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Abstracts and field trip guide

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of the Petrology Group
of the Mineralogical Society of Poland

GANGUE ROCKS:
INSIGHTS FROM NATURE, ANTHROPOGENE, LABORATORY AND SOLAR SYSTEM

October 20-23, 2022 | Rudy, Poland

Katowice-Wełnowiec dump, 13.01.2014

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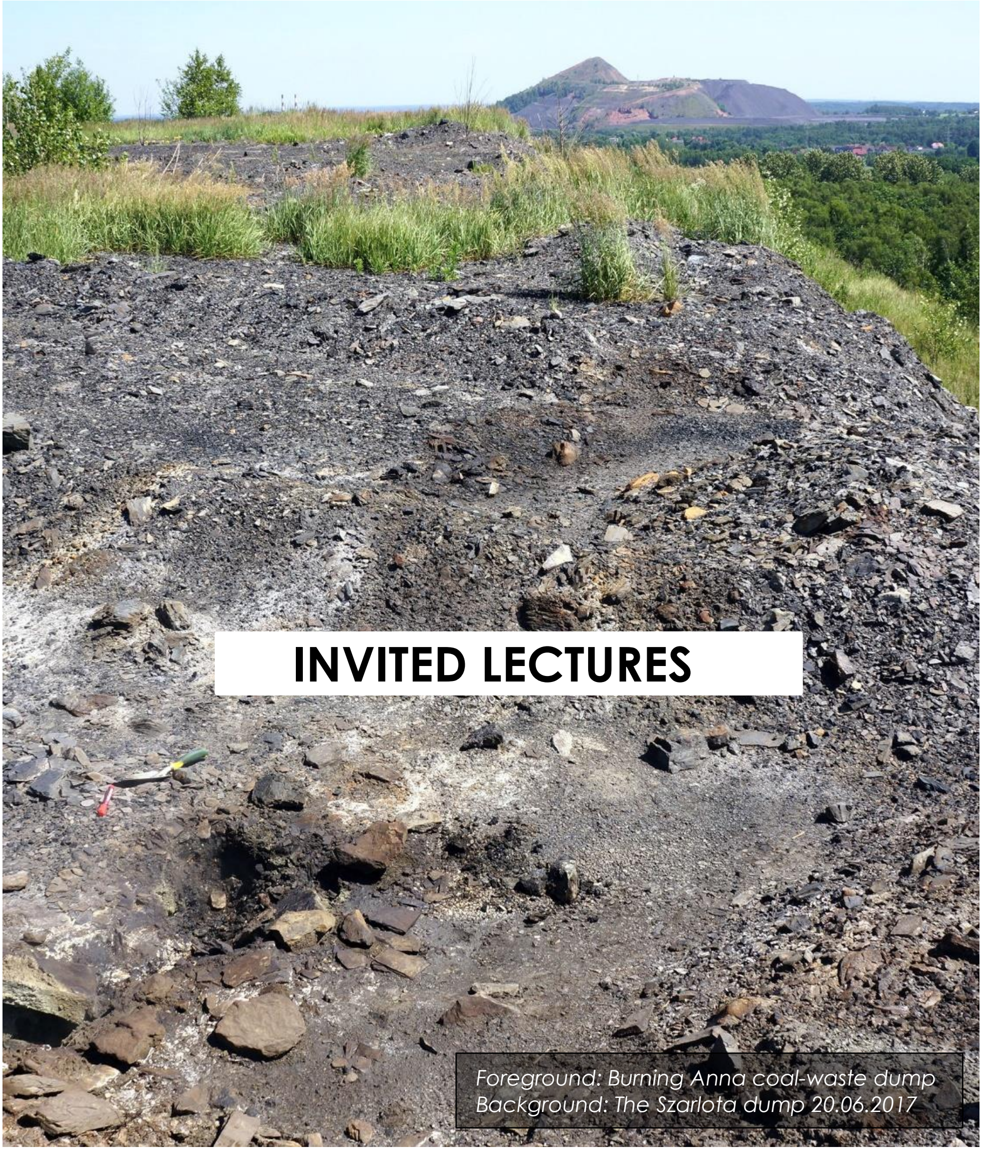

Foreground: Burning Anna coal-waste dump
Background: The Szarlota dump 20.06.2017

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Element distribution as a tool to understand radionuclide behavior within a river system (study from CZ)

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Introduction

The aim of the study was to characterize the relationship between element composition and radionuclides in stream sediments affected by mine water discharges. The study area is situated in the vicinity of Ostrava city in the Czech part of the Upper Silesian Coal Basin (USCB). The first data on radioactivity in the Upper Silesian Coal mines came from Poland in the 1970s (Tomza, Lebecka 1981). Since 1989, the coal industry in Poland has been obliged to monitor the radioactivity of discharged mine waters and sediments (Lebecka at al. 1994; Chalupnik et al. 2001). In 2015, the daily activity of radionuclides discharged into the Vistula (including its inflows) was 420 MBq and 12 MBq into the Odra (Chalupnik et al. 2017). Data on the occurrence of radionuclides in surface water in the Czech part of the Upper Silesian Coal Basin (USCB) are available only to a limited extent from the monitoring programs of state institutions (Hanslík et al. 2005).

Methodology

Two streams into which mine water is discharged were evaluated – Karvinský potok and Stružka. Both streams are situated in the Czech part of USCB. The channel of the Karvinský potok in the Karviná subbasin was artificially modified. Stružka is located in Ostrava subbasin. In-situ ambient dose equivalent rate (ADER) measurements and laboratory gamma spectrometry and X-ray fluorescence data were used to evaluate the downstream distribution of the radionuclides and major- and minor elements in the watercourse. Water samples were analyzed for major ion and element contents.

Results

The ADER measurements show elevated contents of radionuclides with values exceeding 1 000 nSv/h in both streams. The discharged mine waters are Na-Cl type with elevated activity concentration of ^{226}Ra reaching up 0.22 Bq/l and 0.24 Bq/l; the ionic compositions of both rivers are strongly modified

The content of main rock-forming elements in the river sediments of both Karvinsky potok and Struzka reveal increased contents of Al. This reflects increased clay-fraction contents. Contents of Si and Ca are variable with no obvious trends. The activity concentration of all monitored radionuclides (excepting U) decreases rapidly downstream at the Karvinský potok and shows the same trend as Sr and Cr. The activity concentration of radionuclides in the Struzka, as those of Cr, Sr and Mn, first increases but after 1.5. km from the discharge, gradually decrease. The concentration activities of isotopes of Ra and Th closely correlates with the ADER values while those of U isotopes show weak or no correlation.

Conclusion

Based on the correlations between radionuclides and the elements, the Sr is shown to be the most suitable element for the estimation of Ra and Th concentrations. The correlation among radionuclides and elements shows that sorption on clay minerals is not the leading mechanism of radionuclide removal. Significantly more efficient removal occurs within sedimentation ponds which are of great importance in preventing further distribution of radionuclides or potentially hazardous elements further downstream.

In the sediments of both streams, neither Al or Si correlate with Cu, Zn, Ni and As. Cu shows a good correlation with at least 1 isotope of U in both streams. Zn correlates strongly with ^{235}U in Karvinsky potok. This can be interpreted as indicating that some portions of Cu, Zn, Ni and As occur in accessory minerals and some from the discharges or are flushed from the stream surroundings.

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Petrochronology of the REE mineralization of Belcina, Ditrău Alkaline Massif, Eastern Carpathians, Romania

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Mineral deposits associated with silica-undersaturated syenites are an important source of critical metals such as the rare earth elements (REE) and Nb, Zr, P, Ti. Consequently, strongly mineralized alkaline rock suites, such as the Middle-Upper Triassic Ditrău Alkaline Massif (DAM) in the Eastern Carpathians (Romania), are of particular economic interest. What remains to be understood are the specific relations between the degree of mineralization and the underlying processes, the petrology, and the age systematics of such rock suites. Here we report on the textures, chemistry and crystallization ages of monazite and xenotime from the late-stage Belcina carbonate vein REE mineralization in the contact aureole of the DAM.

Phosphates (monazite, xenotime, apatite) of the Belcina carbonate REE mineralized veins are rock-forming, together with Fe-Mg-rich carbonate, thorite, thorogummite, gedrite and plagioclase. Three different textural and chemical types for each the monazites and the xenotimes can be distinguished thus documenting a complex three stage evolution. The relative phosphate age succession (from older to younger) thereby is $xnt_1 > xnt_2 >$ and/or $+ mnz_1 > mnz_2 > mnz_3 + xnt_3 +$ apatite. Taking into account the other important mineral phases, the extended paragenetic succession is $xnt_1 > xnt_2$ (>)+ $mnz_1 + Fe_2O_3+$ Fe-gedrite > mnz_2 + Fe-dolomite > $mnz_3 + xnt_3$ + apatite. Plagioclase does not belong to this succession but is from a textural point of view the earliest crystallizing mineral.

Phosphate chemistry shows that thesecrystallized from hydrothermal fluids whereby each phosphate type follows an independent evolutionary path suggesting growth from (at least) 3 independent and successive hydrothermal fluids. Chemistry and pathways with the DAM suggest that these hydrothermal fluids could be derived from a (subsurface) carbonatitic intrusion.

Mnz_1 - mnz_2 and xnt_1 - xnt_2 ages are tightly cluster at 215.9±1.3 Ma (Norian, Upper Triassic). The third-generation phosphate ages are tentatively younger but associated with large analytical uncertainties and do, therefore, not deliver geologically useful age data.

The mean age of ca 216 Ma is interpreted as timing the carbonate vein formation at Belcina. Thus, the phosphate ages are some 10 My younger than the youngest known igneous activity of the DAM (ca 225 Ma). This, and in line with the fluid chemistry, supports a model of the presence of a late-stage, independent carbonatitic intrusion into the DAM some 10 Ma after the main igneous activity forming the DAM.

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Geochemical study of dump samples from the Troyanovo-3 Mine (Maritsa Iztok Coalfield, Bulgaria) after 16 years of weathering

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Introduction

Mini Maritsa Iztok EAD is exploiting the Maritsa Iztok lignite field (240 km^2) which is of importance for the national energy strategy especially today during crisis times. Three open-cast mines operate in the coalfield (Fig. 1): Troyanovo-1, Troyanovo North and Troyanovo-3 (Tr-3) with annual production of about 20 million tons. Since the start of production in 1962 until 2013, 4278.7 thousands of m^3 of dump materials were removed and backfilled. The geochemical composition and structure of the weathered dump organic matter (OM) from the Tr-3 Mine has been studied.

Geological settings

The lignite-bearing sequence in the Maritsa Iztok Basin (MIB) comprises coal basement of grey-black mudstone and fine to coarse sand, and three lignite seams separated by black clay-blended coal and coaly- and carbonaceous mudstone. The coal is extremely immature (0.2% R_o), brown soft lignite (Rock Eval T_{max} ~380°C); total organic carbon content, dry basis, TOC_{db} = 21.3–56.7 wt%; ash_{db} = 16–45 wt%; total moisture, M_t = 50–60 wt%; sulfur, S_{db} = 3–6 wt%; net calorific value = 5300–7500 kJ/kg).

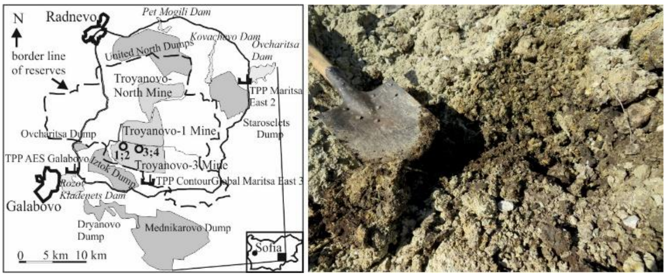

Fig. 1. Scheme of Mini Maritsa Iztok EAD with sampling locations (o) and Sample 3 (field view)

Material and Methods

Four surface dump samples from the Tr-3 Mine dumped 16 years ago were selected from different parts of the dump area (Fig. 1). They had probably been excavated from the mudstones covering Seam II. The samples were air-dried, quartered, crushed, and studied by XRD and Rock-Eval. The soluble portion was prepared by Soxhlet extraction ($CHCl_3$, HPLC grade, ~300 ml, 30 h). Maltenes were fractionated on a Silicagel column in neutrals, aromatics/slightly polars, and polars. The first two fractions were studied by GC-MS. Experimental details are given in Stefanova et al. (2016).

Results and Discussion

The main minerals identified by XRD are mixed layered illite/smectite, kaolinite, quartz, albite, pyrite and gypsum. TOC contents range from 2.30 to 10.39%. S_1 values are low (0.04-0.07 mg HC/g rock), and S_2 values elevated (2.37-12.06 mg HC/g rock). The ranges of T_{max} (389-436ºC), HI (103-176 mg HC/g TOC) and OI (60-129 mg CO_2/g TOC) are close to the values found for the mudstones from the Tr-3 Mine by Milakovska et al. (2022). Two of the samples have OM of Type II/III kerogen, and two of Type II kerogen.

The quantity of soluble organic matter varies from 0.30-1.28 % and is lower than that of the mudstones from the Tr-3 Mine. In the dump extracts maltenes prevail, including resins in the third fraction. The GC-MS studied fractions supply information for compounds of various chemical characteristics. The short/long *n*-alkane ratio varies from 0.16-0.8, indicative of long-chain member dominance. The maxima are at nC_{27} and nC_{29} for long-chain homologues, and at nC_{18}, nC_{17} and nC_{19} for the short chain homoloqgues. Low (0.72-0.87) values of nC_{23}/nC_{31} hint that the OM has not been subjected to any thermal influence.

Two sets of samples are distinguished according to the calculated values for hopane- and sterane biomarkers. The values for two of the sample are characteristic of immature OM. It was possible to calculate only the values for 22S/(22S+22R) $H_{31}\alpha\beta = 0.09$-0.18. The other two samples show mature distribution features that do not conform to the generally immature OM of the MIB lignites. The samples show hopane values for Ts/(Ts+Tm) = 0.36-0.38 and 22S/(22S+22R) $H_{31}\alpha\beta$ = 0.58-0.59 and sterane values for 20S/(20S+20R)$\alpha\alpha C_{29}$ = 0.51-0.57.

Summary

The collected dump samples show different degrees of maturation indicated by TOC and RE parameters and indices. The geochemical characteristics of two samples do not reveal any evidence of elevated OM maturity. The second pair of two samples experienced a thermal impact influence indicated by calculated values for hopane and sterane biomarkers. We are inclined to assume that the elevated OM maturity of the dump samples has been attained naturally in the rock massive but not by smoldering in the dump. The results provide a further indication of elevated maturity from the Tr-3 Mine as previously detected by Misz-Kennan et al. (2021) and Milakovska et al. (2022).

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Speleogenesis vs. dedolomitization (cave "Mravljetovo brezno v Gošarjevih Rupah"; Rovte Hills, central Slovenia)

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Introduction

The paper presents the first results of the bilateral Polish-Slovenian research project CEUS: "The multi-proxy studies of dedolomitization processes and related speleogenesis in central Slovenia with implications for understanding of incipient stages of sulphide mineralizations in southern Poland".

A short presentation of the project

Dedolomitization, dolomite calcitization, or recalcitization is frequently described in literature dealing with the diagenesis of carbonates and, somewhat less frequently, hydrogeology. However, a relationship between dedolomitization processes and/or their products and speleogenesis is still unclear. We aim to describe new speleogenetic processes that may occur in many environments where regional underground watercourses flow through mixed evaporite-carbonate successions. Such a mechanism could be responsible for large-scale porosity and instability in deep-seated carbonates that are important for regional groundwater flow in karst aquifers. This study may also encourage researchers to re-evaluate the relationships between brecciated- and dedolomitic horizons, which are widespread in certain karst regions, and associated caves which have traditionally been explained only by "common" meteoric (i.e., epigene) speleogenesis.

In the area of Vrh Sv. Treh Kraljev (VSTK) in the Rovte region, there are three apparently similar caves ranging from 300 m to 1000 m in length, but each of which formed in different rocks, namely, dolomite, limestone and dedolomite. The research area in central Slovenia provides a unique opportunity to perform multi-proxy studies of dedolomitization processes and associated speleogenesis. The results of our preliminary hydrogeochemical studies in the Rovte region have shown that dissolution of calcium sulphates and dedolomitization are still occurring deep below the surface. Thus, the area we selected represents a unique polygon to investigate the direct relationship between currently active processes of Ca sulphate dissolution, dedolomitization and speleogenesis, and their fossil products.

Mixed evaporite-carbonate successions and the confirmed presence of dedolomite are common in many areas of Poland. In the southern part of the country, sulphide mineralization (e.g., Zn-Pb-Fe, Cu-Fe) occurs in such geological conditions. The research in central Slovenia should improve our knowledge of the incipient stages of formation of the sulphides. In simplified terms, we will essentially test two basic hypotheses regarding speleogenesis related to dedolomite: (1) Fracture-related dedolomite was formed by processes associated with deep-flowing meteoric water that ascended through the evaporite horizon, and thus enriched in calcium and sulphate, caused dedolomitization of the host dolomite with the pathways altered by dedolomitization being more permeable and susceptible to dissolution and thus preferential for later hypogenic- and/or epigenetic speleogenesis; (2) some of the sulphate rock was dissolved deep below the surface under reductive conditions, where hydrogen sulphide (H_2S) was formed in the presence of organic compounds and oxidised to strong sulphuric acid (H_2SO_4) higher up towards the surface. Dissolution of dolomite with strong sulfuric acid formed caves and, as a by-product, calcium sulphate on the cave walls. Subsequently, under the conditions of the "common" meteoric hydrogeochemical environment, the sulphate crusts were dissolved or replaced by calcite, and dolomite in the immediate vicinity of the crusts was also replaced by calcite (dedolomite) due to the common-ion effect. To understand the processes now fossilised in the cave wall rocks, extensive hydrogeochemical studies, including stable isotope studies, of deep wells in the area, and multiproxy studies of caves and the surface are being conducted. Numerical models will be applied to test the likelihood of a dedolomite-related speleogenesis scenario.

Results

The main results obtained during the research so far are:

1) The topographically well-defined VSTK consists of a sequence of Middle Permian to Middle Triassic carbonate and siliciclastic rocks several hundred metres thick with intercalations of evaporites within the Upper Permian and Lower Triassic dolomite sequence found in boreholes.

2) All three caves of the VSTK have a ramiform and/or maze-like pattern and other signs indicating their possible hypogene origin.

3) The wall rock of the Mravljetovo brezno v Gošarjevih rupah (MBGR) cave consists mainly of dedolomite replacing the Middle Triassic dolostone. Dedolomitization of the host rock was most probably the result of interaction between limestone, dolomite and Ca-sulphate rocks in the phreatic zone. Based on oxygen- and carbon isotope values, it is suggested that the dedolomite was precipitated from low-temperature aerobic meteoric water recharging from areas covered with C3 plants. Petrographically, several major textural groups of calcite crystals can be distinguished, indicating not only replacement of dolomite, but also participation in open fissures and perhaps cavities formed by dissolution of dolomite.

