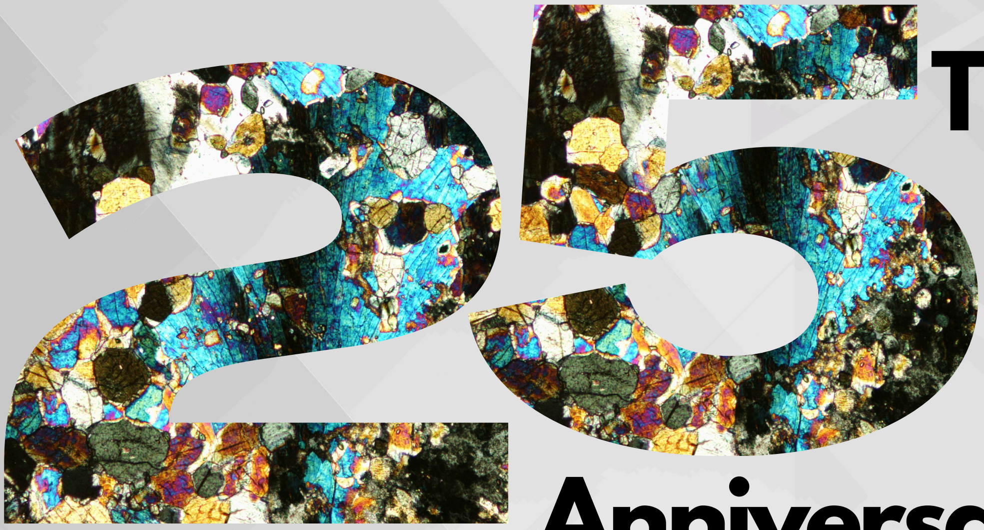

25TH Anniversary of the Microprobe Laboratory

FACULTY OF GEOLOGY UW

17-18 June 2024

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Evgeny GALUSKIN[1], Irina GALUSKINA[1]

[1]*Institute of Earth Sciences, Faculty of Natural Sciences, University of Silesia, Będzińska 60, 41-200 Sosnowiec; e-mail: evgeny.galuskin@us.edu.pl, irina.galuskina@us.edu.pl*

In 2010 we received a 2×2×1 cm sample of larnite rock collected by Mikhail Murashko in 2008 from a large outcrop of pyrometamorphic rocks on Jabel (mountain) Harmun, near the Nabi Musa village in the Judean Desert, the possible burial site of the Prophet Muhammad (Galuskina et al., 2017). In 2012 while working on the new mineral nabimusaite from the arctite supergroup, Dr. Piotr Dzierżanowski discovered in the thin section of this sample an inclusion of chalcocite, Cu_2S, with oldhamite, CaS, grain inside. A thin ~10 µm rim of sulphide with a composition corresponding to the thiocuprate, $CaCu_2S_2$, was found around the oldhamite. This mineral formed as a result of the chemical reaction: $Cu_2S + CaS = CaCu_2S_2$.

The size of the $CaCu_2S_2$ grains did not allow for single crystal structural studies. It was therefore decided to use the EBSD method, but a problem arose - microprobe analyses of this potentially new mineral did not give total close to 100% and were poorly calculated on stoichiometry. This problem was solved by Dr. Piotr Dzierżanowski, who noticed that different grains of $CaCu_2S_2$ had different cathodoluminescence, ranging from bright orange to pale yellow. $CaCu_2S_2$ has been subjected to intense changes both in natural processes at low temperatures and in contact with air. Qualitative analyses of $CaCu_2S_2$ were carried out on freshly prepared grains of the bright orange luminescent mineral.

When choosing the name of the mineral, we had no doubt that it should be named after the scientist who not only discovered it, but also solved the methodological problem related to its chemical composition. In 2014 the new mineral dzierżanowskite was approved by the Commission of New Minerals, Nomenclature and Classification of the International Mineralogical Association.

In 2015, the second discovery of dzierżanowskite was associated with the finding of unusual jasmundite-bearing rocks that formed 1–1.5 m diameter rounded forms (‘paleofumaroles’) in low temperature hydrothermal rocks containing larnite pseudoconglomerates. The jasmundite, $Ca_{11}(SiO_4)_4O_2S$, formed a series of linear crystals in the altered rock. The rock primary minerals were flamite, brownmillerite, fluormayenite and fluorellestadite. The jasmundite contained numerous ovoid oldhamite inclusions surrounded by a rim of dzierżanowskite and other copper sulphides. The discovery of a new genetic type of dzierżanowskite significantly prolonged the time required to prepare scientific manuscript describing the mineral, which was published in Mineralogical Magazine in 2017 after the untimely death of Piotr Dzierżanowski.

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History of the discovery of eringaite

Irina GALUSKINA[1], Evgeny GALUSKIN[1]

[1]Institute of Earth Sciences, Faculty of Natural Sciences, University of Silesia, Będzińska 60, 41-200 Sosnowiec; e-mail: irina.galuskina@us.edu.pl, evgeny.galuskin@us.edu.pl

The Wiluy locality (Republic of Sakha-Yakutia) of grossular, vesuvian and pseudomorph of achtaragdite has been known since 1790, when the academician E. Laksman discovered this interesting mineralogical object and brought samples to many museums. The author of grossular is A. G. Werner, who named the green garnet crystals grossular in 1808.

At present, the classic locality is at the bottom of the Wiluy reservoir, which was created during the building of a hydroelectric power station on the Wiluy River in 1965–1967. However, on the banks of the Wiluy reservoir, outcrops of light aposkarn rodingite-like rocks have been exposed, containing crystals of grossular, vesuvian-wiluite and pseudomorphs of achtaragdite.

Ca-garnets containing Sc_2O_3 have been found in a large xenolith of grossular-vesuvianite rodingite-like rocks interbedded with serpentinites and chlorite rocks hosted in the ~250 Ma Erbeekskaya gabbro-dolerite intrusion outcropping in the Wiluy River, Republic of Sakha-Yakutia (Galuskina et al., 2005). This intrusion belongs to the Siberian Trap Formation.

The history of the discovery of scandium garnet is directly related to Piotr Dzierżanowski. In the early 2000s Zr-Ti garnets of the schorlomite-kimzeite-kerimasite series were found. For a long time it was not possible to obtain good quality analyses, the totals were significantly underestimated. We felt that the measurement conditions and standards chosen were not suitable for the phases studied. EDS analyses of these garnets showed that the main components in their composition are Ca, Al, Fe, Zr, Ti and Si. Piotr solved the problem of the low totals in the analyses of these garnets was by. He found that Sc, whose lines in the EDS spectra overlap with those of Ca and Ti, had not been analysed. For Sc_2O_3 contents up to 5 wt. % it was difficult to see the thickening of the line CaKβ. We did not expect Sc in the composition of garnet, especially since these rocks do not contain other Sc-bearing minerals. The correct development of the technique for measuring Sc in garnets not only allowed us to describe the zonal scandium schorlomite (Galuskina et al., 2005), but after a targeted search we discovered a new garnet called eringaite, named after the Eringa River, a tributary of the Wiluy River. Eringaite was later discovered in meteorites and is thought to be one of the first garnets to form in the solar system (Ma, 2012).

