-(Ce) along with minor amounts of secondary monazite-(Ce) and xenotime-(Y) in interstitial spaces between fluorapatite crystals as well in fractures in fluorapatite.

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Characterization of the bricks from the Medieval castle in Wrocław (SW Poland) and identification of the construction phases by petrographic analysis

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This work describes the mineralogical characterization of historic bricks, sampled from the Medieval castle in Wrocław. The first castle in Wrocław was erected after 1175, on a river island called Ostrów Tumski. The results of archaeological research showed its complex inner structure and allowed to distinguish four main constructing phases. The first and the oldest one corresponds to a huge brick building, so called the 18-side tower house. At the beginning of the 13th century, it was followed by a large reconstruction. As a result, the Brick Palace was erected (the second constructing phase). In the mid-13th century the whole structure was surrounded by a fortified wall (the third constructing phase). In the following fourth constructing phase (80's of the 13th century), the residential core was again rebuilt and replaced by an another palace, so called the 8-side Hall. The aim of our study was to correlate two methods i.e. archaeological studies and petrographic studies of bricks, to identify and discriminate different constructing phases, on the basis of expected differences of the composition of the ceramic artifacts, resulting from different sources of the raw material. Thus, thirty four samples of the bricks, representing all constructing phases, were petrographically studied in details.

At the first glance, all bricks exhibit similar petrographic features. The ceramic body is composed of metaclay micromass, optically inactive to slightly active. Its color is reddish to dark brown in plane polarized light and brown to dark brown in between crossed polars. It contains ubiquitous grains, dominated quartz, with subordinate feldspars and rock-fragments (granitoids and cherts). Muscovite, biotite, hornblende, zircon and rutile are accessories. The silt fraction prevails over the sand grains, gravel fraction is absent. However, the in-depth study demonstrates differences between bricks belonging to individual construction phases. They include in the abundance of accessories, and small deviations from the typical grain-size distribution. The bricks from the 18-side tower house are strongly depleted in the very fine silt, whereas those from the 8-side Hall are enriched in this fraction. Typically, accessory minerals are rather uncommon, very small, up to 0.1 mm. However bricks from the Brick Palace are enriched in micas and hornblende. Their crystals reach up to 0.5 mm in length. Summing up, it can be stated that the petrographic observations confirmed all the distinguished constructing phases.

Acknowledgements: the research was supported by the National Science Centre Project (2012/05/B/HS3/03704)

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From magma genesis to ore formation;
evidence from macro- to nano-scales

KŁODZKO – ZŁOTY STOK INTRUSION

Field trip guide

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Field trip to the Kłodzko – Złoty Stok intrusion

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Introduction

Geological setting

The Kłodzko-Złoty Stok intrusion (KZI) is a composite pluton with a high mafic component. It is often erroneously called a "granite" intrusion, but it actually shows a very close affinity with mafic and lamprophyric rocks found all around the intrusion. The age of the KZI is constrained by zircon dating to be from 340 to 330 Ma (Mikulski, Williams 2013; Mikulski et al. 2013). The intrusion is situated between a few geological units and domains (Fig. 1).

In the NW it contacts the Bardo unit (BU), which is composed of Lower Carboniferous sedimentary clastic and diagenetic rocks with pyroclastic intercalations (Bojanowski et al. 2014), where some dated zircons from bentonite in the Paprotnia beds yielded 334 Ma or 337 Ma age (Kryza et al. 2008). Generally the BU has a stronger contact metamorphic effect than other units. In the NE the intrusion is cut by the Sudetic boundary fault (SBF) of the Alpine orogeny which in this part of the Sudetes replaces the older Variscan intra Sudetic fault (ISF – Aleksandrowski, 1998). In the SE and S, the intrusion contacts gneisses of the Śnieżnik massif (ŚM), which by the ENE part of the contact are tectonically changed into a mylonitic zone called Skrzynka shear zone (SSZ). Jawornickie granitoids (JG) intruded into the ŚM just a few km SE of KZI are 444-450 Ma years old (Białek, Werner 2004), and may have consolidated at 18-23 km depth (Białek, 2001). In the SW, the intrusion is partly cut the by Nysa graben (NG) which is part of the intra Sudetic basin (ISB). The intrusion contacts the Neoproterozoic and Cambro-Ordovician Kłodzko metamorphic complex (KMC); (Mazur et al. 2004). On the eroded surface of the KMC Upper Devonian limestones formed in a marine environment and form the base of this side of the BU. The intrusion's contact with these limestones is included in this excursion.