4) We suggest that most of the passages of the MBGR were primarily formed in phreatic conditions. However, it is not yet clear whether the main channels were initially formed by dissolution of a previously dedolomitized portion of the host dolomite or whether dedolomitization occurred during the intrusion of water with elevated Ca/Mg ratio into previously formed cave channels.

5) Subsequently, the cave was modified and possibly significantly enlarged in the epiphreatic zone (perched conduits with clastic sediments) and in the vadose zone (shafts with active dripping water, ceiling channels formed by condensation corrosion, secondary cave minerals, e.g., gypsum, hydromagnesite, aragonite, dolomite, and phosphates such as cattiite).

6) Chemical analyses of water discharging from the wells indicate that dedolomitization is still ongoing subsurface. Continuous monitoring of climatic conditions in the cave (T, humidity, wind) shows surprising dynamics leading to intense condensation corrosion and probable precipitation of secondary minerals.

The research was supported by the Polish and Slovenian research agencies (NCN and ARRS) through the bilateral Polish-Slovenian research project CEUS (project code in Poland: 2020/39/I/ST10/02357; project code in Slovenia: N1-0226).

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Uncontrolled combustion of coal gangue: An overview of environmental impacts and potential solutions for reuse and rehabilitation in cases from Portugal

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The uncontrolled combustion of coal and coal mining residues has been recognized at a global scale and is known for its deleterious effects related with loss of natural resources and with impacts on environment and human health. The negative impacts are largely associated with the mobilization of volatile compounds and particles to atmosphere and leaching of potentially toxic elements.

Anthracite mining in the Douro Coalfield (Portugal) has occurred for almost 200 years (starting in 1795) and the environmental legacy is represented by more than twenty waste piles composed of coal gangue, drainage systems from underground mines that discharged in natural water streams, and abandoned facilities. The uncontrolled combustion of five coal waste piles, three ignited by forest fires in 2005 and two in 2017, adds a further environmental hazard caused by waste disposal, which often cause acid drainage. From those ignited in 2005, the SPC waste pile still burns today. In those ignited in 2017, combustion was extinguished, and the waste piles rehabilitated in the following two years through remobilization of material, cooling, spreading, landscape modeling and covering. Some of these coal waste piles are located near residential areas, exacerbating concerns about human health.

The comprehensive investigation of the environmental legacy left by coal mining in the Douro Coalfield has been developed by researchers from the Institute of Earth Sciences, University of Porto, and collaborators. This work presents an overview of the characterization and identification of environmental impacts related to the uncontrolled combustion of coal mining wastes in the Douro Coalfield and an assessment of changes induced by the combustion process. This knowledge is needed to find science-based solutions for the reclamation and rehabilitation of these areas. The reuse of mining waste materials will open-up an opportunity to mitigate the environmental impacts and, at the same time, contribute to the recycling of by-products, thus promoting the circular economy of natural resources and sustainability.

The investigations to characterize burned- and unburned materials and to assess the changes induced by combustion included the determination of:

- Petrographic- and mineralogical composition, allowing the identification of changes in organic- and mineral matter and the estimation of combustion temperatures based on newly formed minerals.
- Elemental chemical composition, allowing the assessment of the mode of occurrence of elements, their behavior and fate.
- Concentration of polycyclic aromatic hydrocarbons, distinguishing pyrolytic- and petrogenic sources.
- Acid production potential, integrating mineralogical- and chemical data.

- Petrographic-, mineralogical- and geochemical changes in unburned materials subjected to controlled combustion tests at specific temperatures.
- Radiological parameters, allowing the characterization of radiological risk.

The results establish that the uncontrolled combustion induces changes that exacerbate the environmental hazards, e.g., element mobility, magnetic susceptibility, and radiological risk. Major concerns relate to the emission of volatile organic compounds and particulate matter that disperse in the atmosphere as the waste piles are near inhabited areas. Mobilization of toxic metals through percolation and the Hg content in the superficial materials in the burned area are also of concern.

With regards to the reclamation of these areas, it is essential to extinguish the uncontrolled combustion in the SPC waste pile burning since 2005, principally because it is located close to residential areas with social- and sporting infrastructures. The waste piles ignited in 2017 have been extinguished and rehabilitated. The solution for SPC may consist of a similar approach that includes remobilization, cooling, covering, and landscape modeling offering landscape compatibility, along with installation of a drainage system for leachate collection. In this case, management and monitoring is also essential, principally to avoid new ignitions.

Another solution may be the reuse of the waste materials in construction materials, replacing primary raw materials. At first sight, coal waste material may appear unpromising due to its carbon- and sulphidic contents but some aspects can make them interesting for further investigation: i) The combustion of waste materials in SPC induces graphitization of organic matter and the formation of carbon materials such as carbon nanotubes and graphene sheets (Ribeiro et al., 2010); ii) recent studies have found that some sulphidic mining waste materials are suitable for inclusion in facing bricks (Simão et al. 2022); iii) the combusted material has had their sulphidic content oxidized and material that experiences higher temperatures forms a clinker making it suitable for use as raw material in building products. Therefore, further studies should consider the extraction of carbon materials and the inclusion of both unburned- and burned waste material in the experimental fabrication of construction materials. The major challenge to be faced in the search for solutions for the reuse of these materials is related to their Hg content.

Finally, as at least twenty coal waste piles have been identified in the Douro Coalfield, most of which are enclosed in forested areas, the risk of ignition makes the proper management and monitoring of these areas very important. If a solution for the reuse of these coal-mining wastes is found, it will allow the mitigation of environmental impact and promote a circular economy.

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Depositional setting variability assigned by long chain asymmetric/symmetric *mid*-chain *n*-ketones in Late Mio-Pliocene carbonaceous mudstones (Bulgaria)

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Introduction

The studied carbonaceous mudstones represent core samples from a lignite-mudstone succession showing variations in organic matter (OM) maturity. The borehole, located in the southern part of the Maritsa Iztok Basin (MIB) lignite field in Bulgaria, penetrates Late Miocene-Pliocene sediments (Mlilakovska et al. 2022). The history of the coal-mudstone sequence is complex and is overprinted by variable alteration processes. Elevated OM maturity of the deeper sample (58.0-60.5 m depth) is indicated mainly by hopane distributions. A set of differences was recognized: (i) Position of the samples in the normalized diagram for the fractional composition; (ii) *n*-alkane signature with considerable short-chain *n*-alkane portion ($< nC_{20}$) and low CPI value (1.53); (iii) hopane distribution characteristic for mature OM with 22S/(22S+22R) C_{30} hopane ratio ~ 0.30 and Ts/(Tm+Ts) = 0.30; (iv) *n*-alkan-2-one distribution centred at the n-C_{27} homologue. Briefly, the organic geochemistry involving more mature OM of the deepest sample conflicts with the ordinary maturity trend for the region.

This is not the first encounter with samples showing elevated maturity in the region. Misz-Kennan et al. (2021) reported such for dump samples excavated from mudstones and lignites of Seam I. The main features of samples that had experienced a thermal impact are paler oxidation rims, higher reflectance (0.31-0.53%), irregular cracks, Gaussian *n*-alkane profiles, the presence of alkyl aromatic hydrocarbons and high concentrations of phenolic compounds. Thermal influx along major faults was assumed by Zdravkov et al. (2020) for lignites with increased coalification from the Maritsa-Zapad lignite field adjacent to the MIB; this assumption was based on a 22S/(22S+22R) C_{30} hopane ratio (~0.55) and R_o ~ 0.3-0.4%, both twice as high as previously reported.

Results and discussion

In attempting to follow alteration processes in the borehole, we used *n*-alkan-2-ones as a palaeoproxy (Milakovska et al. 2022). There is an extensive literature to substantiate a product-precursor relationship and to discriminate paleoenvironments using ketones. To our knowledge, correlations applying long chain *n*-ketones with a carbonyl group in the mid of the aliphatic chain attached to an even-numbered carbon atom are missing.

In the separation scheme used by Stefanova et al. (2016), *n*-alkan-2-ones were isolated in the second fraction comprising slightly polar components. They were accompanied by long–chain ketones with carbonyl group at the mid of the chain as in C_{29} *n*-alkan-10-ones (C_9-CO-C_{19}). This *n*-ketone is common in Bulgarian lignites and in lipid extracts from interbedded claystones. It occurs in the waxes of various higher plants and is indicative of the presence of higher plant epicuticular leaf waxes in the palaeomire.

In this study, we enriched the series of long chain "odd"-numbered *n*-ketones with a carbonyl group placed in the mid of the linear aliphatic chain (symmetric) or slightly shifted from the center (asymmetric) (Table 1). In the SIM *m/z* 58 homologues, nC_{29}-nC_{35}, were concomitant to the trivial *n*-alkan-2-ones separation.

Table 1. Long-chain symmetric/asymmetric *n*-alkanone series and homologue abundance

Homologue	Type*	R_1-CO-R_2	M^+	*m/z*	High abundance
29	Asym. Asym.	C_9-CO-C_{19} C_{13}-CO-C_{15}	422	155,295 211,239	Coal Seams I, II, III
31	Asym. Sym.	C_{11}-CO-C_{19} C_{15}-CO-C_{15}	450	183,295 239,255	Sm., 58.0-60.5 m
33	Asym.	C_{15}-CO-C_{17}	478	239,267,295	Sm., 58.0-60.5 m
35	Sym.	C_{17}-CO-C_{17}	506	267,283	Sm., 58.0-60.5 m

*after Cranwell (1984)

In SIM *m/z* 58 of the deepest sample (58.0-60.5 m), the intensities of the symmetric nC_{31} and asymmetric nC_{33} *n*-alkanones even prevail over the C_{29} *n*-alkan-2-ones (Table 1). The distribution maximized at asymmetric C_{33} (C_{15}-CO-C_{17}) is followed by a symmetric C_{31} (C_{15}-CO-C_{15}) with a comparable intensity. The presence of *n*-ketones with oxygen attached to an even-numbered carbon atom, analogous to the C_{29} *n*-alkan-10-one, the most widespread asymmetrical ketone in plants, argues for cuticular wax input into the palaeomire.

Conclusions

In the thermally altered sample 58.0-60.5 m of the borehole, in addition to evidence for elevated maturity rendered by *n*-alkane and hopane distributions, a series of long-chain symmetric/asymmetric *n*-alkanones with an unusual distribution was registered. Today, it is widely believed that *n*-alkanones with a carbonyl group at the middle of the chain are not source specific tracers because they are ubiquitous in the plant kingdom. However, our data show that it may be time to reconsider the informative value of the series as source specific biomarkers for palaeoenvironmental variability reconstruction.

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27th Meeting of the Petrology Group of the Mineralogical Society of Poland

ABSTRACTS

Participants of the 27th Meeting of the Petrology Group of the PTMin
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The vegetation development on smoldering coal-waste dumps in Southern Poland

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Underground smoldering fire on coal-waste dumps creates unfavorable- and extreme ecological conditions for the development of organisms. In high-temperature zones, the vegetation dies, and the soil degrades. In areas where the fire is smoldering, the temperature inside the soil ranges from 35-140 degrees Celsius. Any further rise in temperature leads to a complete loss of water from the soil, which contributes to the destruction of the plant's root systems and, as a result, the entire assimilation apparatus. These smoldering areas can be better known through research on the plant's morphology as they wilt and lose color. Such places provide vital information about impending underground fires. Even though the smoldering coal-waste dumps belong to extreme ecological systems in terms of the environment, various plant species present different life forms, and historical- and geographical groups. The dumps and other anthropogenic objects are characterized by mosaic-like habitats and microhabitats resulting from the form of the terrain created when post-mining waste is stored. They create areas of variable humidity, affecting species' colonization with different ecological requirements (Abramowicz et al. 2021a; Ciesielczuk et al. 2015). As many as 126 species belonging to various synecological groups have been found in a small area of the Czarny Las dump in Ruda Śląska (Upper Silesian Coal Basin; Abramowicz et al. 2021b). Thus, coal-waste dumps constitute an important center of biodiversity occurrence in anthropogenic areas. They also seem to be a unique natural laboratory for conducting various environmental- and biogeochemical studies, as well as observing the dynamics of changes in various phenomena, e.g., smoldering fires.

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Experimental synthesis of $ThSiO_4$ by fluid-induced alteration of chevkinite-(Ce)

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During hydrothermal alteration, the REE-bearing minerals of the chevkinite group have the potential to release not only REE but also high field-strength elements and the actinides, including Th. The initial concentration of Th in a fresh chevkinite-(Ce) varies from 1.0 to 2.9 wt.% ThO_2. A series of hydrothermal experiments using different hydrous fluids ($Ca(OH)_2$, NaOH, NaF and CaF_2) and P, T conditions ranging from 500-600°C and from 200-400 MPa have been carried out. The products included $ThSiO_4$ showing a remarkable range of textures (see Figures). The textures provide significant new information on the incorporation of Th into hydrothermal fluids, the ways in which it is transported, the efficiency of various ligands in promoting the transport and the mechanisms of $ThSiO_4$ deposition. EBSD studies have revealed the structural nature of the $ThSiO_4$ and how it varied with mode of transport. The effects of the invading fluid(s) on the host chevkinite-(Ce) have shown that its structure has been maintained.

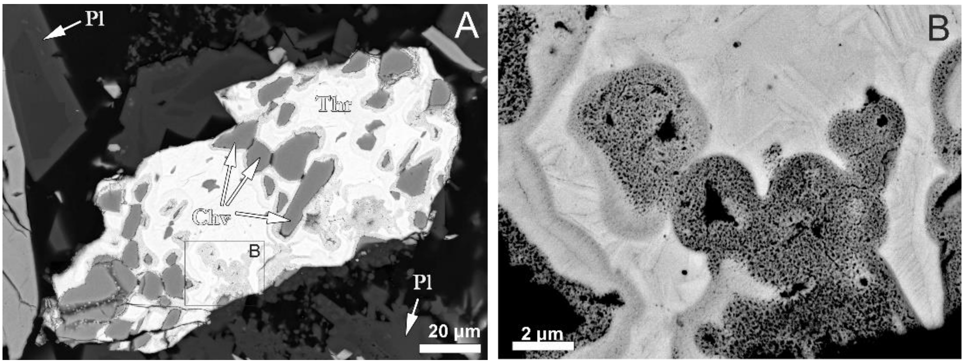

Fig. 1. BSE images: A. Chevkinite-(Ce) largely replaced by $ThSiO_4$, B. Unusual bubble aggregate of spherical forms in $ThSiO_4$

The quantity of Th which comes from altered chevkinite-(Ce) strongly depends on the fluid composition. For example, fluorine in the fluid appears to increase the mobility of the Th.

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The application of fly ash chemical transformation products in environmental engineering

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Volatile organic compounds, pesticides, pharmaceuticals, surfactants, metal anions, metalloids and nonmetals, and radionuclides are typically released into the environment through a spill or inappropriate disposal, allowing the chemicals to get absorbed into the ground or enter the sewage system. Several treatment methods have been developed to remove the above pollutants from water. Due to their cost-effectiveness and efficiency, mesoporous materials, especially those synthesized from coal fly ash (FA), are recognized as the most promising strategy for slowing down the impact of pollutants.

VOCs (benzene, ethylbenzene, toluene, xylene), pesticides (2,4-D, MCPA, carbendazim, simazine), pharmaceuticals (erythromycin, colistin, fluoxetine), surfactants (HDTMA, TX-100), metals and metalloids (Cr(VI), V(V), As(V)), radionuclides (^{238}U, ^{234}U) were sorbed on mesoporous materials synthesized from FA. The synthesized materials included zeolites (Na-X, Na-A, Na-P1), zeolite-carbon and zeolite-vermiculite composites, and mesoporous silica materials.

The novelty of the work is based on the use of fly ash as a precursor to the synthesis of new materials with the structure of zeolites, mesoporous silica materials, zeolite-carbon composites, and on the utilization of the functional materials obtained in environmental engineering. Materials synthesised from fly ash can effectively remove all tested pollutants within the range of concentrations typically found in the environment. The sorption efficiencies found ranged from 50-100%, depending on the initial concentrations of sorbed compounds used, the pH of the reaction environment, the reaction time, and the solid to solution ratio. Sorbents modified with surfactant compounds have higher sorption efficiencies than unmodified materials. Experiments on the regeneration and reuse of sorbents indicate that they can be reused many times without significantly deminishing their sorption capacity.

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From arenisation to speleogenesis - mineralogical evidence from the Stołowe Mountains (Poland and the Czech Republic)

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The research carried out to date has revealed that the development of marginal parts of the sandstone plateaus of the Stołowe Mountains is mainly facilitated by processes operating at depth. Evacuation of the rock residuum leads to the opening of fractures and the gradual subsidence of the joint-bounded sandstone compartments. Although the evidence of *in situ* disintegration of cliff-lines is widespread, including the presence of chaotic boulder fields replacing numerous sections of rock walls, joint-controlled slots, open clefts as well as sandy cones at the outlets of fissures – the weathering processes standing behind the formation of these landform assemblages have remained unspecified. It was hypothesized that the arenization phenomenon – responsible for the chemical alteration of silica cement and quartz-grain boundaries – is of crucial significance. Our goal in this study is to check the role of silica dissolution in the speleogenesis in the Stołowe Mountains.

Several complementary methods have been used to determine the degree of sandstone weathering. A compressive strength evaluation using Schmidt hammer and rock surface moisture measurements have been compiled with scanning electron microscopy (SEM) observations used for assessing micromorphological changes. They were complemented by a classical mineralogical study that utilized polarizing light microscopy, X-ray diffraction, and thermal analysis to fully characterize the rock studied.

Our investigations revealed a high degree of rock weathering, manifested in the form of etching, mainly of syntaxial quartz overgrowths. Microstructures such as v-shaped and irregularly shaped pits up to 1 μm in diameter and large embayments up to tens of micrometers formed on both the syntaxial quartz and primordial grain surfaces are the hallmark of a chemical attack on rock constituents. Moreover, the obtained results show that there is a direct relationship between 1) increased rock moisture content, 2) high degree of weathering and 3) abundance of microstructures resulting from chemical etching.

The biotic factor also plays an important role and cannot be neglected as a contributor to rock weathering. The SEM observation showed that the rock is strongly affected by microorganisms. Therefore, a laboratory bioweathering experiment was also designed to evaluate the microbial contribution to the dissolution of sandstone. Element release and weathering features were observed and compared to features found in naturally weathered sandstones. Microbial biomass was analyzed in terms of elements capturing. In general, this approach was crucial to differentiate the influence of chemical and biotic weathering.