Eringaite, a scandium garnet with the ideal formula $Ca_3Sc_2(SiO_4)_3$, was discovered in 2010 (Galuskina et al., 2010). The empirical formula for eringaite with a Sc_2O_3 content of 11.20 wt. % is:
$(Ca_{2.98}Y_{0.01}Mg_{0.01})_{\Sigma 3}(Sc_{0.82}Ti^{4+}_{0.44}Fe^{3+}_{0.30}Zr_{0.21}Mg_{0.10}Al_{0.09}Cr^{3+}_{0.08}Fe^{2+}_{0.05}V^{3+}_{0.01})_{\Sigma 2.01}(Si_{2.48}Al_{0.30}Fe^{3+}_{0.22})_{\Sigma 3}O_{12}$.

Together with Piotr Dzierżanowski, 31 new minerals have been discovered and described thanks to his direct involvement in the projects.

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25th anniversary of the Microprobe Laboratory at the Faculty of Geology, University of Warsaw – 22nd anniversary of my cooperation with the Jubilate: a short retrospection

Adam PIECZKA[1]

[1]*Department of Mineralogy, Petrography and Geochemistry, AGH University of Krakow, 30-059 Krakow, Mickiewicza 30; e-mail: pieczka@agh.edu.pl*

The first information about the establishment of the Microprobe Laboratory at the Faculty of Geology of the University of Warsaw I received from colleagues Dr. S. Ilnicki and Dr. K. Nejbert in October 2001 at the annual meeting of the Petrology Group of the Mineralogical Society of Poland. In 2002, I was invited by S. Ilnicki to a one-day free microprobe session at the Laboratory, probably so that I could directly become acquainted with capabilities of the CAMECA SX 100 microprobe that had been launched. The session took place in February 2003. I don't know who was the direct initiator of this invitation, but I would like to thank the person very much after 22 years. I think that probably someone at the University of Warsaw, Faculty of Geology community believed in me at that time as a potentially valuable collaborator, in spite of that since the mid-1990s I had been cooperating with the microprobe laboratory at the Institute of Non-Ferrous Metals in Gliwice.

In the following years up to date I have performed microprobe analytics at the University of Warsaw Laboratory for 7 KBN, MNiSzW and NCN grants, including 5 in which I was the Principal Investigator; in total, I had 105 two- to five-day microprobe sessions. The implementation of subsequent projects more and more frequently led to the need to identify new mineral species, unknown to science, found in the studied domestic geological formations. Due to certain equipment limitations and inability to extract very small fragments of these phases to structural studies, I cooperated at that time with a few foreign mineralogists and crystallographers. Obtaining the ability of manual extraction of microcrystals as well as their cutting with the Focused Ion Beam technique, enabled me and my cooperating colleagues from my university, the University of Warsaw, the University of Wrocław, and the University of Silesia to carry out all the necessary researches in national units, including the latter in structural research laboratories at the Faculties of Chemistry of the University of Warsaw and the Jagiellonian University equipped with modern equipment for such research.

The scientific result of this cooperation with the Microprobe Laboratory of the University of Warsaw is about 76 articles and 21 scientific communications (excluding conference abstracts) in indexed foreign journals, mainly *American Mineralogist*, *European Journal of Mineralogy*, *Mineralogical Magazine*, *The Canadian Mineralogist*, etc., 13 in the *Mineralogy* (Mineralogia Polonica) journal, and the discovery of 21 new minerals from Poland [nioboholtite, titanoholtite, szklaryite, pilavite-(Y), bohseite, żabinskiite, maneckiite, graftonite-(Ca), graftonite-(Mn), beusite-(Ca), silesiaite, lepageite, parafiniukite, thalliomelane, kozłowskiite, scandio-winchite, beryllosachanbińskiite-Na, beryllocordierite-Na, heflikite, magnesio-dutrowite, allanite-(Sm)]; currently under the vote of the IMA CNMNC is our new proposal related to dubińskaite – a new mineral of the axinite group. Based on some of the results, I prepared together with foreign and domestic mineralogists classifications of a few mineral groups, e.g. the dumortierite supergroup, the graftonite group and the kristiansenite group. In a sense, these achievements are also achievements of the Laboratory. All of them, but also others more personal, would not have been possible without this basic decision from about 25 years ago to organize the Microprobe Laboratory at the Faculty of Geology of the University of Warsaw, and later to give it the organizational form that can be paraphrased as the Open Access form. For all this, on the 25th anniversary of this Laboratory, I would like to warmly thank its organizers and the current management. I would also like to thank for the kindness of the staff working there: in the beginning Dr. Piotr Dzierżanowski and Lidia Jeżak, and currently Dr. Beata Marciniak-Maliszewska and Dr. Petras Jokubauskas.

Twenty years of the Lithuanian-Polish collaboration on EPMA monazite dating: implications for the Precambrian metamorphic history of Lithuania

Grazina SKRIDLAITE[1], Laurynas SILIAUSKAS[1], Boguslaw BAGIŃSKI[2]

[1]*Institute of Geology and Geography, Nature Research Centre, Akademijos 2a, Vilnius, Lithuania; grazina.skridlaite@gamtc.lt*
[2]*Department of Geochemistry, Mineralogy and Petrology, Faculty of Geology, University of Warsaw, 02-089 Warsaw, Poland; b.baginski1@uw.edu.pl*

The deformed charnockites (Lz1/795) in the extension of the Mazury complex into S Lithuania were the first rocks from Lithuania dated by the monazite approach at the EPMA facility, University of Warsaw in 2005-2006. After a presentation at the EGU General Assembly in 2006, the results were published in Gondwana Research in 2008.

Since the EPMA method allowed dating of monazite grains in areas where metamorphic reactions were recognized (in polished thin sections), it provided a unique opportunity to correlate the obtained ages directly with the defined metamorphic events. The monazite data helped to distinguish high-grade events at 1.81–1.79 Ga, c. 1.73–1.68 Ga, 1.62–1.58 Ga, and 1.52–1.50 Ga in the metapelitic granulites (Lk1 and 5, Pc3, Bl150, Tr11) and charnockites (Vd1, Sh3, Fig. 1) in the Precambrian of western Lithuania. Despite large errors, the results were in perfect fit with relevant zircon ages. Most of the data appeared in the article "Recurrent high-grade metamorphism recording a 300 Ma long Proterozoic crustal evolution in the western part of the East European Craton (Skridlaite et al., 2014, Gondwana Research).