Petrological context

Mineralogical variety

Based on data in Wierzchołowski (1979), Lorenc (1991,1994) and our studies, the KZI is very varied, with a wide range of rocks and mineral parageneses: some relict ultramafic cumulates (Ol-Phl-Hbl pyroxenites > Ol-Px-Phl hornblendites > Ol-Px-Hbl "phlogopitites"), some Hbl-Px gabbros, Bt-Hbl diorites, Bt-Hbl tonalites,

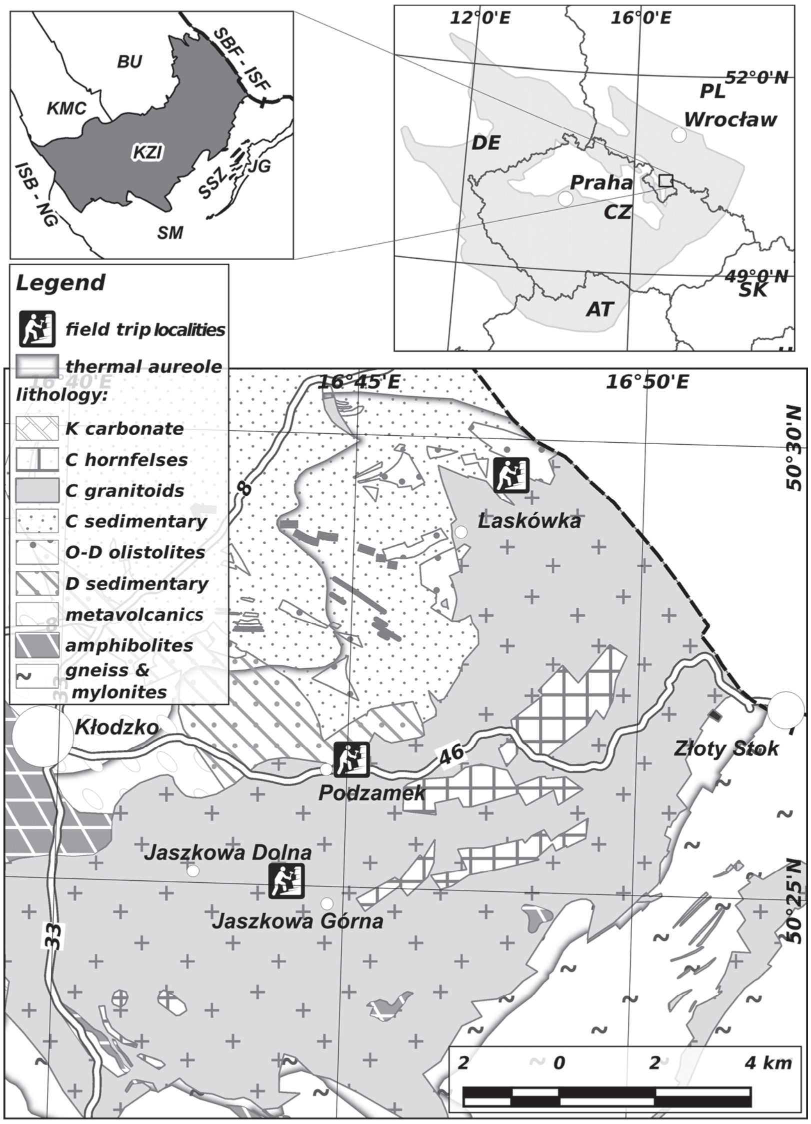

Fig. 1. Upper: surrounding geological units(after Aleksandrowski, 1997) and location in the Bohemian massif; lower: simplified geological map of KZI (based on Finckh et al, 1942; Cwojdziński, 1979ab). Abbreviations: BU – Bardo unit, ISB – intra Sudetic basin, ISF – intra Sudetic fault, JG – Jawornickie granitoids, KMC – Kłodzko metamorphic complex, NG – Nysa graben, SSZ – Skrzynka shear zone, ŚM – Śnieżnik massif, SBF – Sudetic boundary fault.