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Granitic melt-mantle interaction during the subduction of continental crust at mantle depth constrained by reaction experiments

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During subduction, melts and fluids allow elements transfer from the crust to the mantle. An example of this process is described during the subduction of continental crust in the Granulitgebirge (Bohemian Massif). Here melt inclusions are reported in eclogite lenses in serpentinized garnet peridotites and are used to determine the melt nature and the conditions under which this process took place. Based on its major and trace elements signature, the melt most likely originated in the continental crust and its interaction with the mantle took place at about 1000°C and 2.2 GPa. During the deep subduction of the continental crust, this melt interacted with a mafic/ultramafic layer already present in the mantle to produce the eclogites where it is now contained. Although most of the parameters of this metasomatic interaction are constrained, the absence of mineralogical relicts makes the protolith nature still unknown. For this reason, we performed melt-rock reaction experiments that would also contribute to better constrain the formation of garnet-bearing lithologies during crust-mantle interaction in the geological setting observed in the Granulitgebirge.

We performed reaction experiments at 1.5 and 2.2 GPa, 1000-1100°C, using a piston cylinder apparatus. The starting material was a homogeneous mixture comprising a synthetic glass with the same composition as the granitic melt measured in the Granulitgebirge eclogites and two mantle protoliths - a fertile lherzolite and a spinel clinopyroxenite. The first protolith was synthetized in the laboratory starting from a gel at the conditions at which the reaction experiments were conducted (1100°C and 2.2 GPa). The spinel clinopyroxenite was a natural mafic rock (bulk XMg = 0.74) from which clinopyroxene and Al-rich spinel were separated. The chosen melt-rock weight proportion was 1:9 as indicated by the reaction in the Granulitgebirge. In the experiments involving the lherzolite-granitic glass mixture, garnet ($Prp_{71}Alm_{13}Grs_{9}$), orthopyroxene and minor clinopyroxene were produced at the expense of pristine mantle minerals, thus producing an orthopyroxene-rich garnet websterite. Experimental runs on the spinel clinopyroxenite-granitic glass mixture at 1.5 and 2.2 GPa and 1100°C show textural evidence of a reaction that produced mainly garnet ($Prp_{45}Alm_{29}Grs_{24}$) and clinopyroxene coexisting with a residual melt. The products of this second group of experiments for both mineral assemblage and chemistry resemble the Granulitgebirge eclogites arguing for a mafic protolith rather than a peridotite. Other reaction experiments are in progress to better define the effects of pressure and different initial melt/rock ratios on the reactions.

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Occurrence of nitrogen-fixing microorganisms in Polish lignites

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Lignite deposits are habitats for microorganisms such as *Bacteria*, *Archaea*, and fungi. Processes of lignite decomposition under aerobic and anaerobic conditions are widely studied to better understand the formation of microbial gases - CH_4 and H_2. Stimulation of natural microflora from coal habitats can enhance the formation of microbial coal bed methane, which is an alternative biotechnology for energy. The bioavailability of nitrogen in coal habitats is a limiting factor for the growth of microorganisms in many oligotrophic environments (Strąpoć et al. 2011). Therefore, it is very important to better understand the role of nitrogen cycling (e.g., N_2 fixing), and lignocellulose degradation under anaerobic conditions (Leschine et al. 1988).

Miocene detritic lignite from the opencast mine in Konin (Poland) was incubated for 5 years under anaerobic conditions (headspace atmosphere 85% N_2, 10% CO_2, 5% H_2). The growth of the natural microbial community from that coal was stimulated by additions of a solution of trace elements and vitamins, yeast extract, nutrient broth, methanol, and sodium acetate. The activity of microorganisms resulted in the decomposition of lignin. Released biogas contained CO_2, whereas CH_4 and H_2S were not present. 16S rRNA gene sequencing revealed the presence of microorganisms able to fix N_2 in all investigated samples, belonging to the order of *Rhizobiales (*families *Beijerinckiaceae, Rhizobiaceae)*. Further isolation and characterization of microbial genes influencing the N_2 cycle in coal will be investigated for quantitative evaluation of N transformation processes.

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Orogenic peridotites of the Seve Nappe Complex, Scandinavian Caledonides – lithospheric mantle insight into Caledonian Wilson cycle

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Since the 2nd half of the XX century, numerous tectonic models have been discussed to explain the details of the Caledonian Wilson cycle in Scandinavia. However, the crustal metamorphism record is often blurred by overprinting throughout the geological history of the orogeny. Therefore, information from deeper parts of the lithosphere is required to complement the crustal perspective. One of the most important sutures within the orogeny, between the Seve Nappe Complex (SNC; outermost margin of Baltica) and the Köli Nappe Complex (Iapetus-derived oceanic terranes), comprise numerous occurrences of mantle-derived bodies. In this study we present petrological- and geochemical observations from the orogenic peridotites occurring within the SNC as an insight into tectonic processes recorded by the deep lithosphere during Caledonian Orogeny.

Three groups of peridotites were analyzed. The first group comprises serpentinised Spl-facies ultramafics with an assemblage of Ol+Srp+Amph+Spl+Opx(a)±Opx(b). The rocks represent primary mantle lithologies of sub-oceanic affinity (refractory dunitic- to harzburgitic composition) with a record of supra-subduction (SSZ), arc-related setting visible in chemical composition (low Mg#, high Cr# chromite) of zoned Spl cores.

The second group is dominated by dunites/harzburgites with mosaic Ol, common interstitial Chl, tremolite with Na-rich rims and porphyrocrysts of primary Opx. This group of peridotites recorded deserpentinisation of primary mantle lithologies. Differences in the modal- and chemical compositions between localities ($Ol_{Fo93-95}$+Amph+Chl+Mgt+Opx *vs* $Ol_{Fo90-90}$+Opx[a]+Chl+Spl+Opx[b]) suggest that the chemical character of dehydration and recrystallization varied between the areas.

The third lithology is represented by foliated peridotites with retrogressed Grt. This highly refractory lithology (dunites with scarce Opx) comprises isometric post-Grt kelyphite structures, locally recording brittle deformation pre-dating Grt decomposition. Numerous Amph-forming events have been recognised, showing continuous exhumation and fluid infiltration.

Collectively, the studied mantle lithologies provide direct evidence for their primary sub-oceanic affinity with SSZ record (first group), recrystallization of singular bodies (second group; related to subduction) as well as extensional input throughout the cycle (third group interpreted as lithospheric-scale shear zone exhumation). These observations underline the significant role of an oceanic domain in the formation of the Baltican margin, yielding implications for tectonic models of the Caledonian Wilson cycle.

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A vestige of high-pressure-low-temperature metamorphism in the Izera-Kowary Unit (Karkonosze-Izera Block, SW Poland)

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The Karkonosze-Izera Block situated in the NE part of the Bohemian Massif is considered to be a flat-lying metamorphic complex intruded by a multi-stage granitoid intrusion. Its eastern margin is recognized as a Variscan paleosuture zone, locally delineating the extent of the Saxothuringian domain. One of the suture-markers, high-pressure-low-temperature metamorphism, was recently identified in the Karkonosze-Izera Block as a result of continental subduction (Jeřábek et al., 2016).

In this study, three samples of garnet-bearing mica schists from the Polish part of the Karkonosze-Izera Block were examined. The inspected samples are dominated by a mineral assemblage related to regional metamorphism (M2: muscovite, biotite, chlorite, plagioclase, quartz, ilmenite). However, we also documented an older mineral assemblage M1 comprising garnet, chloritoid, phengite, paragonite, chlorite, quartz, rutile and pseudomorphs after lawsonite that we interpret as vestiges of high-pressure-low-temperature metamorphism. Phase equilibrium modelling and classical geothermobarometry methods have been applied to reveal the P-T record of the observed mineral assemblages. Results show that the M1 paragenesis crystallized in pressure-peak blueschist/lawsonite-eclogite facies conditions, reaching 19.0-20.8 kbar at 470°C – 500°C, while the M2 paragenesis crystallized in temperature-peak greenschist/epidote-amphibolite conditions of 5-7 kbar at 525-575°C.

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Magnesium minerals in sulphate speleothems from the “Pomorzany” Zn-Pb ore mine

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Zn-Pb and Fe sulphide ores of the Silesian-Kraków region occur within nearly flat-lying Middle Triassic (Muschelkalk) carbonates. The host rocks of these hydrothermal deposits emplaced in karst cavities are ore-bearing dolomites, reflecting early-diagenetic dolostone recrystallization and limestone dolomitization. The karst and sulphide ores are located along the metasomatic contact between the ore-bearing dolomite and the carbonates.

During exploitation of the Zn-Pb and Fe sulphide ores in the Olkusz mining district, the carbonate (dolomitic mainly) massif was drained, and sulphide oxidation and acid mine drainage developed. Favored by high moisture contents (92-95%) of the mine galleries, sulphate speleothems, stalactites, flowstones and efflorescences started to form. In the “Pomorzany” mine, these comprise epsomites and melanterites with admixted sulphates such as hexahydrite, pentahydrite, chvaleticeite, starkeyite, szomolnokite, rozenite, copiapite, boyleite, bianchite, anglesite and gypsum (Cabała & Bzowska 2008).

With decreasing humidity, the composition of the sulphates changes; the hexahydrites change to pentahydrites, even to four-water starkeites and rosenites. These are stable under high humidity conditions, in mine galleries or karst systems. The contents of hydrated Ca, Mg, Fe sulphates in the Pomorzany ores is < 4%. AAS analyses show that infiltration-building sulphates have high concentrations of Zn ($< 11,594$ mg·kg^{-1}), Fe ($< 78,709$ mg·kg^{-1}), Cd (< 24.8 mg kg-1) and Mn (322.4 mg kg-1) (Cabała & Bzowska 2008).

Oxidation of sulphides and the initiation of Zn, Pb, Cd occurred before or syngenetically with sulphate precipitation in the mining drainage zone. Characteristic of the secondary sulphates is the high proportion of magnesium sulphates, e.g., epsomite $MgSO_4{\cdot}7H_2O$, and hexahydrite $MgSO_4{\cdot}6H_2O$, indicating dolomite dissolution or selective leaching of Mg^{2+} ions. As magnesium is stabilised in unstable, easily soluble sulphate minerals, it is transferred to groundwater in the carbonation zone. The high content of magnesium sulphates is evidence that not only easily soluble sulphides, e.g., sphalerite, pyrite and markasite, but also ore-bearing dolomite are oxidised in the aeration zone. The processes observed in the Olkusz mining district can be regarded as an artificial analogue to one possible model of dedolomitization processes in nature in the past.

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Geochronology and metamorphism of the Mårma Terrane, Kebnekaise region, northern Swedish Caledonides

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The Scandinavian Caledonides record the history from the break-up of Rodinia to the subsequent collision between Baltica and Laurentia. We investigated several lithologies including the Aurek gabbro, banded amphibolite and mylonitic orthogneiss as well as the Vistas granite, gabbro and syenite dyke belonging to the Vássačorru Igneous Complex (VIC) of the Mårma terrane in the Kebnekaise mountains, northern Swedish Caledonides. U-Pb zircon geochronology yielded ages of 609 ± 3 Ma and 614 ± 2 Ma for the Aurek gabbro, 626 ± 7 Ma for the banded amphibolite, 835 ± 8 Ma for the mylonitic orthogneiss, 864 ± 3 Ma and 840 ± 7 Ma for the Vistas granite and granitic dyke, respectively, and 856 ± 3 Ma and 850 ± 1 Ma for the gabbro and syenite intrusions of the VIC. No evidence of later Caledonian metamorphism was found based on the U-Pb zircon geochronology. Nevertheless, U-Pb monazite geochronology from the mylonitic orthogneiss revealed a lower intercept of c. 443 Ma (upper at c. 840 Ma) interpreted to be related to the Silurian tectonometamorphism. Moreover, scrutiny of the U-Pb data from the banded amphibolite revealed an age cluster of at c. 598 Ma interpreted to reflect partial melting.

Thermodynamic modelling revealed that all the studied samples experienced medium- to high-grade metamorphism. Pressure-temperature (P-T) estimates for the VIC samples yielded metamorphic conditions of 7.4-8.1 kbar at 615-675°C (mylonitic orthogneiss) and 6.5-7.5 kbar at 600-625°C (granite). These P-T conditions were achieved during the collisional stage. The banded amphibolite records P-T conditions in the melt stability field at 600-680°C at 10.5-12.0 kbar, related to a rifting setting. The Aurek gabbro instead, experienced high-pressure metamorphism, with P-T estimates of 11.8-12.6 kbar at 480-565°C under eclogite facies conditions. The similarities with the Tsäkkok Lenses (south of Aurek) extends the high-pressure affinities of the Seve Nappe Complex to the north of the Swedish Caledonides.

The magmatic activity between 860 and 830 Ma has been interpreted as a failed rifting attempt of Rodinia. The younger Aurek gabbro is related to the real opening of the Iapetus Ocean and the break-up of Rodinia thus reflecting the age of the emplacement of the dyke swarm (c. 610 Ma).

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Magmatism and metamorphism in the Köli Nappe Complex of Sweden: The tectonic evolution of oceanic terranes in Iapetus

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The Köli Nappe Complex (KNC) forms part of the Scandinavian Caledonides, originating as oceanic terranes within the Neoproterozoic to Palaeozoic Iapetus Ocean in island arc- or back-arc basin tectonic environments along with flych dominated terrigenous basin-fills. Prior to their accretion to the Baltican paleocontinental margin, these oceanic terranes underwent several episodes of rifting, magmatism and ductile deformation. We report preliminary results from an ongoing study to reconstruct the magmatic-, accretionary- and collisional orogenic processes recorded in the KNC in the north Swedish Caledonides.

The most complete sequence through the KNC is exposed in northern Jämtland and Västerbotten, where it comprises late Cambrian- to mid-Silurian volcano-sedimentary successions. U-Pb isotopic ages were acquired by LA-ICP-MS (Laser Ablation Inductively Coupled Plasma Mass Spectrometry) of zircons in metavolcanic rocks of the Lower Köli Nappe. Magmatic zircon shows ages of 470-530 Ma. This fits with previous magmatic ages found for the KNC, though the 530 Ma age in one sample predates all known ages for ensimatic subduction magmatism in Iapetus. These dates constrain the age of magmatism in an ensimatic arc system within Iapetus. Garnet-biotite thermometry and THERMOCALC avP gives P-T estimates of 10-15 kbar and 470-530°C for the Lower Köli.

The Tännforsen Synform is a tectonic lens of the KNC located in Central Jämtland. It is composed primarily of calcareous phyllites and garbenschiffer which have sedimentary flyschoid protoliths, along with minor volcanics. They preserve an inverted Barrovian metamorphic sequence, from greenschist facies in the east to amphibolite facies in the west. Electron microprobe analyses were conducted on three samples of garbenschiffer from the Middle Köli Nappe and two samples of mica schist from the Bunnerviken lens (correlated with the Lower Köli Nappe). Conventional thermobarometry and THERMOCALC avP gives P-T estimates of between 520-575°C at 7.5-9.5 kbar for the Middle Köli, and 570°C at 7.5-10 kbar for the Lower Köli. These results are currently being refined using petrological modelling in Perple_X. This metamorphism probably records the thermal regime during the early stages of development of the Scandian collisional orogenic wedge during Iapetus closure and the collision of Baltica with Laurentia.

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Zonation of copper sulphides within the contact zone of oxidized rocks (Rote Fäule) with reduced rocks in the Radwanice-Gaworzyce Cu-Ag deposit

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The research presents a review of petrographic studies of ore mineralization in the Kupferschiefer-series in the western part of the Fore-Sudetic Copper District. It is the continuation of research conducted in the Radwanice-Gaworzyce deposit in the last few years. Samples used for the revisions were obtained from mining profiles collected during underground fieldwork, as well as from a number of archival boreholes. The occurrence of three geochemical zones was confirmed in all of the examined profiles: 1) An oxidized zone (Rote Fäule), impoverished in ore minerals, but considerably enriched in iron oxides and hydroxides, 2) a reduced zone, enriched in ore minerals but barren with iron oxides and hydroxides, and 3) a transition zone between the oxidized- and reduced zones, with intermediate features between both zones, including the occurrence of relict sulphide mineralization accompanied by iron oxides and hydroxides. Compilation of reflected-light microscopy and electron microprobe investigations produced new geochemical results. The zonation of copper sulphides and the relationships between the variability of mineral textures and characteristics of copper-sulphide alteration within individual geochemical zones are precisely considered in relation to the redox front. All the investigated Kupferschiefer-series profiles are characterized by the prevalence of copper sulphides from the Cu-S group, where chalcocite dominates quantitatively over digenite and covellite and where, in the upper parts of the copper-bearing series, chalcocite is accompanied strongly by bornite, chalcopyrite and minor idaite. Among the most prominent features is the gradual depletion of Cu in the Cu-S group of minerals towards the Rote Fäule front, as well as the depletion of copper in the Cu-Fe-S group minerals outwards from the oxidized rocks. The zonation pattern of Cu-S sulphides is oriented concentrically outwards from the most oxidized towards the less altered parts in the following order: covellite - yarrowite - spionkopite - geerite - anilite - roxbyite - digenite - djurleite - chalcocite. This trend represents the progressive alteration of Cu-rich sulphides and the loss of Cu ions; Cu sulphides become depleted in Cu towards the oxidized zone. As the oxidative potential diminished in the distant parts of oxidized areas, much weaker alteration processes occurred. The remains of copper sulphides in the transition zone and their altered forms of occurrence exhibit leaching processes of Cu ions exemplified by the crystallization of Cu-sulphides increasingly depleted in Cu. Covellite indicates the foremost extent of oxidative alteration processes with a stepwise loss of copper. Analogously, the zonation pattern within the Cu-Fe-S group reflects a decreasing Cu content from bornite through idaite to chalcopyrite. The gradual decrease in Cu content in copper sulphides, and the Cu-S and Cu-Fe-S mineral zonations directing outward from the Rote Fäule zone, are the results of the expansion of the mineralizing fluids. During the propagation of these fluids, the ore mineralization front was moving outwards from the Rote Fäule areas, causing the formation of ore bodies. The printing of this abstract was financed by the the National Fund for Environmental Protection and Water Management (Project: Popularization of knowledge in the field of geology and promotion of the geological survey activities).

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Magma supply and other geological conditions for SMS formation along mid-ocean ridges: implications for ore prospecting along 26-33°N, Mid-Atlantic Ridge

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Slow-spreading ridges host much larger seafloor massive sulfide (SMS) deposits than fast-spreading ridges. The highest-tonnage seafloor massive sulfide (SMS) deposits are hosted in plutonic rocks from oceanic core complexes (OCC), which expose the lower crust and mantle uplifted to the seafloor along detachment faults at slow-spreading ridges. All seven contractors of the International Seabed Authority for sulfide exploration, including Poland, operate on slow- to intermediate-spreading ridge segments with OCCs.

Slow-spread oceanic crust is thinner and more heterogeneous (Elsherif et al., poster session) than fast-spread oceanic crust (Marciniak et al., this session), which affects sulfide differentiation during magmatic processes and metal transport between the mantle and the ocean floor. To better understand sulfide differentiation in slow-spreading ridges, we investigated igneous rocks from two extensively sampled OCCs with high (Atlantis Bank, 57°E, SWIR) and low (Kane Megamullion, 23°N, MAR) magma supply. In large gabbroic bodies of Atlantis Bank, sulfides differentiate mainly through fractional crystallization. Sulfides fractionate early and accumulate at the lower part of gabbroic bodies. In Kane Megamullion with low magma supply, sulfides typically differentiate through melt-mantle reaction, which leads to high sulfide enrichment at the contacts of gabbro and peridotite, often shallow under the ocean floor. This enrichment in melt-mantle reaction could be why most large SMSs along slow-spread oceanic lithosphere with relatively low magma supply.