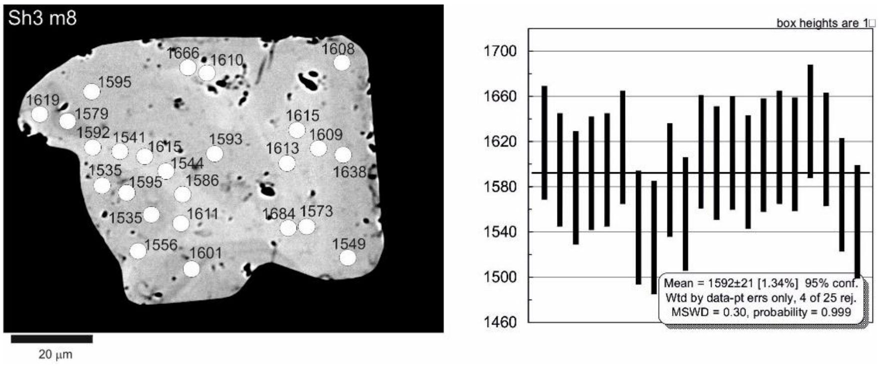

Fig. 1. Photomicrograph of the Sh3 charnockite with its metamorphic age of ca. 1.6 Ga (monazite average age; Skridlaite et al., 2014)

In S and E Lithuania, the EPMA results of mineral chemistry and monazite dating helped to characterize magnetite in the Varena Iron Ore deposit and the surrounding rocks, and to date some rocks and ore-forming events (cf. Siliauskas et al., 2018, etc.).

The monazite dating results allowed us to attribute peculiar granitoids in mid-Lithuania (Pm97) to the chain of ca. 1.45 Ga post-orogenic, AMCG intrusions. Nowadays, when emphasis is put on critical raw materials, continuation of the Lithuanian-Polish collaboration on the EPMA application to the mineral chemistry of ores and accessory minerals and monazite dating can provide excellent results of a broad, international significance.

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Titanite breakdown to rutile during the albitization of the Sakar granitoid batholith, SE Bulgaria: nature and experiment

Daniel HARLOV[1], Anna GUMSLEY[2], Rafał JUROSZEK[3], Beata MARCINIAK-MALISZEWSKA[4], Petras JOKUBAUSKAS[4], Ianko GERDJIKOV[5]

[1]Helmholtz-Zentrum Potsdam, Deutsches GeoForschungsZentrum - GFZ, Telegrafenberg D-14473 Potsdam, Germany;
e-mail: dharlov@gfz-potsdam.de
[2]Institute of Geological Sciences, Polish Academy of Sciences, 31-002 Kraków, Poland
[3]Institute of Earth Sciences, University of Silesia in Katowice, Będzińska 60, 41-205 Sosnowiec, Poland
[4]Faculty of Geology, University of Warsaw, Żwirki i Wigury 93, 02-089 Warszawa, Poland
[5]Faculty of Geology and Geography, University St. Kliment Ohridski', 15 Tsar Osvoboditel Blvd., 1504 Sofia, Bulgaria

Petrologic and mineralogic studies of the Sakar Batholith (Strandja Zone, SE Bulgaria/NW Turkey) revealed that rutile-rich aggregates were formed during albitization at ~600 °C and ~300 MPa. This observation has been tested experimentally.

Four experiments involving fluid-aided alteration of titanite in a granitic system were conducted using cold-seal autoclaves on a hydrothermal line at 280 MPa and 600 °C. A series of four alkali-bearing fluids consisting of $NaCl+H_2O$, $NaF+H_2O$, $Na_2Si_2O_5+H_2O$, and 2M NaOH were used. The starting material included natural titanite and synthetic fluorapatite grains together with a powdered granite mix. Two experiments involving $NaCl+H_2O$ (RT-1) and $NaF+H_2O$ (RT-2) resulted in rutile forming from titanite. The mineral assemblage formed in experiment RT-1 consisted of rutile, Ti-Th-U oxides, and monazite, whereas in experiment RT-2 rutile, fluorite, lorenzenite, albitized plagioclase, REE-enriched rims on fluorapatite, and a glass formed. The comparison between natural observation and the experimental results from this study supports the premise that a $NaCl+H_2O$ fluid was responsible for the albitization of the Sakar Batholith, which further supports the role of NaCl-bearing fluids during the albitization of granitoids.

In general, this study demonstrates that metamorphic/hydrothermal rutile can form from titanite in a granitoid system at mid- to upper-crustal pressures in the presence of alkali-bearing fluids, specifically NaCl- and NaF-bearing fluids. An important implication from these experiments is that the presence of rutile (as opposed to titanite) in granitoid rocks alone is not an indicator of high-pressure conditions, but rather the geochemical relationship between rutile from titanite is more a function of the chemistry of the fluid and host rock, especially if they are Na-rich, rather than the P-T conditions.

EMPA and SEM study of the reaction rims on zircon megacrysts from Devonian kimberlites in the Azov Domain of the Ukrainian Shield

Leonid SHUMLYANSKYY[1], Bogusław BAGIŃSKI[2]

[1]*Institute of Geological Sciences of the PAS, ul. Twarda 4, Warsaw, Poland; e-mail: lshumlyanskyy@yahoo.com*
[2]*Faculty of Geology, University of Warsaw, ul. Żwirki i Wigury 93, Warsaw, Poland; e-mail: b.baginski1@uw.edu.pl*

Zircon megacrysts often occur in kimberlites and, together with other minerals, they constitute an assemblage known as the “low-Cr suite”. They usually reveal ages and isotope systematics similar to the host kimberlite that support their cognate origin. However, this is not the case for the Middle Devonian Novolaspa kimberlite pipe and dyke located in the Azov Domain of the Ukrainian Shield. The U-Pb age of zircon megacryst was found to be 14 m.y. older than the age of kimberlite emplacement. Moreover, alteration rims commonly surround zircon megacrysts, providing evidence for the chemical nonequilibrium between the megacrysts and kimberlitic melts (Tsymbal et al., 2011; Shumlyanskyy et al. 2021a), although some crustal xenocrystic zircons do not reveal any alteration (Shumlyanskyy et al., 2021b).

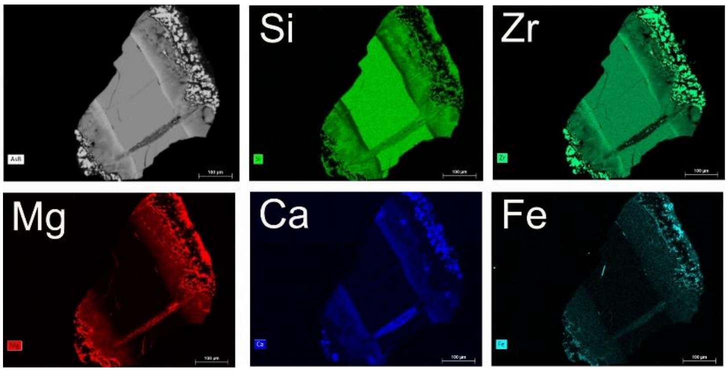

Fig. 1. Chemical maps of the studied zircon crystal surrounded by alteration rims.

The boundary between the unaltered crystal and the alteration zone is very sharp. The unaltered crystal does not reveal any variation in chemical composition close to the boundary. A narrow layer composed of serpentine is located directly on the contact. It is followed by a wide zone composed of fibrous zircon-like mineral. It has a variable composition with different zones situated parallel to the contact with the primary zircon. In places, zircon-like mineral forms tight intergrowths with thin baddeleyite lathes, oriented normally to the initial zircon interface.