Phl-Hbl-(Opx/Ol)-Cpx (Qtz) melanocratic syenites, dominant Cpx-Bt-Hbl monzo-granodiorites/ granodiorites, minor Hbl-Bt monzogranites, some intrusion-associated andesites and dacites with a wide range of mineral compositions: i.e. Pl – 10-90% An (Fig. 4) often oscillatory zoned;Ca-Amph - actinolite/ tremolite – pargasite/ hastingsite; dark mica- phlogopite (*sensu stricto)* – annite; Cpx and Opx with mg# from 90% to <50%. Among the accessory minerals apatite is dominant (in some rocks exceeding 5%), with zircon, allanite, ilmenite or titanite. Magnetite is rare, instead in most rocks accessory (or even 5%) amounts of Fe sulphide phases such as pyrite or/and pyrrhotite are present. Tiny (<few µm) chromite grains often are associated with pyroxene mantled by amphibole. No white micas are present, except a very small amount in the pegmatites. No garnet, cordierite or any other Al mineral typical of S-type granites have been found.

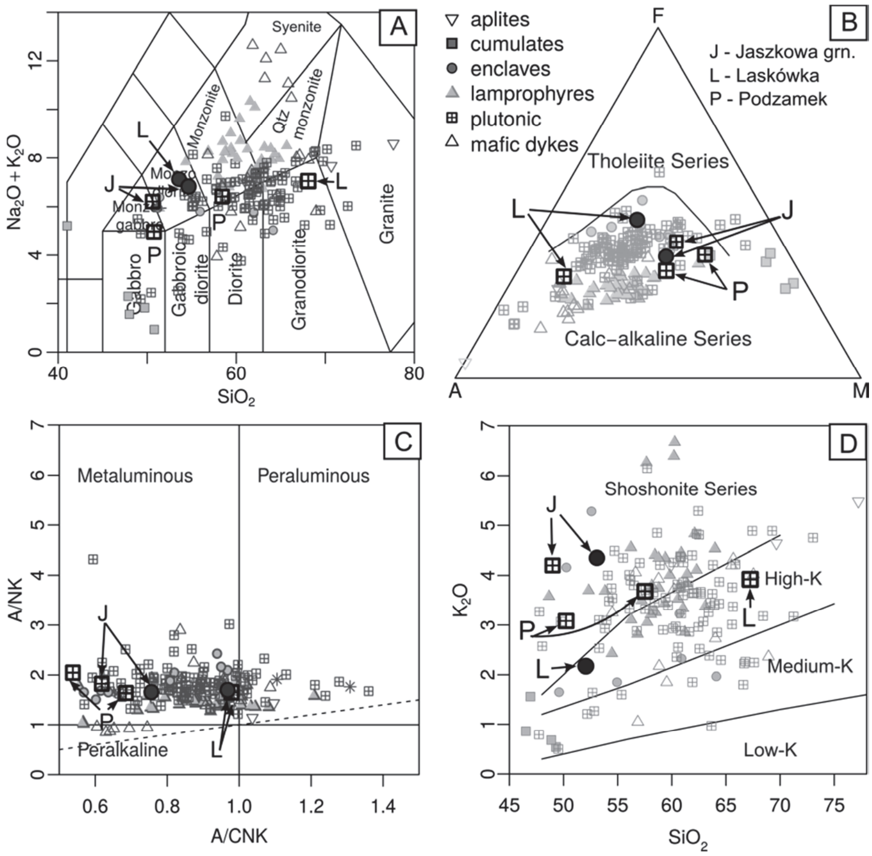

Fig. 2. A - TAS classification of plutonic rocks (Middlemost 1985); B - AFM diagram (Irvine, Baragar 1971); C - diagram of Shand's (1943) coefficients; D - SiO_2-K_2O diagram, lines after Peccerillo, Taylor (1976); (data used from Awdankiewicz 2007, Wierzchołowski 1977; Lorenc 1991,1994; Mikulski et al. 2013 and our unpublished data)