Our results will aid searching for SMSs within the Polish contracted area along the MAR (26–33°N) where a low magma supply shapes the lithosphere structure. The first Polish expedition, a 34-day-long regional survey, starting from Charleston in South Carolina (U.S.) on August 13, 2022 and ending on St. Georges in Bermuda on September 15, 2022, performed acoustic imaging including multi-beam bathymetry and backscatter supported with sub-bottom profiling to characterize three known OCCs (Atlantis Massif, the Southern OCC, Dante's Domes), and two new OCCs in the area. Additional magnetometry sensors may help estimate the serpentinized peridotite to gabbro ratio in OCC footwalls to indicate magma delivery rates. Finally, multi-beam and physicochemical (pH, ORP, temperature, turbidity, CH_4, and O_2) water column analyses served to search for hydrothermal activity.

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The planetary field analog studies in the Rio Tinto mining area, Spain

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Data from martian rovers and martian meteorites indicate that ore minerals are common on Mars, including sulfides such as pyrite. However, detecting sulfide ore deposits from martian spectrometers is difficult in the NIR range due to spectral interferences with silicates. Because of the limited in-situ measurements by the martian rovers, Mars mineralogical studies must be supported by studies of terrestrial analogs. The most suitable analog for studying ore minerals is the Rio Tinto area in Andalusia, Spain, which hosts the most significant known volcanogenic massive sulfide deposits on Earth (1). In Rio Tinto, we have investigated 614 sites along a river bed located 3 m from each other. At each site, we investigated five random samples for pyrite content. The data were interpolated (Fig. 1). By establishing our test field for remote sensing of sulfide deposits on Earth, we will be able to determine abundance thresholds for detecting major sulfide phases on Mars and identify their key spectral features. Firstly, principal component analysis based on a false-color composite of Sentinel-2A were used to enhance pyrite content from remote sensing data. PCA components with the highest topographical and spectral information allowed for lithological discrimination. Secondly, we used PRISMA (2) hyperspectral data in the visible near-infrared and short-wave infrared (VNIR-SWIR; 400-2500 nm with 239 spectral bands). By a preliminary analysis, in the SWIR spectrum, the absorption around 2000 nm is compatible with Pyrite GDS483 (USGS spectral library).

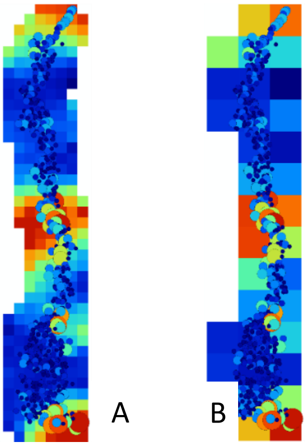

Fig. 1. Interpolation maps of pyrite content based on 614 sampling sites using the ordinary kriging method (SAGA GIS): (A) 10 m corresponds to Sentinel-2 spatial resolution, (B) 30 m to Landsat 8.

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Late Devonian magmatic and hydrothermal activity recorded in ultramafic rocks from the southern part of the Szklary Massif

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Three previously poorly known lithologies have been recently found in the southern part of the Szklary Massif (SM). Natural outcrops of silicified serpentinites (SiSp) have been documented in an abandoned quarry situated on the western slope of Siodłowe Hill. Based on textural, mineralogical, and chemical differences, we distinguished two types of SiSp. Type I contains well-preserved primary minerals cut by numerous veinlets filled with microscale quartz crystals characterized by euhedral growth zones with oscillatory CL zonation. It is moderately enriched in SiO_2 (62-90 wt.%) and depleted in MgO (10-19 wt.%) compared to the protolith. Type II is almost exclusively composed of amorphous- or poorly crystalline silica, with microquartz aggregates being the most abundant form. It shows extremely high values of SiO_2 (83-90 wt.%) and low MgO concentrations (4-8 wt.%). Both types of SiSp have elevated content of REE, Y, Rb, and K (Cieślik et al. 2022).

Further field studies in the southern part of the SM revealed the occurrence of leucocratic intrusion which we initially classified as diorite. The diorite is composed of plagioclase (An_{20-50}), biotite, and Fe-Ti oxides accompanied by titanites and zircons. Accessory minerals include chamosite, apatite, monazite, epidote, allanite, and an unidentified Mg-rich phase. Zircons from the diorite yield a concordia age of 378.0 ± 5.0 Ma (SHRIMP). A single zircon grain has an inherited core for which U-Pb age analysis yields a concordant age of 504.0 ± 7.0 Ma. The most striking feature of the studied rock is unusual element fractionation with respect to the K-rich syenite from Wilków Wielki (see Pietranik & Majka 2017).

A small outcrop of clinopyroxenite provided an unrivalled opportunity to track metasomatic alterations in the SM. Studied samples have well-preserved diopside crystals overgrown by serpentinite. Some parts of the rock contain only tremolite-clinochlore aggregates and others are magnetite-depleted. SEM-EDS observations supported by Raman spectroscopy allowed the identification of secondary (fluid-related?) minerals: dolomite, titanite, apatite, Ca-rich aluminosilicates, and unexpected anhydrite inclusions in tremolite.

We infer that between 340 and 380 Ma, the southern part of the SM was affected by magmatic- and hydrothermal activity that caused local enrichment in incompatible elements and crystallization of a mineral paragenesis unusual for ultramafic rocks.

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Brittle deformation microstructures in eclogites and granitoid HP gneisses, Norwegian Caledonides: Palaeoseismicity triggered by densification?

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Microstructures indicative of brittle fracture under metamorphic conditions are an important indicator of deep crustal or mantle seismicity. This may have been triggered by metamorphic transformations, including hydro-fracturing due to dehydration reactions (e.g., Bukała et al. 2020) or by shear stresses set up by domains undergoing metamorphic densification (Yamato et al. 2022). Feedbacks between fracture, fluid ingress and catalysis of eclogite genesis in previously dry rocks are also important.

Evidence for brittle fracture in garnet and omphacite has been found in the Western Gneiss Region continental eclogite terrain near Flekke in Sunnfjord, Norway, where eclogites and omphacite-bearing granitoid orthogneisses have developed from Proterozoic charnockite and gabbro protoliths. Well-preserved protoliths pass over short distances into domains of eclogite-facies mafic and felsic rocks of up to a few km^2 in extent. In the cores of compositionally zoned garnets, a pervasive network of filament-like features have compositions identical to the rim zone. These are interpreted as healed microfractures and indicate that early (amphibolite-facies) garnet has been catastrophically disaggregated prior to new garnet growth under HP or UHP conditions. Omphacite in the same rocks shows similar channel-like networks. No evidence for lawsonite breakdown that might favour reaction-induced hydrofracturing is known. Estimates of density changes across the eclogite transition based upon P-T pseudosection calculations suggest a rapid increase in bulk rock density in the amphibole- and plagioclase-out interval during continental subduction.

These observations are consistent with recent numerical modelling (Yamato et al. 2022) of brittle deformation due to densification where seismicity is favoured by a large pressure overstep for eclogite formation and the formation of small eclogitic (densified) domains. Large changes in shear stress at the tips of densifying regions could have favoured seismic pumping of fluids that aided eclogitisization. A likely source of the fluids was a large, continental shield brine aquifer (Hughes et al. 2021).

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Iron-rich minerals in lacustrine sediments as indicators of climatic changes as exemplified by the Anthracosia Shales from the Intra-Sudetic Basin

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To decipher the past environmental conditions of the rocks, we need to know their mineralogical and geochemical features. The mineral composition of the Anthracosia Shales (Upper Carboniferous/Lower Permian) from the Intra-Sudetic Basin were initially studied by Wójcik-Tabol et al. (2021). The Anthracosia Shale formation can be lithologically divided into three intervals (I – light grey medium- and fine-grained sandstones intercalated with thin layers of mudstones and shales; II – dark grey and brown shales with higher carbonate contents intercalated with thin layers of sandstones; III – medium- grained sandstones with thin shale layers). In this study, siderite (Fe_2CO_3), pyrite (FeS_2) and vivianite ($Fe_3(PO_4)2\bullet 8H_2O$) are taken into consideration as palaeoenvironmental indicators (Håkanson and Jansson, 1983; Wilkin et al., 1996). Siderite and pyrite found within interval II have TOC contents of up to 2.5% (Nowak, 2003, 2007). The most abundant is siderite, which occurs in the form of 1) contiguous crystals in thin yellowish horizons and 2) crystals dispersed in the fine-grained mineral matrix. Siderite occurs throughout a 10 m-thick interval and coexists with pyrite in a 4 m interval of the section. Pyrite is represented by framboids of size varying from 1.67-42.08 μm. Vivianite was identified by X-ray diffraction in a small amount in interval I. The presence of siderite and pyrite in the Anthracosia Shales may indicate reducing condition in the basin. Pyrite framboids can suggest anoxic – dysoxic conditions in the water mass. The presence of vivianite also suggests a reducing environment and lack of H_2S.

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Tackling the geochronological record of the Variscan metamorphism in the Western Tatras: Outline and perspectives

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The crystalline basement of the Tatra Mountains is composed of pre-Mesozoic crystalline rocks, overlain by a Mesozoic and Cenozoic sedimentary cover and nappes. Metamorphic rocks are the most abundant in the western exposures of the basement (Western Tatra Mts.) and display an inverted metamorphic sequence with high-grade rocks in the hanging wall (Upper Unit) and lower-grade rocks in the footwall (Lower Unit).

The Upper Unit, composed mostly of migmatites and orthogneisses with lenses of eclogites, records near isothermal decompression from 1.6 GPa to 1.0-1.2 GPa at 750-800°C. In contrast, the Lower Unit reached peak-pressure conditions at 0.6-0.8 GPa and 640-660°C (Janák et al. 1996; Moussallam et al. 2012). The Upper- and Lower Units record a clockwise P-T path. Therefore, it is inferred that both were juxtaposed at mid-crustal levels and share only the retrograde path during the late-Variscan exhumation (Moussallam et al. 2012). The timing of the Upper Unit metamorphism was estimated using garnet (Sm–Nd age of 337± 10 Ma), monazite (in-situ U–Pb ages from ca 380 Ma to 340 ± 11 Ma), and a metamorphic zircon U–Pb age of 347± 7 Ma (Burda et al. 2021). In contrast, the geochronological record of the Lower Units is poorly constrained and relies on a single study reporting a monazite age of ca 370 Ma (total-Pb method; Moussallam et al. 2012).

This contribution is related to a project aiming to reconstruct a detailed P-T-t path emphasizing the petrochronological record of the Variscan processes within the Tatric superunit. The fieldwork and preliminary dataset document an eastward increase in P-T conditions within the Lower Unit. The timing of metamorphism will be tackled with high spatial resolution in-situ U-Pb dating of monazite encompassing various textural positions to precisely target distinct metamorphic- and deformation events along the P-T path.

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Quartz-Hematite veins in the Oman Ophiolite: Syn-volcanic or syn-obduction origin?

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In the northern Semail ophiolite, Oman, giant quartz–hematite–pyrite veins < 11 km in length crosscutting the pseudostratigraphy from lower- to upper crust are bordered by chlorite alteration haloes that overprint the spilitized- and epidotized host rocks. The genesis of these so-called Q' veins has been attributed in the literature to two models: (1) Syn-volcanic hydrothermal circulation that fed black-smoker type seafloor massive sulphide (VMS) deposits or, alternatively, (2) syn-obduction ascent of externally derived fluids into the ophiolite nappe long after volcanism had ceased. If the Q' veins are syn-volcanic, they might hold key evidence of how metals are transferred from the deep oceanic crust to the seafloor. However, if the Q' veins formed during obduction, they are irrelevant to VMS processes but instead useful in understanding the emplacement of the ophiolite onto the Arabian platform.

The Q' veins are in pre-existing syn-volcanic faults. They are crosscut only by younger calcite veinlets and brittle fractures but not by any magmatic dykes. The Q' fluid precipitated quartz, hematite, pyrite, chlorite and traces of chalcopyrite, and overprinted older, genetically unrelated quartz–epidote veins. The vein textures are remarkably constant between locations, regardless of whether the veins are hosted by the shallowest lavas, the sheeted-dyke complex or by lower crustal layered gabbros. The amount of quartz can only be explained by cooling and decompression of an ascending fluid.

The composition of early chlorite (Fe# = 0.3-0.6) is partly buffered by the mafic wall rocks, but the latest chlorite is very rich in iron (Fe# = 0.65-0.9), indicating buffering by the ascending fluid. During quartz deposition, the fluid became more reducing, partially transforming hematite to magnetite. The chlorite alteration haloes reveal addition of Co, Ni and Cr to the wall rock and show that the Q' fluid had lower Ca/Mg, Sr/Mg, Ba/Mg and Na/Mg than the syn-volcanic fluids that altered the host rocks to spilite and epidosite.

The formation temperatures of the veins, as reconstructed from fluid inclusions, depend on the hydrostatic pressure at the time of veining. Assuming syn-volcanic pressures, Q' veins in the deep gabbros and sheeted dykes are cooler (110-220°C) than those in shallow lavas (180-324°C). Assuming syn-obduction pressures, the temperatures are even lower, but the differences in depth remain.

Previous studies have demonstrated a syn-volcanic SE-trending paleomagnetic direction in the northern massifs of the ophiolite. Our analyses of the paleomagnetic direction of hematite in the Q' veins indicates a contrasting NW direction, which coincides with the published direction of regional remagnetization in the southern ophiolite massifs.

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Metal migration and ore formation in the slow-spreading oceanic lithosphere: an insight from the Central Sudetic Ophiolite, Poland

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The aim of this project (NCN 2021/43/B/ST10/03343) is to better understand the formation of large seafloor massive sulfide deposits along slow-spreading ridges.

During eight sampling campaigns, we have collected 127 of 235 planned samples, including 12 chromitites, 31 mantle peridotites from Radunia Hill and Tąpadła Pass, 8 ultramafic cumulates from the Tąpadła Pass, 28 gabbros and 9 ferrogabbros from Ślęża Mountain and Kunowska Hill, 15 dikes from the Wieżyca Hill and Kunowska Hill, 4 basalts from Gozdnica Hill, and 20 ocean-floor sediment samples from Kamionki Hill near Pustków Wilczkowski. Some of these samples have been investigated in situ both macroscopically and microscopically. Sulfides occur as irregular or globular grains, from tens of micrometers up to 1-2 cm in size. Magmatic sulfides are typically <500 μm polyphase grains of pentlandite, chalcopyrite, and pyrrhotite with pentlandite predominating in the mantle and pyrrhotite in the crust. Magmatic sulfides dissolved on serpentinisation are often recrystallized as secondary pentlandite or heazlewoodite. Hydrothermal sulfides in the crust, <1 cm in size, are mainly pyrite and chalcopyrite, and some pyrrhotite. Oxides, even magmatic oxides, are more prominent and may reach 2-3 cm in size. Magmatic oxides in the crust are mostly Fe-Ti oxides, ilmenite, and titanomagnetite. Magmatic mantle oxides are mostly chromites, especially in chromitite horizons. They are partially altered to ferrichromites on rims.

We plan to determine whole-rock major element-, trace metal-, and S contents and S isotopic compositions. Sulfides, oxides, and other relevant phases will be analyzed in situ for major-, chalcophile-, and highly-siderophile elements (HSE, namely, Au, Re, and Platinum Group Elements) and for S, Cu, Fe, and Ni isotopic compositions. We will determine the distribution of chalcophile- and HSE metals, S, and their isotopes for the entire ophiolite, its magmatic centers, individual outcrops, specimen, and thin sections. Thus, the project should play a significant role in shaping future research on the migration of S and chalcophile elements across the oceanic upper mantle and oceanic crust, and on potential zones of metal enrichment and ore formation. We should be able to indicate how metals 1) become pre-enriched during magmatic differentiation in the crust, 2) are enriched during hydrothermal migration in the crust, 3) behave during melt-rock reactions within the Moho transition zone and 4) partition between phases during the formation of the chromitite horizon in the sub-Moho mantle.

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Organic compounds leaching from coal wastes (Stożki Rymer Dump, Poland)

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Introduction

Self-heating of coal wastes leads to production of a wode range of compounds that are leachable. This leads to their migration to surface waters and soil. The aim of this simulation studies was to determine the type and characteristics of compounds leached from the selected bituminous coal waste dump. This dump (Stożki Rymer, Rybnik) was subject to many years of spontaneous heating processes, which led to the creation of a wide range of new organic substances, formed as a result of organic macromolecules cracking. In the highly industrialized and urbanized environment of Upper Silesia, there are many sources of organic pollution, such as car traffic, low emissions from individual furnaces and industrial power engineering. Determining what markers are characteristic of the self-heating dumps is crucial in assessing the degree of dump environmental impact. Rainwater penetrating the highly permeable deposit is a medium that can dissolve large amounts of toxic substances and discharge them outside.

Nine samples of coal waste were collected at selected dump sites, ground and macerated in distilled water for 72 hours in order to obtain water extracts. After centrifugation, the organic phase was extracted by solid phase extraction (SPE), and the extract composition was analyzed by gas chromatography coupled with mass spectrometry. The composition of the rock extracts before and after leaching was investigated using the same method. The values of popular geochemical indices and the percentage phenol content in the extracts were calculated.

Results and Discussion

The obtained results allowed to characterize coal wastes strongly washed with water, changes in the values of geochemical indices under the influence of this process and groups of compounds preferentially mobilized to water from dumps undergoing thermal processes. The study of the composition of water extracts of waste obtained in controlled conditions in terms of the content of toxic substances and environmental markers contributed to a better assessment of the scope of migration of substances from post-mining waste. The presence of such compounds as phenols and polycyclic aromatic hydrocarbons (PAHs) in lycheates suggests significant environmental impact of coal waste dumps.

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Petrographic description of ore-bearing martian meteorites: MIL 03346, NWA 5219, and NWA 13367

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We investigate the petrography of selected ore-bearing martian meteorites to better understand the course of evolution of martian magma - particularly with emphasis on processes controlling ore formation and their distribution on the planet. Our first results include one nakhlite (MIL 03346) and two shergottites (NWA 5219 and NWA 13367).

MIL 03346 consists of 75.0 vol.% clinopyroxene, 23.0% mesostasis, 1.5% olivine, 0.49% titanomagnetite $[Fe^{2+}_{1.44}(Fe^{3+}_{0.97}, Al_{0.09}, Ti_{0.50})O_4]$, and 0.01% pyrrhotite ($Fe_{0.89}S$). Clinopyroxenes show zonation from 23% ferrosilite (Fs_{23}), 40% wollastonite (Wo_{40}), 37% enstantite (En_{37}) augite in the core towards $Fs_{46}\,Wo_{33}\,En_{21}$ hedenbergite on the rims. Olivines are 42% forsterite (Fo_{42}) in the cores with Fo_{20} rims. Iddingsitization along their fractures constitutes evidence for rock weathering in the water-saturated environment.