The outer zone is composed of euhedral crystals of baddeleyite, while the interstitial areas are filled with serpentine, diopside, phlogopite, titanite, apatite, and calcite. The alteration was accompanied by the removal of silica and increase of other elements, including Fe, Ti, Mg, and highly incompatible trace elements.

According to Tsymbal et al. (2011), the chemical composition of the newly-formed minerals in the alteration rims indicates their formation at low pressure, decreasing temperature and increasing oxygen fugacity, i.e. during the final stages in the evolution of the kimberlite melt.

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Electron microprobe as a tool in environmental geochemistry

Jakub KIERCZAK[1]

[1] *Department of Experimental Petrology, Institute of Geological Sciences, University of Wrocław, Pl. M. Borna 9, 50-204 Wrocław, Poland; e-mail: jakub.kierczak@uwr.edu.pl*

Environmental geochemistry focuses on studying the chemical composition of various components of the environment (rocks, soils, water, air). It analyzes biogeochemical cycles of elements and more complex chemical compounds, and their impact on ecosystems and human health. Minerals and their synthetic equivalents, formed as a result of intentional or unintentional human activities, play an important role in biogeochemical processes. Therefore, mineralogical sciences are closely related to environmental geochemistry. This close relationship is particularly evident in studies focused on identifying, tracing, and understanding the migration of pollutants within the environment. Knowledge of the phase composition of environmental samples can also be useful in developing methods for removing contaminants from soil and water, such as using contaminant-absorbing minerals.

Studies aimed at determining the mobility of pollutants in the environment are usually based on indirect methods. Typically, these procedures involve assessing the leachability of potential contaminants from soil or waste samples. The test sample is placed in a solution designed to simulate natural environmental conditions, and the content of contaminants in the leachate is then determined. Indirect methods, however, do not identify the main carriers of the contaminants, they are also not able to imagine how the weathering and dissolution proceed in the solid product. These are information that add much value to the environmental research and help to visualize the main pathways of elemental migration. Microanalytical techniques (including electron microprobe) are the perfect tool to provide information on such aspects of environmental studies. Electron probe microanalysis (EPMA), is a direct method for identifying and accurately quantifying contaminants in environmental samples. Based on the analysis of the chemical composition of materials, it is possible to determine the geochemical form in which potential contaminants are present in the studied environmental samples. If these data are supplemented by knowledge of the stability of different mineral phases in the environment, we then have a complete set of information on the mobility of contaminants.

The purpose of this presentation, prepared for the 25th Anniversary of the Microprobe Laboratory at the Faculty of Geology of Warsaw University, is to show examples of the application of electron microprobe analysis to environmental studies of the mobility of metallic contaminants. Research on the distribution and mobility of metallic elements in natural and anthropogenic soils and industrial wastes will be presented, highlighting the applicability of electron microprobe analysis in environmental studies.

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Petras JOKUBAUSKAS[1]

[1]Laboratory of Electron Microscopy, Microanalysis and X-ray Diffraction, Faculty of Geology, University of Warsaw, Żwirki i Wigury 93, 02-089 Warsaw, Poland; e-mail: p.jokubauskas@uw.edu.pl

This presentation is about small incremental steps and activities in facility of electron microprobe and microanalysis (two Electron Probe Micro-Analyzers (EPMA): Cameca SX100 and SXFiveFE), which is currently part of the Laboratory of Electron Microscopy, Microanalysis and X-ray Diffraction at Faculty of Geology, at University of Warsaw.

The title is three decimal numbers [10/ 25/ 40] encoded in hexadecimal numeric system with a hidden meaning of ‘Foreseeing next 15 years based on 15 year experience and current state of the facility’. It is about hidden from eyesight progress of method. It means the increased availability, stability, accuracy and precision – the improvements of these properties as the result of long and systematic on-site research and development in past years and plans for the future. This includes such activities as: spatial room temperature long-term recording and its analysis and following rearrangement of P10 gas installation and air conditioning; upgrading roughing pumps; upgrading vacuum detection system; studying Schottky’s emitter working principles and replacing official operation procedures with physics-based procedures; troubleshooting, fixing and upgrading hardware; reverse engineering data formats and communication protocols; making efforts to include both microprobes in the fundamental international EPMA method research activities and etc.

Most of those listed activities made small incremental improvements or at least raised the awareness of lurking unknown negative impact to analysis and steered analytical procedures to minimize the external variables. As an example, most of analytical conditions in this facility was based on two-side background measurements for peak-background determination 10 years ago. In contrast, currently updated or made from scratch analytical setups are redesigned to use ‘single background measurements with precisely determined universally applicable slope’ strategy (I am sure that we are the only facility in the world doing such a move), which increases accuracy and precision with no analytical time penalty. Also, world-uniqueness of the facility could be claimed for peak overlap correction procedures being applied to extreme: 127 overlap corrections for single setup designed for full analysis of HFSE+REE+silicate/phosphate (43 measured elements in a single setup). The chemical dating analytical setup is another example for stability improvements. That is a repeatable age of 1045 Ma (±10) for Namaqualand Monazite sample independently from the year season or day cycles, without any major tinkering of the setup in the last 5 years.

During last 10 years the character of activities keep shifting from the software solutions toward tinkering of the hardware. Some improvements are already made by upgrading physical parts of EPMA’s and more are planned for the future. Thus, I predict that in next 15 years, this facility will stay competitive price-wise while offering precise, accurate analysis with further increased efficiency and reliability.

Islamic glazed pottery from Dülük Baba Tepesi (south-east Turkey): technology and provenance

Małgorzata DASZKIEWICZ[1], Eva STROTHENKE-KOCH[2]

[1]*Institut für Prähistorische Archäologie, Freie Universität Berlin, Fabeckstrasse 23-25, 14195 Berlin and ARCHEA Warszawa; e-mail: m.dasz@wp.pl*
[2]*Forschungsstelle Asia Minor, Universität Münster, Georgskommende 25, 48143 Münster; e-mail: eva.strothenke@uni-muenster.de*

Laboratory analysis was carried on pottery found at Dülük Baba Tepesi. A total of 47 sherds were selected for analysis, among them were 27 fragments of glazed pottery (one example see Fig. 1). The latter included samples taken from vessels, coated only with a single-colour glaze; some of them featuring sgraffito decoration. Samples taken from vessels with overglaze and underglaze decoration were also analysed.

Analysis of the glazed pottery included: macroscopic assessment of sherds, analysis of vessel wall cross-sections using a polarising microscope, analysis using a scanning electron microscope, as well as qualitative and quantitative analysis of the glaze's and sherds' chemical composition using an electron microprobe.

The aim of this analysis was to:

- determine the chemical composition of the glaze,
- estimate the chemical composition of the sherd matrix,
- examine the glaze/sherd interface,
- determine one of the aspects of the vessel firing process (single firing/multiple firing).

Chemical composition was analysed using a Cameca SX-100 microprobe (EPMA operator: dr. Petras Jokubauskas, Faculty of Geology, University of Warsaw).

Measurement accuracy was checked by measuring certified reference materials (CRM) used for glaze/glass analysis, such as: NIST SRM 610, NIST SRM 616 and Corning Standard Glass D.