Textures

The rocks are highly heterogeneous, textures mostly changing over a few or tens of meters where the granitoid can be coarse-grained, fine-grained or porphyritic, with mafic magmatic enclaves, streaks and aplite dykes. Numerous andesite, dacite and lamprophyre dykes intrude the pluton, and many magma mixing textures are preserved. The dense spatial coverage of outcrops makes it possible to estimate the variety of intrusive rocks and the afore-mentioned textures can be observed in most randomly chosen outcrops.

Geochemical composition

The KZI suite has a very wide compositional range where it is difficult to identify any dominant trend. However most analyses occupy the metaluminous, calc-alkaline (Fig. 2) classification field. It is clear that the diversity of rocks was caused by a number of repeated magma processes such as fractionation and mixing, and not by one process alone. The primary magmas were generated in different regions of an ultra-heterogeneous mantle source. Plate convergence in an Andean-type subduction setting is most likely, judging from: the prolonged duration of magmatism (lasting at least 10 Ma according to zircon dating), the high amount of water in primary melts and all magmatic suites, and the Nd and Sr isotopic data (Fig. 3) where more mafic but colder members (and richer in H_2O) have a more "crustal" signature inherited from ocean water released from the subducted slab and subducted sediments.

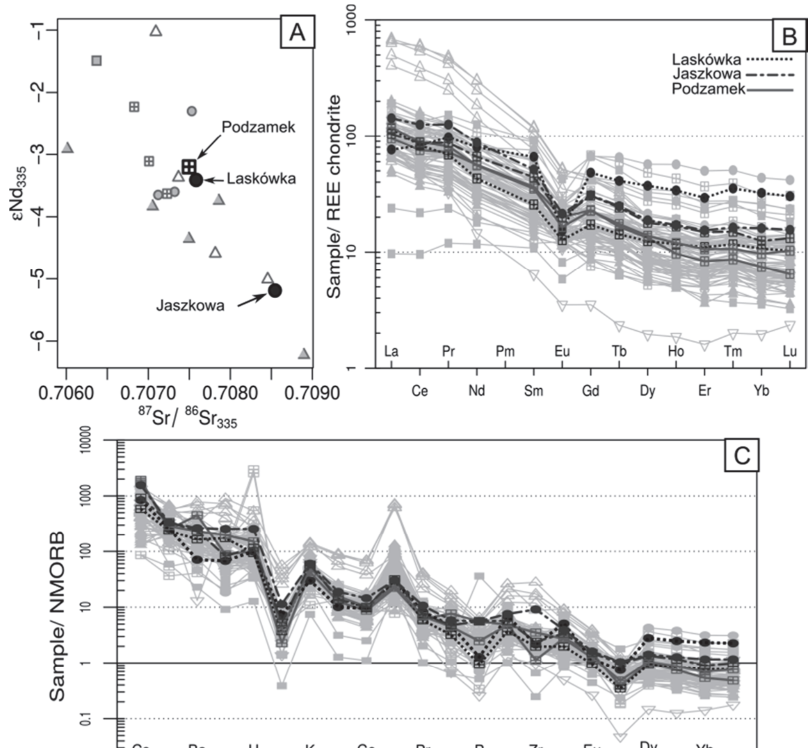

Fig. 3. An epsilon Nd vs $^{87}Sr/^{86}Sr$ initial; B - REE spider diagram normalized to chondrite (Nakamura 1974); C: spider diagram of trace elements of KZI rocks normalized to NMORB (Sun, McDonough 1989); symbols are the same as in previous diagram; data from Awdankiewicz (2007) and our unpublished material.

We have prepared three easily accesible (jump out of the bus – pick up the rock) stops to show key processes in the formation of the Kłodzko-Złoty Stok intrusion as we understand it.