NWA 5219 contains 67.7% clinopyroxene, 29.8% maskelynite, 1.6% merrillite, and 0.75% oxides: ilmenite $[FeTiO_3]$ and titanomagnetite $[Fe^{2+}_{1.64}(Fe^{3+}_{0.59}, Al_{0.1}, Ti_{0.67})O_4]$ as well as 0.15% pyrrhotite $[Fe_{0.93}S]$. Clinopyroxenes are augite ($Fs_{25\text{-}26}$ $Wo_{31\text{-}32}$ $En_{42\text{-}43}$) and pigeonite ($Fs_{40\text{-}61}\,Wo_{11\text{-}16}\,En_{27\text{-}45}$). Maskelynite precipitated at the expense of plagioclase due to the shock that the rock underwent is $An_{55}Or_{1.8}$.

NWA 13367 is made of 47.8% olivine, 35.6% clinopyroxene, 12.5% maskelynite, 3.0% merrillite, 1.0% oxides: ilmenite $[FeTiO_3]$, Mg-Al-chromite $[(Fe^{2+}_{0.8}, Mg_{0.2})(Cr_{1.7}, Al_{0.2}, Fe^{3+}_{0.1})O_4$, and Ti-chromite $[(Fe^{2+}_{1.15}, Mg_{0.17})(Cr_{0.92}, Al_{0.22}, Fe^{3+}_{0.2}, Ti_{0.34})O_4]$. Remaining 0.1% is pyrrhotite $[Fe_{0.98}S]$. Olivines are $Fo_{62\text{-}65}$. They can be distinguished by brownish color, possibly caused by shock-induced oxidation of some portion of Fe^{2+} into Fe^{3+}. Clinopyroxenes, poikilitically enclosed by olivines, are $Fs_{27\text{-}31}Wo_{7\text{-}14}En_{58\text{-}63}$ augites.

Ultimately, we will investigate at least 15 meteorites, which will then be analyzed in the context of large-scale remote sensing data delivered by martian satellites. The project aims to find out how ore formation proceeds on Mars and what factors determine ore distribution.

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Geochemistry of thermal waters and seismogenic faults in the central Colca River basin, Western Cordillera, Peru

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Thermal waters in the central part of the Colca River basin discharge in springs and geysers draining Mesozoic to Quaternary sedimentary and volcanic formations at elevations ranging from 1380 to 4330-4750 m a.s.l. Related to tectonic- and volcanic activity, this thermal system is heterogeneous and complex with divergent hydrogeochemical- and physical properties, variable isotope compositions, different reservoir temperatures, and different associated precipitates around thermal springs. The main groups of thermal waters include waters that are 1) chloride-rich (dominant), 2) sulphate-rich and 3) bicarbonate-rich. The contrasting geochemistry of the thermal waters, and variations in host rocks, result in highly variable mineral phases precipitating on surrounding rock surfaces, dry plants, and soil (Ciesielczuk et al. 2013; Tyc et al. 2022).

Active crustal faults located in this area (e.g., Benavente et al. 2017; Gaidzik et al. 2020; Gaidzik & Więsek 2021) play a crucial role in this complex hydrogeological thermal system (Tyc et al. 2022), They act as 1) barriers to infiltrating meteoric waters, 2) pathways for hydrothermal solutions and gases, and 3) passages for heated waters ascending to the surface.

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Novel biomarkers from Upper Cretaceous coals and siltstones from the North Sudetic Basin, Poland

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The Late Cretaceous succession of siliciclastic sediment from the Czerna Formation in the North Sudetic Basin (SW Poland) consists of sandstones, dark grey mudstones and shales with coal intercalations. The wide variety of lithofacies indicates variable conditions of sedimentation: coastal, lacustrine, paludal and lagoonal (Leszczyński 2018). The oldest part of the Czerna Formation consisting of lacustrine organic-rich sediments was exploited in 1842-1881 in several small mines located north of Lwówek Śląski (Milewicz 1988).

One sample of dark grey mudstone with lignite fragments from the inoperative sandstone quarry in Rakowice Małe, and five samples of coals and siltstones from the active sandstone quarry in Żeliszów, were chosen for gas chromatography-mass spectrometry analyses. All samples were thermally immature (the mean vitrinite reflectance (Rr) values ranged from 0.34-0.41%).

Here we report the occurrence of 7-*p*-Cymenylferruginol (both 7α- and 7β-isomers), which was the dominant natural product in extracts, along with two novel minor additional isomers, namely 3α- and 3β-*p*-cymenylferruginol, and two hydrocarbons, 7α- and 7β-*p*-cymenyldehydroabietane. The most likely source of these compounds in the Cretaceous appears to be from Taxodiaceaepollenites (Simoneit et al. 2021). The natural products survive unchanged, back to the Late Cretaceous, and we documented numerous additional aromatic hydrocarbon derivatives based on interpretation of their mass spectra.

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The impact of seasonality and meteorological conditions on $PM_{2.5}$ carbonaceous fractions: advantages, weaknesses and interpretation pitfalls

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$PM_{2.5}$ samples were collected in Legnica (SW Poland) to evaluate seasonal differences and to identify the possible pitfalls of using these data for air pollution monitoring purposes. As using a sole method to track sources of air pollution is rather limited, we opted to combine different techniques. For this purpose, concentrations of $PM_{2.5}$, carbonaceous fractions (TC/OC/EC), as well as carbon isotope compositions ($\delta^{13}C_{TC}$) of total carbon and FTIR spectra of $PM_{2.5}$ were evaluated together.

We observed statistically significant differences between the heating and vegetative seasons for $PM_{2.5}$ and TC/OC/EC concentrations, with higher levels during winter, resulting from the increased activity of local emission sources and specific meteorological conditions. Calculated POC and SOC values also displayed strong seasonal variabilities. Interestingly, OC/EC ratios did not show seasonal differentiation, even though differences were observed when OC and EC are considered separately, hinting that the widespread use of this ratio may lead to incorrect interpretations. For $\delta^{13}C_{TC}$, results showed a seasonality with an average $\delta^{13}C_{TC} = -25.3\pm0.4‰$ for the heating season and $\delta^{13}C_{TC} = -26.9\pm0.5‰$ for the vegetation season. An isotope mass balance (IMB) model indicated coal as the main source of pollution in the winter, and a mixing of coal, transport, and bio/organic origins in the summer. However, the interpretation for summer should be rather excluded as an interpretation pitfall. FTIR spectra of $PM_{2.5}$ for winter samples confirmed the conclusions drawn from carbon isotopes, as well as from the TC/OC/EC concentrations. FTIR spectra for the vegetative season differed from those in winter, and agreed with the other proxies, confirming a slightly higher biogenic origin for carbonaceous particles.

We suggest that a broad look at the air pollution and a multi-proxy approach are prerequisites for drawing reliable conclusions when evaluating the environmental status of the atmosphere and avoiding pitfalls when interpreting data.

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The first ion microprobe (SHRIMP) dating of zircons from the Sejny Gabbronorite-Anorthosite Massif, Mazury Complex (NE Poland)

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The Mesoproterozoic Sejny gabbronorite-anorthosite massif (SM) in NE Poland, intruded into the late Paleoproterozoic Mazowsze Domain in southeastern Fennoscandia. The SM, hidden under 600 m of Phanerozoic sedimentary strata, was drilled by the Sejny IG1 and IG2 boreholes. In the present study, a new set of age determinations on zircon grains from AMCG components (anorthosite, gabbro and jotunite) and from granite veins cutting the Sejny AMCG rocks is presented.

The new age results obtained using a SHRIMPIIe/MC ion-microprobe indicate that the SM intruded in several magmatic pulses with peaks at ca 1514 Ma and 1504 Ma. This is confirmed by concordia ages of 1513.2 ±4.4 Ma, 1514.3 ±5.4 Ma, 1504.4 ±7.6 Ma, 1503 ±4.8 Ma and 1504.8 ±5.5 Ma recorded for anorthosite, gabbro and jotunite. The new SHRIMP data from the SM indicate an age of emplacement significantly younger than the 1549 ±5 Ma age determined previously (U-Pb ID-TIMS single zircon dating; Gawęda et al. 2005). The new ages are coeval with ages obtained for the nearby Suwałki anorthosite massif and rapakivi granitoids (Wiszniewska & Krzemińska 2021).

The presence of rare and slightly older entrained zircon antecrysts (1527 ±11 Ma), reflects a two-step crystallization – in a deep-seated magma chamber and continuous crystallization during the rising of the melt and emplacement of the SM.

Finally, abundant granitic aplites and pegmatites, with sharp contacts with the host SM rocks, define a time frame for the Sejny massif solidification. The crystallization age of an individual aplitic vein was determined at 1484 ±17 Ma. Microgranites with numerous inherited zircon cores (1830.2 ±7.3 Ma and 1502 ±1.4 Ma) were generated by re-melting of the late Paleoproterozoic source of the Mazowsze Domain and by re-melting of the SM rocks.

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Rapakivi-type quartz monzonite from the Pietkowo IG1 borehole, NE Poland: a new A-type granitoid occurrence in southernmost Fennoscandia

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This study concerns the rapakivi-type quartz monzonite from the Pietkowo IG1 borehole in the Polish part of southernmost Fennoscandia.

The U–Pb dating, obtained using a SHRIMPIIe/MC ion-microprobe, indicates that the Pietkowo IG1 quartz monzonite was emplaced at 1495-1491 Ma with concordia ages of 1491 ±5 Ma, 1492 ±5 Ma and 1495 ±4 Ma. The limited number of results from the cores of larger zircon grains provided an older concordia age of 1513 ±7 Ma implying a two-stage crystallization (in the magma chamber and during rapid melt uprising and emplacement).

The Pietkowo IG1 quartz monzonite shows a specific rapakivi-type texture and weakly metaluminous, transient ferroan/magnesian and alkali-calcic nature. The elevated contents of alkalis ($K_2O > Na_2O$), F, Ga and high-field-strength-elements (HFSE) and the high FeO_t/MgO ratio of the Pietkowo quartz monzonite are compatible with other A-type granite occurrences in Fennoscandia, e.g., the Salmi (SW Russia Karelia) and Ahvenisto (S Finland) rapakivi batholiths, and the slightly older granitoids of the Mazury Complex (1516-1499 Ma; NE Poland; Wiszniewska & Krzemińska 2021). The presence of magnetite and titanite in the Pietkowo rock indicates crystallization under oxidizing conditions. The quartz monzonite is classified as A_2 sub-type, whereas the Nb/Y ratio indicates a within-plate tectonic setting.

The Pietkowo IG1 rapakivi-type quartz monzonite is an example of, so far, the southernmost Mesoproterozoic granitoid massif of A-type affinity in Fennoscandia.

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Late Paleoproterozoic sedimentation and Mesoproterozoic metamorphic event evidenced by integrated zircon- and monazite geochronology: A case study of Gdańsk IG1 paragneiss, N Poland

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The amphibolite-facies Grt-Bt paragneiss derived from the Gdańsk IG1 deep drill hole located on the coast of the southernmost Baltic Sea, north Poland, was investigated. In addition to zircons dated using a SHRIMPIIe/MC ion-microprobe, monazite crystals were dated by the microbeam chemical technique either as grain separates or in thin sections.

The zircons are characterized by detrital cores surrounded by metamorphic rims and overgrowths. The age probability-density distribution peaks for detrital zircon are at ca 2700, 1927, 1868, 1840, 1819, 1770, 1735 and 1652 Ma. The detrital zircon age clusters in the range of 1650-1880 Ma match well with the time frame of common magmatic activity in the Baltic Sea area. Thus, the Gdańsk IG1 metasediments were likely sourced from the surrounding region comprising the Transscandinavian Igneous Belt (TIB 0 (1855-1845 Ma); TIB 1 (1810-1760 Ma)), the southernmost Baltic Sea area, and Öland- and Lithuanian rocks of the West and Mid Lithuanian Domains (WLD and MLD). The zircon population at 2.10-1.90 Ga and the subordinate late Archaean population at 2.7 Ga match ages from the western margin of Sarmatia (i.e., Osnitsk-Mikashevichi Igneous Belt and Belarus-Podlasie Belt). The youngest grains were probably derived from AMCG suites in Finland and Lithuania.

Zircon-rim and monazite isotope analyses record a metamorphic event at ca 1485 ±9 Ma, and 1498 ±6 Ma, respectively, corresponding with the time of AMCG magmatic activity recognized previously in the basement of N Poland. Monazite exhibits three overlapping populations based on Th-U-total-Pb geochemical dating. Y-enriched parts (pale on BSE images) of monazite provide an age of 1494 ±23 Ma, confirming the isotopic recognition. Numerous older fragments identified within monazite grains (1539 ±13 Ma and 1596 ±17 Ma) reflect earlier stages of metamorphic evolution before garnet breakdown.

The youngest detrital zircon constrains the deposition of the Gdańsk sediments to a time after ca 1650 Ma, but prior to their metamorphism at ca 1600 Ma.

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Metarhyolites from the Kamieniec Metamorphic Belt: geochemical and zircon isotopic constraints on the Early Palaeozoic magmatic event in the Saxothuringian

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The Kamieniec Metamorphic Belt (KMB), a longitudinal fragment of crystalline basement located in the Fore-Sudetic block, comprises a volcano-sedimentary succession dominated by mica schists with intercalations of scarce paragneisses, marbles, quartz-graphite schists, eclogites and bimodal volcanics. The succession underwent cold subduction in Variscan times and records HP-LT metamorphism under lawsonite eclogite facies conditions.

The chemical composition of the rocks corresponds to rhyolites of subalkaline, strongly peraluminous composition (normative corundum), enriched in LREE over MREE-HREE ($[La/Sm]_{CN}$ 2.8-5.5, $[Gd/Yb]_{CN}$ 1.0-1.5) and depleted in HFSE. Variations in major- and trace elements suggest fractionation of plagioclase, biotite, apatite, ilmenite, and cordierite with some zircon and perhaps monazite. The metarhyolite zircons deliver the dominant late Cambrian age of 512.4 ± 4.1 Ma (magmatic event), while the inherited Neoproterozoic- and Archean ages (c. 560, 630 and 2588 Ma) point to Cadomian and ancient detrital components mixed and recycled from the source to the felsic melt. Discrimination diagrams show that felsic melts were most probably generated from immature sediments (greywackes, psammites originally deposited in arc environments, e.g., active continental margin) and emplaced in a post-collisional to post-orogenic (transitional) setting. Presumably, anatexis followed syn-collisional crustal thickening of a limited degree and was triggered by heat input from the upwelling asthenosphere.

The KMB metarhyolites show several similarities with other late Cambrian, S-type, peraluminous (meta)granites from the Saxothuringian domain in the West Sudetes (e.g., the Rumburk granites, the Izera-Kowary gneisses). The generation of rhyolitic magma seems to correlate with intrusions into the transitional crust at the peripheries of the continental crust. Thus, we consider the origin of the KMB metarhyolites to be another facet of magmatic pulses concurrent with the gradual change of the tectonic environment marking the end of the Cadomian orogeny (arc-Gondwana continent collision) and the onset of Cambro-Ordovician rifting.

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Amphibolites from roof pendants of the Kudowa massif: A mineralogical- and geochemical study

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The study focused on amphibolites from roof pendants of the Kudowa massif (Central Sudetes, SW Poland). The rocks are fine-grained with metamorphic foliation (dominant S2 foliation, locally with relics of an older foliation S1). They are mostly composed of amphibole (70-80 vol.%), plagioclase (< 30 vol.%), mica, chlorite and subordinate or accessory apatite, epidote, garnet, titanite, rutile and ilmenite. Amphiboles show zoning with rims composed of Mg-hornblende (Al^{IV} 0.41-1.87 pfu; X_{Mg} 0.47-0.70; $[Na+K]^A$ 0.10-0.60 pfu), and cores mainly of pargasite (Al^{IV} 0.27-1.95 pfu; X_{Mg} 0.49-0.73; $[Na+K]^A$ 0.04-0.60 pfu). The accompanying plagioclase shows a wide range of An content with rims X_{An} 0.19-0.64 and cores 0.10-0.60. The composition of rare garnet is almost homogeneous (X_{Alm} 0.56-0.62; X_{Sps} 0.09-0.11; X_{Prp} 0.09-0.12; X_{Grs} 0.16-0.22).

The conditions of metamorphism were estimated by combined amphibole–plagioclase±quartz thermobarometry. Depending on the sample, pressure ranged from 4 kbar at 600°C to 8-12 kbar at 650°C. For the garnet-bearing sample, P-T conditions from 6.3 kbar at 530°C to and 8.3 kbar at 570°C were obtained (Amp-Plg-Grt geothermobarometer).

The amphibolites are characterized by low contents of SiO_2 (44.5-44.5 wt%), high TiO_2 (1.26-2.84 wt%), Al_2O_3 (13.3-15.6 wt%), MgO (7.19-8.81 wt%, mg# 0.35-0.48). The chondrite-normalized REE diagram shows moderate enrichment in LREE over MREE and HREE (La/Sm_{CN} 1.22-1.24; La/Yb_{CN} 1.85-1.99) though one sample is depleted in LREE (La/Sm_{CN} 0.58; La/Yb_{CN} 0.56). On the N-MORB-normalized diagrams, the profiles show weak negative Nb anomalies. The discrimination diagrams mostly display subalkaline, N-MORB to E-MORB affinities.

The results of our study suggest a dominant E-MORB-like source of magma perhaps with some subduction zone-derived components, as implied by the negative Nb anomaly. There are also no signs of significant thermal influence due to the Kudowa massif on the rocks, and only minor alteration in composition may possibly be due to hydrothermal activity originating from the massif.

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The origin of lead artifacts from Novae – applications of Pb isotopes in research on the provenance of artifacts from N Bulgaria.

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Introduction

The objects of the research are lead samples from the archaeological site of Novae (N Bulgaria). The samples are fragments of architectural elements (e.g., columns, water pipes, etc.). One of the samples is a lead bar. The aim of the research is to try to determine the provenance of the ore used in the smelting of lead used by the ancient Romans. For this purpose, lead isotope analysis with the use of MC-ICP-MS equipment was used. The results are in the ranges: ^{208}Pb/^{204}Pb: 38.40-38.87; ^{207}Pb/^{204}Pb: 15.61-15.68; ^{206}Pb/^{204}Pb: 18.46-18.75. The results were compared with literature data and databases from OXALID and with the results for galena from Madan (Bulgaria), Trepca (Kosovo) and Rudnik Mine in Serbia. The results of the analyses indicate that the ore for making the bar comes from a different place than the ore used for the rest of the samples. This is indicated by a significantly lower values ^{208}Pb/^{204}Pb and ^{206}Pb/^{204}Pb. The rest of the samples seem to belong to one complex. Comparing the results of the lead samples to the OXALID data, it is seen that the samples do not correlate well with any of the ore sources in Bulgaria. For most of the samples, the results are similar to those of ores from deposits located in SE or SEE Bulgaria. For the bar sample, deposits from NW or NWW Bulgaria are suggested. A comparison of the lead results with the ore results from Rudnik Mine (Serbia) indicates that it may be a potential place of ore origin. There is a very good correlation with most of the Novae results. Comparing the results from Novae to the results of ores from other areas where the Romans could extract ore (Italian, German, Alpine or French deposits), any correlation is very small or absent. All these facts make it most likely that the ore comes from local sources (Bulgaria or Serbia). Comparing the archaeological dating of the studied samples to the theoretical sources of ore, it is seen that, over time, the Romans changed the source of the ore for lead production. This is indicted by the different origins of the bar, the youngest examined object (4th century AD).