Analysis revealed the use of alkaline as well as alkaline-lead and lead glaze. Firing was carried out once or multiple times, but this was not strictly correlated with the type of glaze. The glaze was applied directly to the vessel surface or over a slip.

Fig. 1. One of the analysed pottery fragment (MD7747)

Circa 2580–2574 Ma LIP-scale mafic magmatism in the Zimbabwe and Kaapvaal cratons – the oldest continent-continent collision no more?

Ashley GUMSLEY[1], Michiel DE KOCK[2], Katarzyna DUDZISZ[3], Martin KLAUSEN[4], Emilie LARSSON[5], Beata MARCINIAK-MALISZEWSKA[6], Johan RÅDMAN[5], Ulf SÖDERLUND[5]

[1]*Institute of Earth Sciences, University of Silesia in Katowice, Sosnowiec, Poland; ashley.gumsley@us.edu.pl*
[2]*Department of Geology, University of Johannesburg, Johannesburg, South Africa*
[3]*Institite of Geophysics, Polish Academy of Sciences, Warsaw, Poland*
[4]*Earth Sciences Department, Stellenbosch University, Stellenbosch, South Africa*
[5]*Department of Geology, Lund University, Lund, Sweden*
[6]*Faculty of Geology, University of Warsaw, Warsaw, Poland*

The timing of the amalgamation of the Zimbabwe and Kaapvaal cratons in southern Africa along the Limpopo Belt has long been debated. Arguments for this timing range from the late Neoproterozoic through to the late Paleoproterozoic. Most arguments are interpreted through the timing of metamorphic events and the deformational history within the Limpopo Belt itself and usually suggest a Neoproterozoic origin for amalgamation (e.g., Zeh and Kirchenbaur, 2022). However, studies utilising the large igneous province (LIP) barcode technique suggest amalgamation either in the Paleoproterozoic based on matches between the Mashonaland Sill Province (LIP) and the coeval ca. 1.9–1.8 Ga LIP events within Kaapvaal (i.e., the Black Range dykes, Waterberg sills, Soutpansberg sills and Soutpansberg lavas (Söderlund et al., 2010). However, paleomagnetic studies of these different mafic magmatic units between Zimbabwe and Kaapvaal have been used to argue for an even later amalgamation (Hanson et al., 2011). Here we present new U-Pb ID-TIMS crystallisation ages of ca. 2580–2574 Ma from an ENE-trending mafic dyke and a mafic sill on the southeasternmost region of the Kaapvaal Craton in northern KwaZulu-Natal, South Africa. These units cut across a ca. 2646 Ma NNE-trending mafic dyke. These ca. 2580–2574 Ma ages are coeval with the ca. 2579–2574 Ma Great Dyke of the Zimbabwe Craton, as well as the related Umvimeela and East satellite dykes, also in Zimbabwe. However, using further geochemical and paleomagnetic data on these mafic intrusions, we show no similarity between the mafic events in Zimbabwe and Kaapvaal. In fact, it appears over 3000 km of displacement was observed between these LIP events at this time. Such a conclusion renders the oldest known continent-continent collision invalid in the Neoarchean. This conclusion is supported by petrography, rock magnetism and paleomagnetic field tests, which demonstrate the primary nature of this paleomagnetic pole.

Acknowledgements

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Some features of a microprobe study of the unique Krymka chondrite (LL3.1)

Vira SEMENENKO[1], Kyrylo SHKURENKO[1], Nataliya KYCHAN[1]

[1]M.P. Semenenko Institute of Geochemistry, Mineralogy and Ore Formation of the NAS of Ukraine. 34, Acad. Palladin Avenue, Kyiv, Ukraine, 03142; e-mail: cosmin@i.ua

The Krymka meteorite fell in 1946, January 21 as a swarn of fragments with a total about 40 kg, in the Nikolayev region of Ukraine. The meteorite belongs to unequilibrated chondrites and contains xenoliths, a relic of protoplanetary dust in form of primitive fine-grained material, evidence of shock effects of varying intensities: from weak to completely shock-melted *in situ* zones. Most xenoliths are presented by a new type of cosmic material and are unknown on Earth as individual meteorites.

The presence of xenoliths and fine-grained material with a high level of mineralogical, chemical and isotopic heterogeneity, associations of low-temperature and high-temperature minerals bring the main difficulties in study of the meteorite. The use of scanning and transmission electron microscopy, microprobe and secondary ion mass spectrometer are essential for proper characterization of such unusual space material.

Our previous microprobe studies of the Krymka chondrite at a period 1973-2018 (Semenenko et al., 2022) were carried out in different countries by the following instruments: MAP-1, JCXA-733 JEOL Superprobe, JEOL JXA-8200 (Ukraine, Kyiv), Cameca SX-50 (France, Paris), JEOL JXA 8900 (USA, Washington) and JEOL JXA-8600MX (Germany, Muenster). The precise chemical composition was determined only for coarse grains (≥3µm). Compositions mostly of fine grains (≤ 3 µm) were analyzed with the SEM EDS.

The bulk composition of the primitive fine-grained material was obtained using a defocused beam (20 µm diameter). Although we cannot use this method to determine the xenoliths bulk chemistry because of the presence and random distribution of coarse silicate grains, the microprobe can still provide useful information for comparison with similar material, studied by the same method, or to approximate their chemical similarity to other types of meteoritic matter.

Despite the structural, mineralogical and chemical complexity of the Krymka chondrite, its microprobe study has yielded the following new data about origin and evolution of cosmic matter: a) some fine-grained xenoliths directly testify to the early fractionation of metal-silicate dust at the level of nanometric grains and to the accretionary nature of the initial dust balls, as probable nuclei of chondrules within the protoplanetary disk; b) the xenoliths preserved signs of chemical and mineralogical diversity of protoplanetary material, probably generated in the nebular zone, distinctive from that of known types of chondrites. The most important of these are xenolites containing graphite- and bitumen, first found in meteorites. Their textural, mineralogical and chemical features testify to at least two sources of C-containing material and different ways it entered the xenoliths; c) shock-transformed parts of the meteorite, especially completely shock-melted areas demonstrate the chondritic material behavior in accordance with a level of the shock pressure, temperature and cooling rate, caused by preterrestrial impacts.

Study of the Krymka chondrite is now accompanied by new discoveries of rare objects, that confirm its uniqueness and scientific value. Additional studies need to be carried out using a modern microprobe, electron microscope and ion mass-spectrometer to expand knowledge about fundamental processes of the evolution of the Solar System, in particular the Earth, as well as its mineral resources.