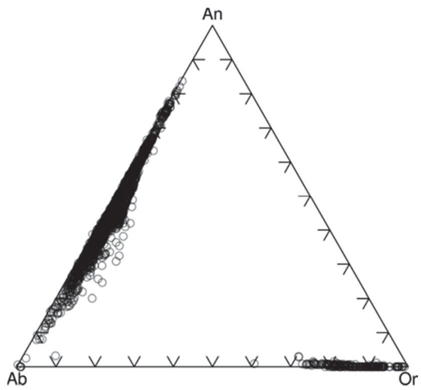

Fig. 4. Feldspar composition in KZI rocks

At Stop 1 we will see felsic plutonic rocks (Hbl-Bt-monzogranites/ granodiorites) with mafic magmatic (diorite) enclaves and xenolithes.

Dominant rocks of intrusion (Cpx±Bt-Hbl granodiorites) with beautifully preserved mingling textures (microsyenite/lamprophyre) will be seen at Stop 2.

At Stop 3 we will show the contact of the intrusion with carbonate rocks and the mineralogically diverse skarns formed. In the vicinity, melanocratic Bt-Hb-Ol-Cpx and Bt-Hbl-Opx-Cpx Qtz syenites similar to durbachites outcrop.

Stop nr 1: Laskówka (16.79075 E 50.48837 N)

At the northern boundary of the village of Laskówka, on the east side of the road to Bardo, leucocratic granodiorites outcrop in a small quarry. Granodiorites are typical of the Laski – Laskówka vicinity, with some rare more leucocratic granite subtypes locally. Most of the rocks from the vicinity contain enclaves, most of which are magmatic mafic (MME), but a few are rather xenoliths of wall rocks.

The MME have a dioritic mineral composition, but contain much more Hbl and Bt than the host granodiorite. Thus the chemical classification is not robust and approaches the monzo- fields (Fig. 2A).

Some of the enclaves lack chilled margins, and have sharp boundaries (Fig. 5B).

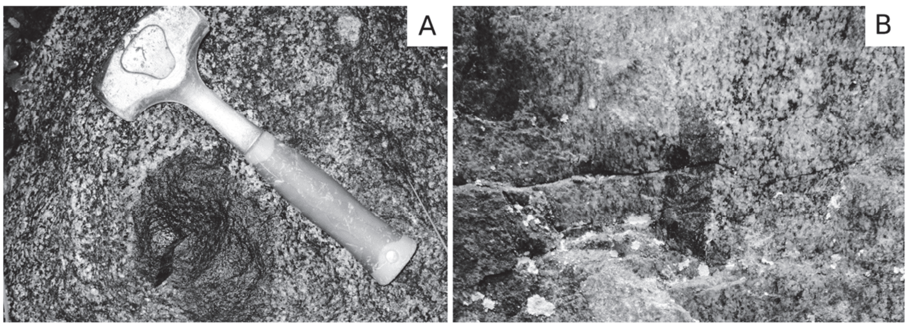

Fig. 5. Laskówka enclaves: A – MME; B – xenolith. Magnification similar for both photos. The hammer for scale, ca. 25 cm in length.

Stop nr 2: Jaszkowa Górna (16.72816 E 50.41093 N)

In Jaszkowa Górna 100 m north of the main road we will follow a track to the old chapel, where the best developed mingling textures between porphyritic granodiorite and lamprophyric melts outcrop. The outcrop is very important for several reasons. Firstly the rocks provide evidence of unconsolidated granitoid magma mixing with lamprophyre magma. Mafic streaks are difficult to classify as lamprophyre on mineral compositions alone. They look at first sight more like micro-poikilitic-syenites (huge Kfs crystals hosting a Px, Amph and Bt). However a more detailed textural study and the very close affinity in geochemistry of major and trace elements and Rb-Sr and Sm-Nd isotopes with the lamprophyres, especially those from Mąkolno and lamprophyroids from Rogówek, leave no doubt as to the lamprophyric origin of the streaks. Secondly, microenclaves composed mostly of amphibole agglomerates with mantled Cpx are very common in most of the KZI granitoids. Enclaves alone show no affinity with the lamprophyres, as Hbl tends to re-equilibrate to plutonic conditions and the Kfs and Pl components are often lost to the granitoids. Evidence of such enclave generation by lamprophyre melt is one more argument that mixing of granitoid and lamprophyre magmas was much more common than previously thought.