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A *ca* 3.3 magmatic event in the Saglek Block, Labrador

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Reliable interpretation of field relationships is crucial for understanding the evolution of areas with complex geological histories. Here we present zircon data from gneisses of the Saglek Block, Canada which have a complex magmatic- and deformational history from *ca* 3.9 Ga to 2.5 Ga. The Saglek Block predominantly consists of the Archean Uivak gneiss that is mostly tonalite-trondhjemite-granodiorite (TTG), with lesser amounts of intermediate- and mafic components. It has been divided into the Uivak I grey gneisses with compositions that vary from tonalite to quartz monzonite and the Uivak II augen gneisses that include Fe-rich granitoids and associated diorites (Bridgwater et al.1976). Although isotopic ages for Uivak I are consistently greater than *ca* 3.6 Ga, estimates for Uivak II protoliths vary widely between *ca* 3.6 and 3.3 Ga (Sałacińska et al. 2019; Wasilewski et al. 2021).

This study presents new zircon ages utilizing Secondary Ion Mass Spectrometry (SIMS). Augen gneiss on Mentzel Island matching the definition of Uivak II gneiss has an age of *ca* 3.3 Ga, similar to Maidmonts gneiss (Sałacińska et al. 2019) and Illuilik gneiss (Wasilewski et al. 2021). It is intruded by granitic sheets at *ca* 2.7 Ga and *ca* 2.5 Ga, during high-temperature metamorphism. Augen gneiss intrudes Uivak I on nearby Maidmonts Is. where new dating demonstrates the formation of gneissosity before 3.3 Ga. Geochemical variation between samples of *ca* 3.3 Ga gneiss from different areas can be attributed to the involvement of different source rocks.

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Monazite reaction history in an eclogite

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Monazite is a common accessory phase in metamorphic rocks. However, it is very rare in eclogites. We studied high-pressure (HP) rocks from the Vestgötabreen Complex, Svalbard to better understand the monazite reaction history in metamafic rock and its relationship to other phases. Monazite is present in the matrix (Fig. 1a) or forms rare, small inclusions (< 30um) in the Ca-rich garnet rim (Fig. 1b). Tabular- or elongated pseudomorphs in the matrix comprise monazite, allanite-I, apatite and epidote (Fig. 1a), whereas the monazite inclusions are surrounded by allanite-II and apatite coronas (Fig. 1b).

Mineral chemistry, pressure-temperature (P-T) estimates and textures indicate that the observed pseudomorphs including monazite can be a product of florencite- and lawsonite breakdown reactions which are the common LREE sinks in HP rocks. These two reactions could have happened at similar P-T somewhere between peak-P (23.5 kbar at 507°C) and peak-T (21.4 kbar at 553°C). The growth sequence may be as follows: florencite>monazite>allanite-II, with lawsonite breakdown providing an extra source of LREE to produce allanite-I and calcium to form Ca-rich garnet rims. Our study suggests that monazite can grow in eclogites under HP conditions due to the breakdown of the LREE-bearing phases as an alternative mechanism to metasomatic growth (e.g., Schulze et al. 2015).

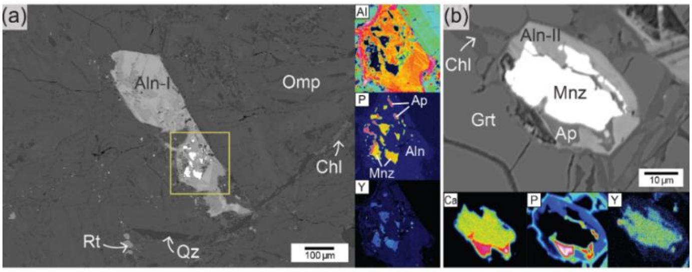

Fig. 1. BSE images and X-Ray maps of (a) pseudomorph and (b) inclusion in the garnet. Aln – allanite, Ap – apatite, Chl – chlorite, Grt – garnet, Mnz – monazite, Omp – omphacite, Qz – quartz, Rt – rutile

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Lunar zircon from Apollo 15 and 16: shock nanostructures and implications for geochronology

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Meteorite collisions are ubiquitous processes in the Solar System. Shocked zircons contain characteristic microstructures that may be indicative of the age and shock conditions of impacts on the Earth's Moon (e.g., Crow et al. 2017). However, many shock-related microstructures in lunar zircons and their mechanisms of formation are not well understood and, hence, implications for impact conditions and age dating are unclear. Here, we studied eight lunar zircons and associated phases with transmission electron microscopy to unravel their histories.

We observed a complexity of shock-related features in zircon: (1) Planar and non-planar fractures, (2) wide zircon rims around baddeleyite cores, (3) polycrystalline or granular textured zircon, in most cases with sub-µm-size inclusions of ZrO_2 (monoclinic baddeleyite and cubic zirconia), (4) irregular networks of amorphous domains, (5) locally-recrystallized domains, (6) inclusions of FeS associated with FeNi metal particles at triple junctions in granular zircon and baddeleyite. Often, different shock-related microstructures overprint one another, indicating different stages of an impact process, or even multiple impact events.

Among the listed features, (1) and (4) can be attributed to the effect of shock wave propagation and shock deformation/amorphization of the lattice, (2) and (3) are attributed to shock heating and mineral reactions triggered by temperature and (5) reflects post-shock annealing and recovery of the damaged lattice. Inclusions containing FeNi alloys (6) can be explained by a localized melting and mixing if material during an impact event and, possibly, the presence of meteorite material. Interestingly, the variety of deformation microstructures had little to no effect on zircon and baddeleyite isotopic ages identified earlier (Vanderliek et al. 2021).

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Evidence for emergent land on the early Earth recorded in low-δ^{18}O zircon signatures from the Napier Complex, East Antarctica

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The nature of surface environments in the Eoarchean (4-3.6 Ga) is recorded mainly in isotopic systems. At the time, the Earth was covered by oceans with little evidence of emergent land (Rosas, Korenanga 2018). Since exposed land may be a prerequisite for prebiotic chemical evolution and the development of life, identifying the time of its emergence is of great importance. The recognition of sub-mantle δ^{18}O (<4.7‰) magmas provides such evidence, as their genesis requires interaction with meteoric water rather than seawater (Troch et al. 2020). Zircon crystallizing from such magmas would preserve these low-δ^{18}O signatures.

This study included three Eoarchean orthogneisses from the eastern Tula Mountains, Napier Complex, East Antarctica. Analyses of oxygen isotope compositions were performed on zircon domains already dated by Król et al. (2020). Two >3.5 Ga gneisses are characterized by high Y-HREE-Nb-Ta, consistent with genesis of their protoliths through melting of crustal sources at low pressures <1.0 GPa. These rocks contain magmatic zircon with sub-mantle δ^{18}O of *ca.* +2 ‰. Such values resemble those typical of hot-spot or extensional environments, where meteoric water can interact with magmatic systems at shallow depths, for example Yellowstone and Iceland (Troch et al. 2020). The discovery of isotopically light δ^{18}O values in >3.5 Ga zircon from the Napier Complex points to the existence of shallow magmatic-hydrothermal systems driven by meteoric water in the early Archean. This, in turn, provides evidence that land had emerged above sea level prior to 3.5 Ga. This study therefore provides isotopic evidence for the earliest-known emergence of land, and for the formation of conditions suitable for life.

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Conditions prevailing during the formation of 14th-17th century metallurgical slags from Polichno near Chęciny, Poland

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Analyses of historical metallurgical slags are the best way to obtain information about the conditions under which metals were produced in historical times. Based on the chemical- and phase composition, it is possible to draw information about the minimum smelting temperature, the viscosity of the metallurgical melt, and the oxidation-reduction conditions under which smelting was carried out.

This study focuses on determining the atmosphere during smelting in the Old Polish Industrial District based on the 14th-17th century smelting slags in Polichno near Chęciny. Geochemical (XRF, ICP-MS) and mineralogical (SEM-EDS, EPMA) analyses of the samples allowed to determine the liquidus- and solidus temperatures and the oxygen- and sulfur fugacities of the slags during smelting.

Slags from Polichno were divided into five main types (POL1-POL5). An additional sample with macroscopically visible galena grains (POL6) was distinguished separately. Both glassy (POL2-3) slags and hypocrystalline slags (POL1, POL4-5) were found. In the glassy slags, crystals of quartz/cristobalite, pyroxenes, litharge, galena, and metallic Cu and Pb were observed. In hypocrystalline slags, wollastonites, arsenides, sulfides, and metallic Cu were most frequently observed. In POL6, slag quartz/cristobalite, galena, anglesite, cerussite, and glass containing an increased concentration of PbO were identified.

Based on high-temperature experiments, the liquidus temperature was determined to be 1100°C for glassy slags and 1200°C for hypocrystalline slags. The solidus temperatures were ca. 800°C and 1100°C, respectively. The phase composition of sample POL6 indicates that it was most likely formed during the roasting of lead ores before the primary smelting process.

Once the temperature range was determined, Predominance Area Diagrams (PAD) were constructed based on thermodynamic calculations. They allowed to reconstruct the values of oxygen- and sulfur fugacities during smelting. The oxygen fugacity (logP O_2) during smelting in Polichno ranges from -19.74 (800°C) to -4.30 (1200°C). The sulfur fugacity (logP S_2) ranged from -9.36 (800°C) to -2.50 (1200°C).

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Preliminary studies of spinel group minerals in Neogene andesites from the Pieniny Klippen Belt (Poland)

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Neogene andesitic rocks form small-volume hypabyssal dykes and sills that accompany the Pieniny Klippen Belt (PKB; Birkenmajer 2003). The PKB is a very narrow geological unit that separates the Outer and Inner Carpathians and comprises tectonically deformed Mesozoic to Neogene sedimentary rocks.

The presence of magnetite in the andesites was first described by Małkowski (1921), while research by Hubicka-Ptasińska (1970) provided data on the characteristics of Fe and Ti oxide minerals. It was found that the magnetites from Mount Jarmuta underwent maghemitization and martization, while the magnetites from Mount Wżar underwent igneous corrosion without the former changes. Detailed studies of andesite from Wżar recognized two generations of euhedral Fe-Ti oxides, the first, titanomagnetite and titanomaghemite (< 0.3 mm) and the second, titanomagnetite (< 0.05 mm). Michalik et al. (2005) also noted the presence of titanite and ulvöspinel (ulvite) in samples from the vicinity of Szczawnica.

Micro-petrographic studies have shown the presence of small and large magnetite crystals (Hubicka-Ptasińska 1970), the latter often containing sulphide inclusions (pyrite, pyrrhotite, chalcopyrite). Moreover, the minerals were seen to vary depending on the location of the andesites. In the Mount Wżar area, anhedral magnetites (< 150 µm) occur intergrown with augite, and fine (< tens of µm) magnetite occurs in the opacitic rims of amphiboles (in intergrowths with pyroxenes, plagioclases, and quartz). In the area of Szczawnica – Krościenko, ilmenite lamellae were observed in large (< 300 µm) euhedral magnetite crystals. In addition, ulvöspinel is seen to be intergrown with ilmenite, feldspars, amphiboles, quartz, and magnetite.

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Gold from a NYF-type pegmatite from the Piława Górna quarry, Góry Sowie Block, SW Poland

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The Piława Górna quarry is a well-known occurrence of anatectic pegmatites in the Góry Sowie Block, Sudetes, SW Poland (Szuszkiewicz et al. 2013). The pegmatite system could be classified as the rare-element class of pegmatites (Černý & Ercit 2005) and represents mixed NYF (Nb-Y-F) + LCT (Li-Cs-Ta).

Gold was found in Pb-Bi sulphides of late hydrothermal mineralization within a blocky feldspar zone of a NYF-type pegmatite dike. The mineralization forms thin (< 1 mm) veinlets along microcline cleavage surfaces and small thin (< 2 cm in diameter) nests in fractured quartz. Cosalite ($Pb_2Bi_2S_5$) pyrite (FeS_2), bismuth (Bi) and chalcopyrite ($CuFeS_2$) are primary ore minerals. Bismuthinite (Bi_2S_3) and galena (PbS) are secondary minerals after cosalite, and bismite (Bi_2O_3) is secondary after bismuth. Gold forms irregular grains, up to 100 μm large (usually < 10 μm). In reflected light, the gold is isotropic, yellow, and has a reflectance of about 77%. It often crystallizes in microcracks in quartz and in fractures along cleavage planes in feldspars. Gold is younger than cosalite and older than bismuthinite and galena. EPMA chemical analyses revealed that the tested grains are an alloy of gold and silver forming electrum with the chemical composition of $Au_{0.71\text{-}0.77}Ag_{0.23\text{-}0.29}Bi_{0.00\text{-}0.01}$. Within the largest gold grain, a thin (3 μm) inclusion of silver (Ag) was found. The silver is isotropic, shows a white color and a very high reflectance of about 93 %. The presence of gold and silver was confirmed by making a map of the surface distribution of elements.

This is the first finding of gold in the pegmatites from Piława Górna and in the entire Góry Sowie Block.

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Migration of chalcophile metals and isotope (S, Fe, Cu) fractionation through an oceanic crust-mantle transition zone (ICDP OmanDP)

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The drill holes CM1A and CM2B of the International Scientific Drilling Program (ICDP) Oman Drilling Project uncover an unprecedented opportunity to study metal migration at the crust-mantle boundary of an ancient fast-spreading mid-ocean ridge system where arriving primitive MORB melts extensively react with the mantle. The layered gabbro sequence is underlain by a sequence of massive dunites in some cases intercalated with gabbro (here called Moho Transition Zone, MTZ), followed by mantle harzburgites.

The sulfide, S, and Cu concentrations increase downwards in the gabbros (from ~0.004 to 1.0 vol.‰, from 341 to 832 ppm, from 110 to 280 ppm, respectively), are high at gabbro-dunite contacts (0.1 vol. ‰, ~480 ppm, 100 ppm) and decrease (<0.001 vol. ‰, ~63 ppm, 20 ppm) downwards in the mantle harzburgites. At least half of the sulfides are secondary, especially in serpentinized rocks, but magmatic pyrrhotite-pentlandite-chalcopyrite are well-preserved in the lower crust sequence and at gabbro-dunite contacts.

The $\delta^{34}S_{\text{whole-rock}}$ supports a predominantly mantle signature with minor seawater addition (+1.9 to +2.3‰, +3.6 to +5.5‰). With $\delta^{34}S$ in pyrrhotites (+0.14‰ to +1.46‰), chalcopyrites (–0.78 to +0.73‰), and pentlandites (–0.27 to +2.35‰), a bulk sulfide $\delta^{34}S$ (+0.4 to +1.4‰) is similar to the whole-rock $\delta^{34}S$ (+0.6 to +0.9‰). Sulfides show variable Fe and Cu isotope signatures, i.e., pyrrhotite (+0.51 to +2.11‰), chalcopyrite (+0.76‰ to +0.83‰ of $\delta^{56}Fe$ and −0.56 to +0.43‰ of $\delta^{65}Cu$, respectively) and pentlandite (+0.9 to +1.82‰). However, bulk $\delta^{56}Fe_{\text{in-situ}}$ for magmatic sulfide grains (+0.22 to +1.33‰) are close to mantle values (+0.025±0.025‰, Craddock et al. 2013).

The enrichment in sulfides, S and Cu in the MTZ seems to be magmatic, possibly through a melt-mantle reaction between gabbroic veins and mantle as we proposed previously for the slow-spreading oceanic lithosphere. However, seawater-derived fluids likely remobilized sulfides from the mantle sequence during serpentinization and the primary sulfide phases have been altered.

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Hemicellulose detection in sedimentary organic matter using methanolysis-GC-MS

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Cellulose has been identified in lignites, including both detritic coals and xylites, but the preservation potential of hemicelluloses, which are less resistant to decay during early diagenesis than cellulose, is generally considered very low. Here we present the finding of hemicellulose in Miocene xylites (fossil wood) and Cretaceous xylo-detritic coals from Poland. Based on chemical analysis, the lignites contained important holocellulose (22-37 wt.%), α-cellulose (wt. 8-29%) and hemicelluloses (wt. 7-13%). The main building blocks of hemicelluloses in fossil softwood based on methanolysis-GC-MS study are mannose and glucose, with lesser amounts of xylose, galactose and arabinose as well as minor rhamnose and fucose. In fossil hardwood, xylose is more abundant than mannose. The preservation of hemicelluloses in fossil material may occur due to structural interconnection between lignin, cellulose and hemicellulose (*i.e.*, lignocellulose), common in extant wood and potentially more resistant to decomposition (Marynowski et al. 2021). Our results show that hemicelluloses can persist for millions of years under favorable conditions with only minor structural changes due to slow microbial- and/or diagenetic decay. During growth and post-mortem, wood degradation by fungi may be the crucial factor changing the structure of the hemicelluloses, whereas hemicellulose can be preserved when depositional conditions are anoxic/dysoxic, optimally in salt water.

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Chemical- and petrological heterogeneity of lithospheric mantle beneath N Patagonia (Argentina) - case study of Cerro Chenque xenoliths

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Mantle-xenolith-bearing, back-arc Pliocene-Quaternary alkali basalts occur in N Patagonia, Argentina. The Cerro Chenque (Rio Negro province) trachybasaltic lavas carry small (< 10 cm in diameter) xenoliths of anhydrous, spinel-bearing harzburgites, dunites and less abundant clino-, orthopyroxenites, and websterites.

The peridotites are protogranular, but their texture is not well equilibrated, e.g., clinopyroxene (Cpx) crystals enclose numerous remnants of orthopyroxene (Opx). All the phases forming xenoliths are Mg-rich (olivine Fo=90.5-93.5%; Mg#^{Opx}=0.90-0.94; Mg#^{Cpx}=0.91-0.95) but are not in chemical equilibrium with each other. The composition of spinel is extremely variable (Mg#=0.65-0.85; Cr#=0.00-0.70). Two types (Group I and II) of REE patterns occur in Cpx and Opx: (1) In Group I, the REE pattern is U-shaped in both pyroxenes, REE contents vary significantly (e.g., La=0.5-50 primitive mantle values, PM); (2) in Group II, Cpx has a convex-upward REE pattern (La=5-7 PM), Opx is LREE-depleted. Clinopyroxene in both groups has positive Th-U and negative Ti anomalies. Sulfides in the peridotites are scarce and small (av. 17 μm in diameter) but, in one sample, numerous grains of sulfides are gathered in a very small area. Sulfides from orthopyroxenite are numerous but small (av. 9 μm) whereas, in clinopyroxenite, they are less abundant and larger (av. diameter 37 μm). Sulfides from peridotites and orthopyroxenite are pentlandite-dominant ($Po_{8-17}Pn_{81-85}Ccp_{2-8}$), whereas sulfides from clinopyroxenite are dominated by pyrrhotite ($Po_{89}Pn_{9}Ccp_{2}$).