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New-mineral and critical-element potential of pyrometamorphic rocks of fire-encompassed post-mining as derived from EPMA studies

Łukasz KRUSZEWSKI[1]

[1]*Institute of Geological Sciences, Polish Academy of Sciences, Twarda 51/55, 00-818 Warszawa, Poland; e-mail: lkruszewski@twarda.pan.pl*

Introduction

Spontaneous coal fires, both in post-mining heaps and natural environments, induce largely dynamic conditions, thus triggering formation of numerous mineral phases. Among these are new and potentially new mineral species. Here I juxtapose some of such findings from coal-fire environment – the "Marcel" mine heap in Radlin (USCB, Poland) – and (burnt) bitumic shale site at Lapanouse-de-Sévérac (LdS; Sévérac-d'Aveyron, Rodez, Aveyron, Occitanie, France). The first site characterizes in persistent fires, due to long-term heap reconstruction, being active since at least 2000. The Radlin site new-phase potential is large, and astonishingly similar to that of the famous La Fossa crater of the Vulcano island, Lipari, Italy.

Example phases

Various exhalative zones in Radlin are responsible for the formation of (1) Cu-(AuAgI)-rich mineralization, with chalcanthite, tenorite and euchlorine associated with dolerophanite. The latter also occurs as a Se-rich variety that could, however, represent a new Cu selenite-sulfate. Additional associate is a Cu sulfide iodide. Iodine is also present as a major component of red-orange crystals covering salammoniac (also known from the nearby "Szarlota" heap in Rydułtowy) that represent an unprecedented combination of bismuth and iodine; this phase is most likely an ammonium iodobismuthate. Another unique find is an ammonium phosphimidate and potassium sodium dithionate(V) chloride. The LdS site, on the contrary, mostly bears high-temperature (pyrometamorphic) slags, with V-analogue of fluorapatite (now known as pliniusite), "magnesiograndiferrite" – $Mg(Fe,Al,Cr,Mn)_4O_7$ – and other Mg-Fe(Cr) oxides, "ferro-ferri-shulamitite" – $Fe^{2+}_3TiFe^{3+}Fe^{3+}O_8$, a Mg-Ti-[]-analogue of batiferrite – $(Mg,Mn)Ti_2\{(Ti,Fe)[]\}Fe^{3+}_8O_{19}$, "Ba-petalite" – $BaAl(Si_3Al)O_{10}$, "K-petalite" – $KAlSi_4O_{10}$, and an amphibole-like phases with example ideal formula of $Ca_5Mg(Al,Fe^{3+})Si_5(O,OH)_{17}(OH)$.

Critical element potential

Critical-element potential of the USCB pyrometamorphic minerals was studied, i.a., using the trace-mode EPMA method. The most frequent positive determinations concern Co, Ga (usually in Fe-rich oxides), and V. Germanium is rarely found (a single cuspidine sample being a prominent exception), probably due to high volatility of its compounds like $GeCl_4$ and/or GeH_4. Finding a strongly Sb-enriched melilite-group representative is somewhat unexpected. Other interesting, rare elements, like In, are less frequently observed.

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The crystal structure of gypsum under high pressure

Julia ALBERSKA[1], Agnieszka HUĆ[1], Marcin STACHOWICZ[1]

[1]*Faculty of Geology, University of Warsaw, Żwirki i Wigury 93, 02-089 Warszawa; e-mail: j.alberska@student.uw.edu.pl, a.huc@uw.edu.pl, marcin.stachowicz@uw.edu.pl*

Gypsum ($CaSO_4{\cdot}2H_2O$) is the most common sulphate mineral on Earth, occurring mainly in evaporite deposits. At ambient pressure, it crystallizes in the monoclinic *C*2/*c* space group with lattice parameters: a=6.2858 Å b=15.2141 Å, c=5.6801 Å, β=114.09°, V=495,89 Å^3. It features a layered structure with water molecules separating the $CaSO_4$ groups. In this work we present the results of single crystal X-ray diffraction (XRD) experiments. The crystal structure was determined for synthetic and natural gypsum crystals at room temperature, at ambient pressure and in a diamond anvil cell under pressures of 2 and 4 GPa. The natural crystals originated from Dobrzyń nad Wisłą and Wieściszowice in Poland.

High pressure experiments on minerals aim to recreate the conditions of the planet's interiors. Nazzareni et al, (2010) found that gypsum undergoes a pressure-induced phase transition at a pressure of 4 GPa. Above this value, the stable form of $CaSO_4{\cdot}2H_2O$ exhibits a slightly different symmetry, crystallizing in the $P2_1/n$ space group (Nazzareni et al., 2010; Tsung‑Lung and Pei‑Lun, 2018).

In this study we optimized the experimental methodology for future synchrotron XRD experiments to determine the redistribution of electron density in gypsum under high pressure.

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Microstructure of hydrocarbon contaminated cohesive soils observed in the SEM

Dorota IZDEBSKA-MUCHA[1], Emilia WÓJCIK[2]

[1]*Department of Engineering Geology and Geomechanics, Faculty of Geology, University of Warsaw, Żwirki i Wigury 93, 02-089 Warsaw, Poland; e-mail: dim@uw.edu.pl*
[2]*Laboratory of Applied Geology, Faculty of Geology, University of Warsaw, Żwirki i Wigury 93, 02-089 Warsaw, Poland; e-mail: wojcike@uw.edu.pl*

Scanning electron microscopy (SEM) is nowadays a wildly applied technique in geotechnical investigations of cohesive soils and also provides a useful tool in discussing the impact of environmental factors and anthropogenic pollution on the behaviour of clays.

A qualitative microstructural analysis of cohesive soils of different genesis and contaminated with petroleum compounds, was carried out using SEM. The research was conducted on 1) alluvial soil subjected to chronic contamination with petroleum substances in a long term, 2) glacial till incidentally contaminated with diesel fuel in a short term, 3) model samples of glacial till contaminated with diesel fuel in laboratory.

The direction of microstructural changes in all three cases studied was similar. The microstructure of the alluvial clay soil exposed in situ to chronic hydrocarbon contamination (1) transformed from anisotropic mixed turbulent-laminar type into homogeneous matrix one. Detailed quantitative analysis of the pore space indicated redistribution of pore space – porosity, pore number and shape (Izdebska-Mucha and Trzciński, 2021). In glacial tills, exposed in situ to short term hydrocarbon contamination (2), the clay matrix changed to less aggregated – loosely packed, with domination of the edge-to-face types of contacts and increase of inter-microaggregate pores content. According to the quantitative analysis, the contaminated soil micro-fabric proved to be more isotropic and less oriented, displayed more open porosity and larger voids than in non-contaminated soil (Izdebska-Mucha et al., 2011). In the laboratory-contaminated glacial till (3), in comparison to the non-contaminated soil, the clay matrix was more loosely arranged, some aggregates disintegrated, silty grains were separated from the clay matrix, the number of face-to-edge contacts increased. On the surface of the clay particles, a thin layer of a substance, probably hydrocarbons, was observed (Gawriuczenkow et al., 2022). The contaminated soil presented less cohesive structure which was reflected in reduction of soil strength parameters (Dobak et al., 2022).

The study confirmed that the presence of petroleum hydrocarbons changes the geological and engineering properties of cohesive soils. These changes involve both qualitative and quantitative characteristics. Changes in microstructure of the hydrocarbon contaminated soils revealed in SEM analyses support the results of mechanical tests. The presence of hydrocarbons, which cause lubrication at particle contact, directly explains the decrease of soil friction angle and leads to reduction of soil stability.