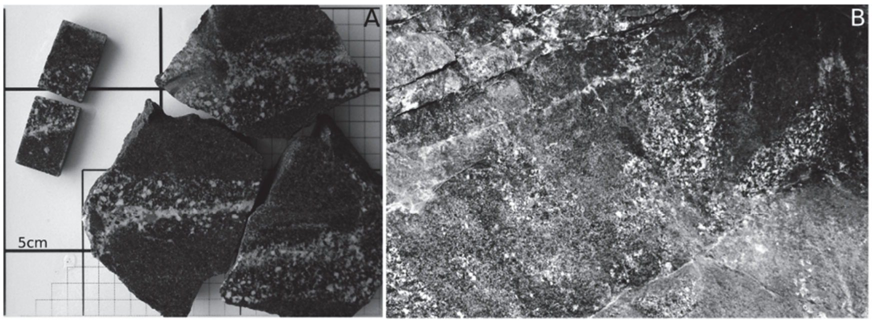

Fig 6. A: cut slabs perpendicular to surfaces between streaks and granodiorite; B: *in situ* picture of the same rocks. Samples from Jaszkowa Górna outcrop. Magnification similar for both photos.

Stop nr 3: Podzamek (16.74562 E 50.43383 N)

Melanocratic Qtz syenites outcrop *in situ* on the old track. More basic types can be found in boulders in the stream. There are a few occurrences of syenites: Qtz- bearing (Bt-Hbl-Opx-Cpx Qtz syenite) and Qtz-free (Bt-Hbl-Ol-Cpx syenite), where the latter contains in addition accessory minerals such as baddeleyite.

Some of the most interesting aspects are:

Cpx as might be expected is overgrown on the rims by amphibole, Cpx is not in equilibrium with Opx – according to the Kd_{Fe} (Putirka 2008). Zoned plagioclases contain up to An_{70} composition. Kfs has a very high concentration of Ba (up to 3.4%) in innermost parts. Kfs in Qtz syenite forms a weak granophyric texture, most commonly observed in granitoids contacting skarns.

Syenites have micro-enclaves composed of phlogopite, Opx, tiny chromites and minute pyrrothite.

Among the accessory mineral phases, apatite-(Cl) is dominant, zircon, ilmenite and some monazite are abundant, and baddeleyite, U-Th oxide, chromite and pyrrothite are less common.

From the mineralogical and geochemical points of view the melanocratic syenites show some affinity to lamprophyres and could possibly be a plutonic type of lamprophyre.

The main stop is in a small abandoned marble quarry. It was opened just at the contact between the intrusion and sedimentary rocks of the Bardo unit, predominantly composed of detrital fine-grained rocks (from wackes to siltstones) with some inclusions of carbonates (which we see in the quarry). At the contact we can observe, as a result of contact metamorphism, scarn rocks. These are structurally complex. We can find them as small (up to a few dozens of cm) pockets composed mostly of calcite, garnet (grossular, andradite and schorlomite), diopside-hedenbergite clinopyroxenes and prehnite. In faults and cracks we can observe scarn rocks as pseudo-veins or elongated bodies a few meters long and a few cm thick. As minor phases we can find vesuvianite, wollastonite and tremolite-ferroactinolite amphiboles. Contact metamorphism conditions in this part of aureole were estimated to be ca. 600°C (Bagiński 2002).

Acknowledgements: This work was supported by project N N307 634840 financed by MNiSW.

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From magma genesis to ore formation; evidence from macro- to nano-scales

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AUTHOR'S INDEX

Erratum

Chemical composition of glasses and associating mineral species in various pyrometamorphic rocks from coal-mining dumps of the Lower Silesia by Łukasz KRUSZEWSKI, Justyna CIESIELCZUK, Magdalena MISZ-KENNAN, Monika FABIAŃSKA, pages 70-71 of this volume.

On page 71 of the volume the statement on financial support is missing in the abstract. Upon the authors' request, the following lines should be added after the main text of the contribution:

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