Strong variations in rock-type and in the chemical compositions of minerals forming Cerro Chenque xenoliths suggest a heterogeneous upper-mantle structure beneath N Patagonia. Clinopyroxene is secondary and was produced due to Opx reaction with a metasomatic silicate melt. The heterogeneity in the composition of Cpx may result from the chromatographic effect during melt-rock reaction, whereas Group II xenoliths would have been affected by less differentiated melt; the chromatographic reaction did not affect the modal contents and compositions of the sulfide phases.

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Diversity in zircon preservation in Eoarchean rocks of the Itsaq Gneiss Complex, SW Greenland

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U-Pb geochronology of zircon is commonly applied to dating of Archean cratons as, despite metamorphism and deformation, zircon grains generally preserve igneous ages of the protoliths. This is especially important in reconstruction of the geological history of cratons that have experienced polymetamorphism, as is the case of the Itsaq Gneiss Complex (IGC) of SW Greenland. This study compares Eoarchean samples from the Isukasia- and Færingehavn terranes which underwent both Eo- and Neoarchean metamorphism (Nutman & Bennett 2018).

Two samples were collected from the Isukasia terrane, from either side of the Isua Greenstone Belt. Zircon grains from the inner sub-terrane of Isukasia preserve igneous morphology with oscillatory zoning in prisms and pyramidal terminations; minor rounding and thin rims indicate limited metamorphic reworking. The $^{207}Pb/^{206}Pb$ zircon age obtained by Secondary Ion Mass Spectrometry (SIMS) is *ca* 3.71 Ga. Zircon grains from the outer sub-terrane of Isukasia have very well-preserved igneous morphologies, but also contain abundant inclusions and signs of metamictisation and fluid alteration. The $^{207}Pb/^{206}Pb$ zircon ages are scattered, with a subgroup at *ca* 3.79 Ga that provides a minimum age for the host granitoid. The older age may be disturbed by subsequent events as other samples from the area have ages >3.8 Ga (Kielman et al. 2018). Zircon from the Færinghavn terrane sample have well-developed metamorphic rims around rounded igneous cores. The $^{207}Pb/^{206}Pb$ zircon age of these grains is ca 3.64 Ga, with metamorphism at *ca* 2.7 Ga. Variety in zircon structures is a response to different degrees of 2.7 Ga metamorphism from lower amphibolite facies in the north part of the IGC, to granulite facies in the south.

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Geochemical- and petrological investigations of coal waste from the Rymer Cones dump (Upper Silesian Coal Basin, Poland)

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Waste generated during bituminous coal mining in Rymer mine in Niedobczyce (Upper Silesian Coal Basin, Poland) were deposited in a nearby dump that originally had the shape of three cones some 60-65m high. Self-heating processes led to the formation of various harmful pollutants. In attempting to stop the heating, the waste material was relocated, and two cones were combined into one (Cone no. 1). Despite many attempts, the dump still has an elevated temperature. Currently the dump covers an area of 13ha, and its capacity is 2 mln m^3 of waste (Misz-Kennan et al. 2015).

Organic matter is present in the waste in the form of laminae, lenses, and as small particles disseminated among other minerals, mostly clay minerals. The content of organic matter is highly variable within the range 0.0-82.4%. Organic matter is dominated by macerals of the vitrinite group. These macerals in samples unaffected by heating or only slightly oxidized have the features of unaltered macerals and a reflectance of ca 0.6%. Samples affected by heating have a paler colour, irregular cracks or paler-colored oxidation rims. Their reflectance reaches 1.6%. The content of liptinite and inertinite macerals is usually < 10% (Misz-Kennan 2010; Misz-Kennan & Fabiańska 2010).

Organic matter in rocks sampled in the thermally active zones shows extensive changes in organic geochemistry such as *n*-alkanes with the Gaussian distribution pointing to a pyrolytical origin, depletion in biomarkers, high contents of phenols reflecting thermal destruction of vitrinite, and a wide range of polycyclic aromatic hydrocarbons. This pyrolytical fingerprint is also found in the dust emitted to the air and deposited on nearby plants (Fabiańska et al. 2016).

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Petrographic classification system for organic particles affected by self-heating in coal waste (An ICCP Classification System, Self-heating Working Group – Commission III)

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Self-heating of coal wastes is one of the major environmental hazards associated with co-mined non-coal rocks produced in coal mining areas, collectively referred to as coal-waste dumps. The waste, composed primarily of claystones, mudstones, and sandstones, and less frequently of carbonates and conglomerates. as well as of inferior/low grade coal, contain various amounts of organic matter. The organic matter occurs as lamina, lenses, and small particles disseminated among minerals. Its oxidation may lead to self-heating and self-combustion that affect both minerals and organic matter within the coal waste dump.

The range of oxidative and thermal alteration of macerals induced by self-heating and self-combustion is dependent on the properties of the organic matter (maceral composition and rank) and other factors, including the presence of pyrite, compaction of wastes, shape of the dump, direction of winds, atmospheric precipitation, and frequency of heavy rainfalls. Duration and rate of self-heating and self-combustion have a strong impact on the individual appearance and optical properties of organic matter particles and thus on their forms.

In 2020, the Self-Heating Working Group of the International Committee for Coal and Organic Petrology (ICCP) completed development of a coal petrographic classification system for the various forms of transformed organic matter present in the coal-waste dumps, which permits determination of their link with *in-situ* self-heating and self-combustion conditions. The classification of transformed organic particles is composed of six interconnected levels. Level 1 determines the nature of the particle (organic or mineral). Level 2 determines the degree of alteration of organic particles (unaltered, altered, and newly formed). Level 3 determines the type of organic particles identified under organics at levels 1 and 2: non-altered represented by huminite, vitrinite, liptinite or inertinite macerals groups; altered represented by porous or massive particles; newly formed represented by pyrolytic carbon, bitumen, chars, graphite, and coke. Level 4 determines the optical properties of particles in terms of fluorescence (fluorescent, non-fluorescent). Level 5 determines the optical texture of the particles (isotropic, anisotropic). Level 6 determines associated optical appearance related to the particle examined. This level applies only to altered particles and newly formed particles. The following forms are categorized in the classification: fractures, fissures, cracks; paler/darker oxidation rims; plasticized edges; bands; devolatilisation pores; paler particles. It has to be emphasized that a given particle might contain more than one form from level 6, i.e. it might have cracks and paler oxidation rims around the cracks.

The ICCP-based classification system of transformed organic particles in coal-waste dumps reflects the complexity of organic forms present at various self-heating and self-combustion conditions in relation to their original maceral composition, coal rank, heating rate, and duration. It enables understanding of the thermal history of the dump, the detection of the fire fronts, as well as the lateral and vertical distribution of oxidatively and thermally affected material in, and dump management and potential reclamation. This is exceedingly important as organic particles affected by self-heating and self-combustion display the potential to leach hazardous substances of concern to the environment.

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HP-LT metamorphism recorded by the Leszczyniec Unit, northern Bohemian Massif

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The Karkonosze-Izera Massif in the Sudetes, Bohemian Massif, is represented by a Variscan nappe stack composed of (par)autochthonous orthogneisses (Cm_3-Or_1) and a volcano-sedimentary succession (D_2-C_1) overridden by lower- and middle allochthons comprising metavolcanosedimentary rocks (Or-?D/D_2). The latter two allochthons are dominated by mica schists and phyllites with minor intercalations of marbles and metapsammites as well as basic- and felsic metavolcanics. Notably high pressure-low temperature (HP-LT) metamorphic rocks were identified within these units, including garnet-bearing blueschists at the iconic Kopina locality. The uppermost tectonic thrust sheet, namely the upper allochthon or the Leszczyniec Unit, is represented by a bimodal suite of mafic and felsic intrusive and extrusive rocks (Or_1) of debated origin. Previous qualitative pressure-temperature estimates on the Leszcyniec Unit suggested epidote-amphibolite facies conditions of metamorphism (Kryza & Mazur 1995). Notably, these authors reported the occurrence of rare Na-bearing amphibole (winchite) in the Leszczyniec metabasites. Careful re-investigation of the Leszcyniec metamafic member revealed the abundance of Na-amphiboles forming rims on Ca-amphibole or anastomosing channel-like microtextures within Ca-amphibole dominated matrix. Sodium amphiboles are primarily represented by ferro-ferri winchite and riebeckite. Phase equilibrium modelling suggests HP-LT equilibration conditions at ~10-11 kbar and 450°C. The developed mineral assemblages and the mutual textural relationship between Ca- and Na-amphiboles suggest an anticlockwise metamorphic evolution of the Leszczyniec Unit with an initial medium pressure-medium temperature phase followed by the HP-LT event. Such a metamorphic pattern implies tectonic erosion of the upper plate and down-dragging of its parts simultaneously with the subduction of the Saxothuringian margin.

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Composition of ravatite from the burning coal-waste dump near Bytom, Poland

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Ravatite (phenanthrene, $C_{14}H_{10}$) is a sublimation product found in a burning brown-coal seam near Ravat/Tadzhikistan (Nasdala and Pekov, 1993). Other crystallized aromatic hydrocarbons such as Freitalite (anthracene, $C_{14}H_{10}$) and Hoelite (anthraquinone, $C_{14}H_8O_2$) from the Königin Carola mine dump, Freital, Saxony, Germany are formed during pyrolysis of coal at low oxygen fugacity as a sublimation from gas phase (Witzke et al. 2021). Usually, these minerals occur as crystals a few millimetres in size and show an intense violet- or whitish-violet to white colour and have a strong rubbery odour (Nasdala & Pekov 1993; Witzke et al. 2021). These purple- to whitish-purple organic minerals were collected from a burning bituminous coal-waste dump nearby Bytom city (Poland) in those parts initially affected by the fire. The temperature ranged from 30-60°C, and significant humidity from 75-90%. The crystals were growing on dry-wet parts of the coal-waste surface. Measurements of the occurrence of selected gases indicate the presence of over-standard concentrations of benzene. The remaining gases do not exceed the acceptable standards, but their concentrations are relatively high compared to air in a clean environment. The GC-MS analysis of clean Ravatite crystals revealed other compounds such as anthracene (~10.9%), dibenzothiophene (~2.4%), fluorene (~1.5%), methylphenanthrenes (~1.5%) and other minor compounds such as dibenzofuran (~0.3%), methyldibenzofurans (~0.4%), methyldibenzothiophenes (~0.3%) or methylfluorenes (~1.1%) in addition to phenanthrene (~81.7%) which is the main component of ravatite. Moreover, ravatites contain other compounds such as fluorenone, anthrone, 1-phenylnaphthalene, fluoranthene or $n\text{-}C_{17} - n\text{-}C_{20}$ *n*-alkanes. Previously, dibenzothiophene was found only in thermally affected coal waste. When pyrite decomposes to elemental sulphur or sulphide ion during self-heating, it is later incorporated into the PAHs structure as happens during the vulcanization process, which may explain the presence of these sulphur heterocycles in the crystal structure. The pyrolysis effect can be seen from the Gaussian distribution of *n*-alkanes.

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Dating of coal-seam fires provide insights on tectonic events

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Coal-seam thinning, and disappearance is recorded in both the Polish and Czech parts of the south-western part of the Carboniferous Upper Silesian Coal Basin. Associated gangue rocks are altered, variably coloured, and with increased fracturing, porosity, and reduction of physical and mechanical properties. As these phenomena make coal-seam exploitation difficult and unprofitable, an understanding of their cause is important from both applied and scientific points of view.

Samples of gangue rocks overlying the vanished coal seams were collected from the Jastrzębie-Bzie Coal Mine and the Gołkowice GIV core. Based on the results of organic geochemistry, petrography and mineralogy, it can be concluded that the main reason for the disappearance of the coal seam was a deep-seated spontaneous coal-seam paleofire (Ciesielczuk et al. 2021a&b). One of the indicators of such is the presence of several groups of immature biomarkers that do not fit the sedimentary environment or the maturity level of Early Pennsylvanian coking coals.

The fire was dated at 19.2-19.8 Ma using paleomagnetism and ^{39}Ar-^{40}Ar dating of muscovite grains separated from red siltstone and whole-rock grey siltstone. Oxygen necessary for self-heating and self-ignition of the coal seam could have been enabled by normal faulting acting as a response to trust-loaded deflections of the Carpathian foreland during plate collision. Accurate isotope- and magnetostratigraphic dating of gangue rocks affected by thermal activity provided the age of tectonic processes in the Carpathians in the early Miocene (Nawrocki et al. 2022).

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Metamorphic record preserved in the Nowa Wieś eclogite (Śnieżnik Massif, SW Poland): Combined phase diagram modelling, Grt-Cpx thermobarometry and quartz-in-garnet elastic barometry

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The Śnieżnik Massif comprises mostly orthogneisses alternating with metasedimentary sequences that record different metamorphic conditions, varying from amphibolite- to eclogite facies. Among them, small bodies of eclogites with an unclear metamorphic history occur. Some authors suggest that their peak metamorphism reached nearly ultrahigh-pressure (UHP) conditions of ~2.6-3.0 GPa and 800-930°C (e.g., Majka et al. 2018), while others propose that they were subjected to eclogite facies metamorphism of ~1.9-2.2 GPa and ~700-750°C (e.g., Štipska et al. 2012).

In this study, we focused on deciphering the peak metamorphic conditions preserved in the Nowa Wieś eclogite using phase equilibrium modelling, Grt-Cpx geothermobarometry and quartz-in-garnet elastic barometry. The peak metamorphic assemblage consists of Grt + Cpx + Ph + Ky + Ru + Qtz. Garnet chemical composition ($Alm_{33-36}Grs_{22-26}Pyr_{39-43}Sps_{1}$), clinopyroxene (max. X_{Na} = 35-37%) and white mica (max. Si_{apfu} = 3.37) were used to estimate peak metamorphic conditions (P: 2.7-3.1 GPa, T: 800-900°C). Similar results were obtained using Grt-Cpx geothermobarometry (P: 2.6-3.2 GPa, T: 780-860°C). Furthermore, about 40 inclusions of quartz entrapped in various garnet grains were measured using laser Raman spectroscopy. The spectral shifts of the 464 cm^{-1} quartz band were used to calculate entrapment pressure, yielding results of ~2.1 GPa. The entrapment temperature used for the calculations was 850°C. The cause of the discrepancies between the results obtained by elastic barometry and phase equilibrium modelling will be the subject of further research.

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Late Cretaceous and Eocene detrital zircons from the Menilite and Krosno Beds in the Transdanubian Range and the Apuseni Mountains in the Polish Outer Western Carpathians

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Samples for isotope U-Pb dating of detrital zircons were collected from 19 outcrops of Menilite Beds and from 34 outcrops of Krosno Beds representing different tectonic units of Western Outer Carpathians in Poland. Analytical spots were chosen within the outermost parts of crystals after careful examination of the internal texture of each zircon grain in cathodoluminescence images. The isotopic dating was performed on the SHRIMP IIe/MC ion microprobe at the Polish Geological Institute-NRI in Warsaw. The TEMORA standards were measured after every three spots which were analyzed in six scans.

Among older grains, the youngest zircons of Late Cretaceous and Eocene-Early Oligocene isotope age were identified. The Late Cretaceous zircons occur within the Krosno Beds from the eastern part of Polish Carpathians only. On the other hand, the Eocene-Early Oligocene zircons were identified in both lithostratigraphic units and in the entire studied area. The primary source of Late Cretaceous zircons was in the Apuseni Mountains where magmatic rocks of this age occur (Balintoni et al. 2014). Volcanic rocks of the Transdanubian Range in Hungary (Kovacs et al. 2007) were the source of the Eocene-Early Oligocene zircons.

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Phytoavailability of Ni, Cr, Co and Mn in fertilized ultramafic soils

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Ultramafic soils are characterized by relatively high contents of Ni, Cr, Co and Mn, low Ca/Mg, and low N, P, and K contents - traits that make them unfavorable mediums for plant growth. Therefore, the cultivation of ultramafic soils should be accompanied by careful monitoring for the transfer of metals to plants. This is not the case in Poland where the cultivation of ultramafic soils is common, although they are rather rare. The aim of the study was to determine the effect of fertilizers on the phytoavailability of Ni, Cr, Co and Mn for *Brassica napus* as well as on mineralogical changes of selected soil minerals which are the Ni, Cr and Co carriers (i.e., spinel-group minerals, chlorite).

The effect of fertilizers on the phytoavailability of Ni, Cr, Co and Mn for *B. napus* was studied by means of a pot experiment. Pots were filled with serpentinite derived ultramafic soil collected in the Gogołów-Jordanów Massif. Ten seeds of *B. napus* were sown and after germination, 5 seedlings were cultivated. The following treatments were prepared: (a) control (ultramafic soil), (b) ultramafic soil with manure, (c) ultramafic soil watered with humic acid solution, (d) ultramafic soil with KNO_3, (e) ultramafic soil with lime, (f) ultramafic soil with $(NH_4)_2SO_4$, and (g) ultramafic soil with $Ca(H_2PO_4)_2$. After harvesting, plants were digested, and chemical compositions analyzed. Some soil properties were also measured (i.e., buffer properties and acid neutralizing potential, pH). Furthermore, soil solutions from pots were collected before seeds sown and before harvesting. Chemical extractions of soils with several solutions ($CaCl_2$, $MgCl_2$, CH_3COONH_4, DTPA+$CaCl_2$, EDTA, $Sr(NO_3)_2$) were adopted to determine the mobility of Ni, Cr, Co and Mn in the soils.

The following conclusions can be drawn from the study: (a) lime and manure are characterized by the highest acid buffer properties, (b) Polish ultramafic soils may be N and P limited, (c) the pH and concentrations of metallic elements in soil solution change with the development of plant growth and type of fertilizer used, (d) Ni, Cr and Co concentrations in soil solution may be controlled by interactions between humic acids and smectite, and the source of humic acids, (e) humic acids may contribute to Cr liberation from spinel and chlorite in ultramafic soils, (f) EDTA and DTPA+$CaCl_2$ extractions are suitable for estimation of Ni, Co and Mn accumulation by plants, (g) manure is the source of available P, possibly due to struvite formation, (h) Mn is translocated in *B.napus* and responsible for chlorosis in $(NH_4)_2SO_4$ treatment, (i) the highest Ni, Co and Mn yield is observed in $(NH_4)_2SO_4$.