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Preliminary studies of internally mixed aerosols in urban area

Tetiana KALINICHENKO[1], Mariola JABŁOŃSKA[1]

[1]*University Laboratories of Atmospheric Survey, Faculty of Natural Science, Institute of Earth Sciences, University of Silesia, Będzińska 60, Sosnowiec, 41-200, Poland; e-mail:tetiana.kalinichenko@us.edu.pl, mariola.jablonska@us.edu.pl*

Introduction

As the consequence of dynamical and chemical transformation processes in atmosphere, particles of aerosols generally consist of internally mixed particles (Posfai and Molnar, 2000). Individual aerosol particles from the urban area of Katowice conurbation were investigated by scanning electron microscopy with EDS analysis.

Methodology and results

Dust samples were collected by aspirator 'Life 1 One' 14.07.2023 during flight from Katowice (Muchowiec) to Będzin using a mobile laboratory located in a manned hot air balloon and investigated by SEM with EDS (Quanta250, FEI: HV, U=15keV, BSE, Ø 3.5-9µm, EDS, t=30''). In our observations, the main components include sulphates, silicates and Fe-bearing particles. The large amount of the aerosol particles was found to be internally mixed with Na chloride aerosol particles in different ratio (see, for example, Fig.1).

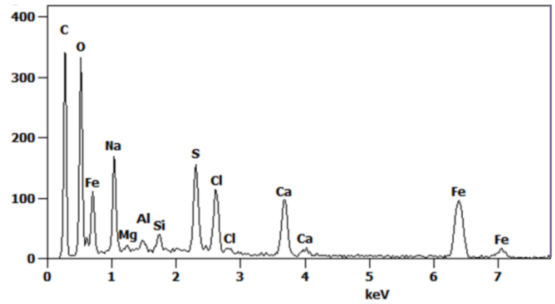

Fig.1. EDS Spectra of internally mixed particles

The ternary diagram within a complex material composition was constructed (Fig.2). Necessary to note that the most part of internal mixed chloride particles are associated with sulphates. Up to 20% of silicates were observed in the chemical composition of sulphate particles. Particles containing anthropogenic iron are also mixed with sulphates and small amounts of silicates and in some cases mixed with chlorides.

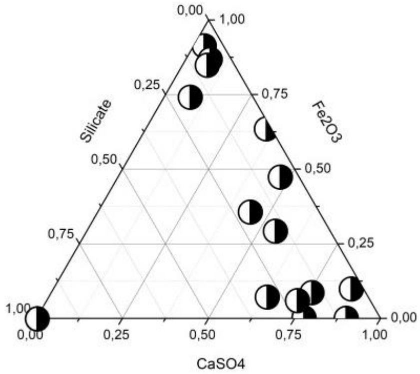

Fig.2. Ternary diagram for main component of urban aerosols

Silicates and aluminosilicates particles, like quartz, feldspars, clays, and others, are bigger than intermixed ones.

Conclusions

The internally mixed aerosols could be produced by processes within clouds, including droplet coalescence. Samples taken up to an altitude of 1,900 m amsl contain sulfates and chlorides probably originated in-situ in the urban atmosphere as a result of gas-to-particle conversion.

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ESRI ArcGIS software for remote research by the EPMA

Monika NOWAK[1], Beata MARCINIAK-MALISZEWSKA[2]

[1]*Institute of Geology, Adam Mickiewicz University, ul. Bogumiła Krygowskiego 12, 61-680 Poznań; e-mail: mnap@amu.edu.pl*
[2]*Laboratory of Electron Microscopy, Microanalysis and X-Ray Diffraction, Faculty of Geology, University of Warsaw, Żwirki i Wigury 93, 02-089 Warsaw; e-mail: b.maliszewska@uw.edu.pl*

The COVID-19 pandemic and repeated lockdowns have necessitated the use of remote methods for conducting scientific research in many cases. This was also the case with the scientific task NCN Miniatura 4: *"Record of chemical interactions between peridotitic xenolith and ascending magma – transformations of xenoliths from the lithospheric mantle present in the Cenozoic volcanic rocks from the area of Lower Silesia and Opolian Silesia"*. It was crucial to establish good communication between researchers from Warsaw and Poznań to accurately set measuring points for chemical analyses.

The IT revolution in geography has contributed to the rapid development of GIS techniques and related software. The widely used ESRI ArcGIS is a commercial software utilized in various scientific and business applications. Primarily, ArcGIS is used for creating field maps (Nowak and Muszyński, 2020). Additionally, it can be effectively used to determine the percentage of rock components in planimetric analysis (Nowak et al., 2011). Despite previous efforts, by 2022 a full correlation between a digital scan of whole thin section taken in polarized light, planimetric maps created in ArcGis, BSE images, and EPMA measurement points had been not achieved. The georeferencing error reached several hundred microns. It was crucial to establish precise benchmark points to fit the digital scan to the local coordinate system used in the Cameca SX100 microprobe (x, y coordinates) and the local ArcGIS coordinate system.

Initially, points marked by fineliner on the glass slide were used as benchmark points, each marked with a separate colour for identification. However, this system turned out to be ineffective, the dot made with a fineliner had too large a surface to serve as a benchmark, and searching for individual colours in the polarized light using EPMA was too time-consuming and confusing. Later, four characteristic points on the surface of the rock were used as benchmarks. These benchmarks, for example: edge of the sample, the longer axis of the mineral, and the edge of the peridotite xenolith, arranged in a square shape, were easily identifiable in digital and BSE images, enhancing accuracy during the georeferencing process. The fitting error has been limited to few microns. Remote measurements were carried out as follows: 1) The information from Poznań contained characteristic benchmark points on specific thin sections, along with the location of the designated measurement profiles. 2) In Warsaw, during standard chemical analyses, the x and y coordinates of the benchmark points were also recorded. 3) Upon receiving the results, in Poznań, the measuring points were automatically linked to planimetric maps, enabling the planning of additional measurement sessions. Despite limitations in connecting to other measuring devices or metric system, using ArcGis software enabled the successful completion of the scientific task Miniatura 4. A total of 110 measurement profiles were conducted in 45 microscopic thin sections, ranging from 1.35 mm to 36.5 mm in length. The EPMA studies served as the basis for planning precise LA-ICP-MS studies and determining changes due to host-rock interaction with peridotite xenolith.

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Characteristics of monazite-(Ce) as a product of experimentally induced hydrothermal transformation of chevkinite-(Ce)

Kacper M. URBANIK[1], Bogusław BAGIŃSKI[1], Ray MACDONALD[1], Daniel E. HARLOV[2]

[1]*Department of Geochemistry, Mineralogy and Petrology, Faculty of Geology, University of Warsaw , Żwirki i Wigury 93, 02-289, Warszawa (Poland); e-mail: k.urbanik2@student.uw.edu.pl*
[2]*Section 3.3, Deutsche GeoForschungsZentrum GFZ, Telegrafenberg, 14473 Potsdam, Germany*

The appearance of monazite group minerals among the products of hydrothermal alterations of chevkinite-(Ce) is rare under natural conditions. While the coexistence of these minerals is often observed, monazite-(Ce) occurring as a product of chevkinite-(Ce) breakdown is uncommon.

Chevkinite group minerals (CGM), titanium-rare earth element (Ti-REE) silicates, occur in diverse geological settings. Recent research has focused on REE behaviour during the hydrothermal alteration of alkaline rocks, crucial for understanding rock formation and REE ore deposits. Experiments on chevkinite-(Ce) were conducted using a cold-sealed autoclave in a high-pressure hydrothermal setup, simulating alkaline rock mineral assemblages and hydrothermal fluids. Conditions ranged from 500 to 600°C and 200 to 400 MPa, with durations of 21 to 63 days.

These experiments produced various REE-bearing mineral phases, including britholite-(Ce), fluorbritholite-(Ce), monazite-(Ce), and minerals of the epidote supergroup. Other LREE-rich phases such as gagarinite-(Ce) and titanite were also synthesized. These findings shed light on mineral transformations and REE mobilization during hydrothermal processes in alkaline rocks. Monazite-(Ce) appears in 6 out of 24 experiments, in samples CF-8, CF-12, CF-15, CF-17, CF-21, and CF-24. In terms of composition, all the analyzed crystals show an almost complete dominance of the phosphate (monazite-xenotime) component (Fig. 1). Among the products, monazite-(Ce) appears in two forms. These are tiny crystals forming rims on the edges of chevkinite-(Ce) or larger 15-20 µm discrete crystals. Comparing the EPMA analysis results of the samples from the experiments, it can be observed that the composition of monazite-(Ce) is identical to that of crystals of this mineral found in natural occurrences (Macdonald at al. 2017; Savel'eya and Karmanov, 2007) associated with hydrothermal alteration of chevkinite-(Ce).

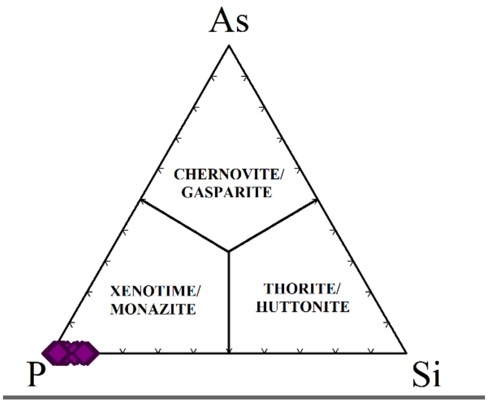

Fig. 1 Composition of monazite-(Ce) from the experiments; As–P–Si triangular diagram

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A SEM-EDS study of detrital Cr-bearing pyropes from terrigenous deposits of the Middle Bug area (Ukrainian Shield): implication for understanding their provenance

Oleksii VYSHNEVSKYI[1]

[1]M.P.Semenenko Institute of Geochemistry, Mineralogy and Ore Formation NAS of Ukraine; Akademika Palladina Avenue, 34, Kyiv - 142, Ukraine, 03142; vyshnevskyy@i.ua

Introduction

Detrital pyrope is widely distributed in sedimentary deposits of Neogene and Quaternary age within Podolian and Ros-Tikich domains of the Ukainian Shield and in several placers was found together with diamond microcrystal's and other high pressure minerals. But primary sources have not yet been found and the type of parental rocks is still not clearly identified. Given this, the question of its provenance is of great interest.

Using a JEOL JSM-6700F/JED-2300 technique, the morphology, chemistry and mineral inclusions of Cr-bearing pyropes from the sediments of the Middle Bug area were studied. In total, five samples of about one hundred grains each, were examined.

Results

Morphology. Usually pyropes have a size of 0.3–0.6 mm. Mainly these are variously shaped fragments of larger crystals with a smooth shiny or sculptured surface, sometimes they have an isometric form (Fig. 1a, b).

Chemistry and compositional zoning. Among the studied garnets there are two chemically different types: Cr-saturated (Cr_2O_3 >0.5 wt %) pyropes and Cr-poor (Cr_2O_3 <0.5 wt %) almandine-pyropes. The first ones are significantly dominant. They form a continuous series of compositions with Cr_2O_3 content from 0.5 to 5.4 wt %, but the vast majority (~80 %) reveals 1.0 to 2.5 wt % Cr_2O_3. They have a concentration of CaO (3.7 to 5.1 wt %), FeO (6 to 10 wt %) and a Mg-number [Mg/(Mg+Fe)] of 0.79 to 0.87. In some samples an elevated content of TiO_2 (up to 0.7 wt %) is recorded. According to Grütter's classification scheme most of Cr-saturated pyropes are classified as lherzolitic (group G9) and only about 10 % are pyroxenitic and websteritic (group G4).

A purposeful microprobe examination of several hundred grains showed that in each sediment sample 1 to 2% of pyrope crystals are chemically inhomogeneous. In them, Fe regularly increases, while Mg decreases across the grain, while other components (Ti, Ca, and Cr) show no change. The Fe-Mg zoning is strongest in a narrow area of 40 to 100 µm width near the grain rim. The maximum and minimum values of Mg (1.38–2.34 apfu) and Fe (0.45–1.09 apfu) content and their ranges in each studied crystal are individual and differ from each other, but their average gradients are approximately the same and are about 0.01 apfu per 10 µm.

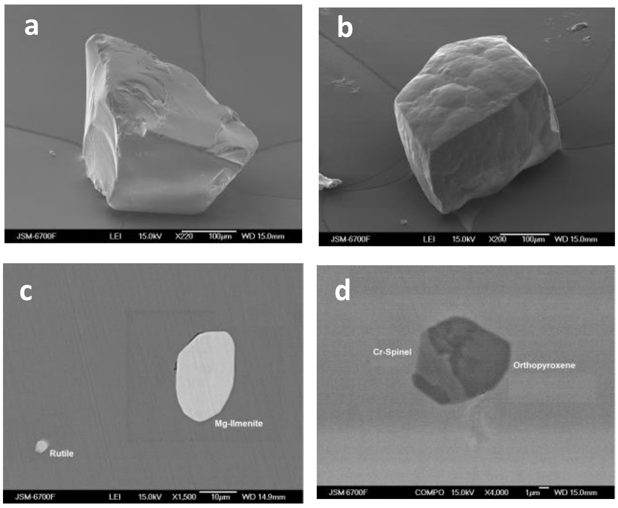

Fig. 1. Typical morphology (a, b) and mineral inclusions (c, d) of Cr-bearing pyropes from sedimentary deposits of the Middle Bug area.

Inclusions. More than a dozen mineral phases have been identified as inclusions (Fig. 1c, d) in the pyropes studied. These are: rutile, ilmenite, armalcolite, Al- and Cr-spinel, loveringite, mathiasite, pentlandite, olivine, enstatite, diopside, pargasite, albite, apatite, ferromagnesite.

Conclusion

In terms of a chemical composition, character of zoning and set of mineral inclusions, detrital Cr-bearing pyropes from sedimentary deposits of the Middle Bug area are most comparable to pyropes of orogenic garnet peridotites. Given this, we consider the latter or similar types of rocks as the most probable primary source of detrital Cr-bearing pyropes within this region.

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