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Missing metal reservoir: Sulfide enrichment at the Contact Series of the Balmuccia peridotite massif (Ivrea-Verbano Zone)

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The accumulation of hydrous basaltic melts in lower crustal melting-assimilation-storage-homogenization zones is an important process controlling metallogeny in collisional settings like the Ivrea-Verbano Zone in Italy. Here, to understand the chalcophile metal migration in subcontinental settings, we investigated the exceptionally sulfide-rich and fresh ~80-m-thick Contact Series (CS) sequence (peridotite-pyroxenite-gabbronorite; Mg# of 66-62), outcropping along the primary igneous contact between the Balmuccia mantle peridotites (Mg# of 91-90) and the lower crustal gabbronorites of the Mafic Complex (Mg# of 65–58).

The sulfide-bearing rocks are clinopyroxene-(plagioclase)-orthopyroxene cumulates with minor alteration by secondary silicates or serpentinization confirmed by low LOI contents. In general, the lower Mg# correlates with high modal sulfide abundances reflected in the bulk rock Cu, Ag, and S contents. The mantle peridotites are sulfide poor (0.15 vol.‰), showing 111±31 ppm S (1SD) and 20±9 ppm Cu, whereas CS rocks (3.0 vol.‰) reveal higher average contents of 3133±1944 ppm S and 180±130 ppm Cu. In the CS, we revealed two sulfide assemblages. Adjacent to the igneous contact, sulfides comprise pyrrhotite-pentlandite-chalcopyrite indicating a typical magmatic origin, whereas ~50 m away from the contact, towards the Mafic Complex, pyrite-chalcopyrite-pyrrhotite-pentlandite sulfide assemblages suggest circulation of post-magmatic fluids. The most external CS zone (~70 m from the igneous contact) shows significantly lower contents of sulfides (0.27 vol.‰), expressed by S (167±23 ppm) and Cu (11±16 ppm). The lowermost Mafic Complex gabbronorites are highly depleted in sulfides (0.02 vol.‰) compared to the CS with <10 ppm S and <2 ppm Cu.

The bulk S isotope signatures ($\delta^{34}S$) for the mantle peridotites range from –0.7 to +0.7‰, whereas those for the CS show more heterogeneous signatures ranging from –1.6 to +0.5‰, with one exception of –3.3‰. Mass balance calculations of bulk $\delta^{56}Fe$ of polyphase sulfide grains range from –0.2 to –0.1‰. Both S and Fe isotopes indicate mantle sources (0±2‰; 0±0.2‰, respectively).

The sulfide-bearing ultramafic rocks of the CS at the subcontinental crust-mantle contact may constitute a primary reservoir, at the base of continental crust, for long-lasting metal fertility and remobilization of sulfides by sulfide-undersaturated melts.

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X-ray absorption near edge structure (XANES) analysis of secondary phases formed during experimental bio-weathering of metal-bearing wastes

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The dissolution of metallurgical waste exposed to bio-weathering conditions results in (i) the release of elements from waste components (phases), (ii) the presence of anirreversible fingerprint on the solid surface and (iii) the formation of secondary phases. As the sulfides are important carriers of potentially toxic elements incorporated in metallurgical waste, tracking their dissolution is particularly relevant for environmental risk assessment.

Sulfide-rich metallurgical waste was subjected to long-term weathering under humid conditions with (i) water, (ii) a sterile growth medium and (iii) siderophore-producing bacteria *Pseudomonas fluorescens*. Based on the chemical composition of leachates and an applied geochemical model, secondary phases were theoretically predicted, whereas the application of X-ray absorption near edge structure (XANES) analysis was crucial for the precise analysis of formed precipitates (chemical composition and proportion of phases). The XANES spectra were obtained at the ASTRA beamline (SOLARIS synchrotron) in transmission mode. Spectra of the samples of interest were analyzed by fitting them to a linear combination of reference spectra using the Athena program. As suitable references, the pure compounds from the geochemical model and minerals were used. The measurements were carried out at *K-edges* of S, Fe, Zn, Cu. The analysis of spectra measured at the S K-edge demonstrated that in the sample after treatment (LS-B), the total amount of sulfates increased in comparison to the sample before treatment (LS). In addition, the existence of sulfur at different oxidation states confirmed the presence of an intermediate sulfur species occurring during sulfide dissolution. Analysis of the spectra measured at the Zn K-edge showed a small increase (3%) in the zinc sulfate phase fraction for the sample after the treatment. However, the linear combination analysis of spectra measured at the Fe K-edge showed that in the sample before and after treatment, Fe atoms were mostly bound in Fe-bearing sulfides (around 60%), whereas the rest of the Fe atoms were bound in Fe_2O_3 and $FeSO_4$. This study reveals the importance of applying powerful analytical techniques such as XANES for establishing the geochemical stability of waste materials in the environment.

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Accelerated mycorrhizal bioweathering of Cu-bearing metallurgical slags: Evidence from dissolution rates and weathering features

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Metallurgical slags originating from copper processing may continue to represent a risk to the environment through the mobilization of metals. On the other hand, these materials may be considered as secondary metal resources if treated properly. Significantly, different phase dissolution sequences can be distinguished due to specific waste characteristics and various dissolution conditions. Consequently, an increased interest in smelting waste (bio)dissolution has appeared in recent years.

This study experimentally simulated the exposure of different smelting wastes (amorphous AS vs. crystalline CS and HS, sulfide-rich LM vs. sulfide-poor materials CS and HS) to various (bio)dissolution conditions and the behavior of these mineralogically diverse samples was compared. Study conditions included sample exposures to and comparisons of acidic abiotic conditions (sterile growth medium) and acidic biotic conditions (growth medium with fungus *Aspergillus niger*). In biotic experiments, one aliquot was filtered through 0.22 μm (dissolved fraction), whereas the second aliquot was submitted to perchloric acid ($HClO_4$) digestion at 80°C. Such an approach allowed us to differentiate the dissolved fraction of metals from that bound to the fungus biomass.

This study demonstrated that *A. niger* had a large influence on the dissolution of metallic elements (up to 8.4% of Zn, 1.2% of Pb and 2.6% of Cu released from AS). In addition, fungus biomass makes an important contribution towards metal uptake (up to 57.4% of Zn released from CS, 27.6% of Pb released from LM and 29.1% of Cu released from AS were incorporated in biomass). The impact of the abiotic acidic medium on the mobilization of metals was up to 5 times lower compared to the biotic contribution (fraction <0.22 μm). When the fungus biomass was considered, element mobilization was up to 240 times higher than dissolved amounts of metals. The amorphous slag (AS) sample was generally the most susceptible to mycorrhizal bioweathering, whereas dissolution of crystalline materials varied between the elements indicating that dissolution was dependent on phases incorporating specific elements.

We conclude that any indication of influential factors affecting the dissolution of smelting wastes cannot be generalized as individual phases react differently under specific conditions, and any reaction is strongly governed by the type of agent used and by the volumetric proportions of phases present in a waste sample.

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Age differences between separate magma pulses in two laccoliths (Halle Volcanic Complex): Insight into processes of silicic magma formation

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The Halle Volcanic Complex includes several laccoliths emplaced during a Carboniferous-Permian flare-up (Breitkreuz & Kennedy 1999). The ages for the laccoliths range from 301±3 Ma (Landsberg) to 292±3 Ma (Petersberg) and, here, we focus on these laccoliths. The whole-rock chemical composition of samples from several depths in both laccoliths, combined with textural analysis, suggest that the laccoliths formed in several magma pulses. In this study, we have checked if a complementary record is also preserved in the chemical composition of accessory phases, e.g., zircon and apatite. Altogether, seven depths have been analyzed from two laccoliths, including electron-microprobe analyses of zircon and apatite and U-Pb SHRIMP dating of zircon. Zircon is chemically homogenous within and between laccoliths and has similar sets of inclusions. On the other hand, apatite shows variable contents of few elements. Nd contents decrease with depth in both laccoliths and apatite from Petersberg has more Cl, whereas apatite from Landsberg has more Na. The implication is that apatite chemistry is better at recording magma evolution than zircon. SHRIMP ages scattered over 30 Ma for a single sample suggests the presence of antecrysts and lead-loss or, alternatively, indicates formation of the laccoliths over a prolonged period of time. This is confirmed by diverse concordia ages obtained for the uppermost pulse (289.7±2.8 Ma) and the lowermost pulse (297.1±1.7 Ma) in Petresberg.

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Reactive melt percolation in lithospheric mantle: What it is

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Lithospheric mantle (LM) beneath oceans consists of peridotites which are formed by decompression melting of asthenosphere upwelling beneath mid-ocean ridges. Beneath continents, the peridotites of LM record melt extraction followed by episodic migration of melts which react with surrounding rock, affecting its composition (these processes are termed as *metasomatism*). Melt migration through peridotites of LM can be channelized or intergranular. In this abstract, the intergranular melt migration inducing metasomatism, commonly termed *reactive melt percolation*, is discused.

Reactive melt percolation is the process of melt migration in interstices among the grains of the host peridotite and concomitant melt-rock reaction. If the rock is below its solidus, the interstices are clamped and do not offer the interconnected network of channels necessary for melt percolation. When the rock starts to melt, the volume of solid grains is reduced, and an interconnected network of interstitial melt is formed. The geometry of that network depends on the volume of the melt and its wetting characteristics. As the newly formed melt is in equilibrium with the host rock, it must migrate from the place of origin to react with the surrounding rock. This is usually due to pressure gradients, causing melt migration towards low-pressure regions.

Reactive melt percolation in LM was first described in the peridotite massifs. These offer insight into relationships among mantle rocks in sections ranging from tens of meters to kilometers. The classical studies come from Ronda in Spain where the relationships among channelized and pervasive silicate melt flow, and their effect on host rock chemical characteristics, have been described in a series of papers by J. L. Bodinier and his co-workers (e. g., Van der Wal & Bodinier 1996). The recent studies based on mantle peridotite xenoliths in basalts suggest that the asthenosphere rocks replacing delaminated roots of orogens are a favorable location for reactive melt percolation in LM beneath continents (Puziewicz et al. unpublished data).

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Composition and sources of saccharides in street dust, topsoils and aeresols from Sosnowiec, southern Poland

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PM_{10}, street dust and topsoil samples collected seasonally from the city of Sosnowiec were analyzed using gas-chromatography – mass spectrometry (GC-MS). In all samples, the dominant compounds identified were anhydro-, mono- and disaccharides. However, their distribution differs between the different types of samples as well as varies depending on the season.

Sources of saccharides from PM_{10} were primarily (a) biomass and low-rank coal burning, (b) pollen grains and (c) fungal spores (Marynowski et al. 2020). Biomass burning compounds are the dominant group during the winter, early spring and late autumn and are represented by anhydrosugars: levoglucosan, mannosan and galactosan, as well as vanillic acid and dehydroabietic acid. Pollen-grain tracers identified were monosaccharides including fructose and glucose, disaccharide (sucrose) as well as D-pinitol. Their highest concentrations were observed in the spring, during the growing season. Two sugar alcohols (mannitol and arabitol) and a disaccharide (trehalose) were used as indicators of fungal spores with their highest concentrations in the summer and autumn in the peak of fungal spore production and most active growth (Marynowski et al. 2020).

For street dust and topsoil samples, only two groups of organic tracers have been recognized – pollen grains and fungal spores. Pollen-grain tracers include glucose and sucrose. Trehalose is the most dominant compound among the fungal-spore tracers followed by mannitol and trace amounts of arabitol. Interestingly, no significant differences were observed in the concentrations of individual compounds depending on the season. The lack of biomass- and low-rank coal burning tracers may be related to their possible degradation by bacteria or fungi (Arya et al. 2022).

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Development of holistic exploration solutions enabling chromites with improved physicochemical parameters to be obtained for use in the production of high-alloy additives

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Exploration for podiform chromite deposits has been a challenge because of their random distribution in ultramafic formations, syngenetic nature, similar density to hosting rocks and lack of associated alteration (Mosier et al. 2012).

PROXIS Sp. z o.o. from Poland executed a project “Development of holistic prospective solutions enabling obtaining chromites of improved physicochemical parameters, used for the high-alloy additives production” (Project no. POIR.01.02.00-00-0166/16-00 co-financed within the Smart Growth Operational Programme 2014-2020, Measure 1.2. "Sectoral R&D programmes - INNOSTAL"). The scope of the project included geological mapping and sampling, laboratory mineralogical-, petrographic-, geochemical- and physicomechanical analysis of collected samples, rock analysis with a portable XRF, geoinformatics (remote sensing) analysis with development of an algorithm for detecting chromite-bearing rocks, application of structural analysis results, relevant selection of geophysical methods followed by geophysical surveys, drilling tests with analysis of core samples verifying previous research, correction of the geo-it algorithm and development of a comprehensive method for prospecting chromites during the stage of development works.

The developed innovative method enables:

- Prospecting fields with difficult access due to complex topography.
- Significant acceleration of mapping due to hyperspectral diagnostics narrowing the search area at an early stage to about 40%.
- More accurate prediction of location of geophysical profiles saving time and costs.
- Limiting invasiveness of the prospecting project due to more accurate identification of drilling locations at the stage of exploration reducing the number of drillings by a minimum of 20%.

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Automorphic tourmaline in phyllite from Podmąchocice, Holy Cross Mountains, Poland

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The presence of very low- and low metamorphic rocks in the Holy Cross Mountains was first time described in 2006 (Salwa 2006). The phyllites are composed of quartz, white mica, chlorite, pyrophyllite, siderite, pyrite, dolomite, rutile, hematite, apatite, xenotime, and monazite. The metamorphism is strictly related to tectonic deformations and, thus, the growth and distribution of new minerals was controlled by deformational processes. The phyllites are cut by veins of quartz, quartz-kaolinite/dickite, quartz-chlorite-apatite and siderite-dolomite.

Recent studies of phyllite thin sections have revealed the presence of number of new minerals, among them tourmalines. Three types of tourmaline occurrence have been identified. The first type is represented by clearly rounded, detrital grains of < 0.5 mm in size. The second type involves autigenic crystals growing on detrital tourmaline grains. The third type comprises automorphic crystals with sizes < 10, rarely 30 µm. The latter two types show a clear ordering of the crystal's direction of growth. Their chemical composition indicates dravite. Some of crystals are zoned, with detrital grains visible inside them.

The autigenic tourmaline crystals may be of pyroclastic origin, but their spatially ordered growth and the regeneration of detrital grains indicate a close relationship with the evolution from diagenetic- to low-grade metamorphic conditions.

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Former melt inclusions from UHP gneisses of the Seve Nappe Complex, Scandinavia Caledonides

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Abstract

Ultrahigh pressure metamorphism has been recently reported in the Seve Nappe Complex (SNC) of the Scandinavian Caledonides (Klonowska et al. 2017). This study is focused on former melt inclusions (nanogranitoids, Bartoli et al. 2016; Cesare et al. 2015) and anatectic processes occurring during the ultradeep subduction of paragneisses from Åreskutan, SNC.

The mineral assemblage of the paragneiss is Kfs+Grt+Qz+Pl+Bt+Wm+Ky+Sil+Ru. Garnets occur as porphyroblsats or aggregates of coalesced crystals up to 3 mm in diameter and they are randomly spread in the matrix. Clusters of inclusions are present in most of the garnets, and they are composed of small multiphase inclusions (MPI), less than 5 µm in size and represent former fluid. MPI consist of various carbonates such as calcite, siderite, magnesite, biotite, pyrophyllite rarely quartz, graphite microdiamond, or rutile and a residual fluid made of CO_2 and CH_4. Within the clusters, relatively larger (5 – 20 µm) and rarer inclusions are nanogranitoids (NG), composed of Qz+Bt+Kfs+Pl±Carb. Seven re-homogenization experiments at different conditions were conducted in a multi-anvil apparatus to remelt NG and determine the composition of the anatectic melt. The best homogenization was acquired at 850 and 900˚C at 4.5 GPa. The entrapped melt is rhyolitic, with high alkali content (~10 wt% N_2O+K_2O). The H_2O and CO_2 content of the remelted NG analyzed by NanoSIMS is respectively ~ 5 wt% and 1200–25000 ppm.

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Cadmium immobilization mechanism in industrially contaminated wetland soils

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Cadmium (Cd) is a toxic element that easily enters the food chain due to high mobility in soils. In waterlogged soils, the low solubility of CdS leads to Cd immobilization. Conversely, CdS is prone to oxidative dissolution after water drawdown, oxidizing about 20 times more rapidly than pure ZnS (Barrett and McBride 2007). Here, we present a Cd immobilization mechanism in surface (4-20cm) layers of periodically saturated organic soils involving the formation of Zn-Cd sulfide aggregates. Focused ion beam (FIB) technology with scanning (SEM) and transmission electron microscopy (TEM) were used to unravel the organization of the metal sulfides at micro- and nanoscale resolutions (Smieja-Król et al. 2022).

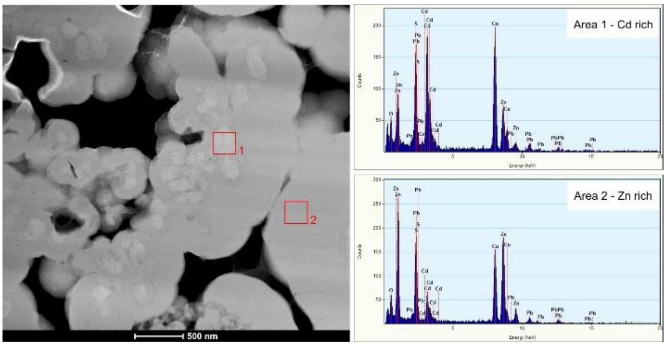

Fig. 1. STEM HAADF image of Zn-Cd sulfide aggregates with Cd-rich multiple high-contrast cores in Cd-poor ZnS

The TEM observations reveal that the aggregates are nanocrystalline (<5nm), and that the Zn-Cd sulfide solid solution exists in a sphalerite polytype over a whole Zn/Cd range. A complex core-shell structure was found in which high-Zn outer layers encapsulate Cd-rich sulfide core (Fig.1). The formation of the Cd-rich core structures seems to be self-sustainable and specific to (Zn,Cd)S precipitation in changeable redox conditions, limiting Cd mobility.

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from the National Science Centre, Poland.

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A revised crystal structure for the rare earth fluoride gagarinite-(Ce) from experimental synthesis by fluid-induced alteration of chevkinite-(Ce)

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The Rare Earth Element (REE) fluoride, gagarinite-(Ce), $^{A}\mathrm{Na}^{B}(\mathrm{REE,Ca})_2\mathrm{F}_6$ has been synthesized in an experiment designed to examine the fluid-induced alteration of chevkinite-(Ce). The experiments were conducted at 600°C and 400 MPa for 21 days, 550°C and 200 MPa for 63 days and 600°C and 200 MPa for 42 days. The formula of crystallized gagarinite-(Ce) analogue is $(\mathrm{Na}_{1.10}\mathrm{Ce}_{0.69}\mathrm{Ca}_{0.44}\mathrm{Nd}_{0.31}\mathrm{La}_{0.26}\mathrm{Pr}_{0.12}\mathrm{Sm}_{0.04}\mathrm{Sr}_{0.03})_{3.0}\mathrm{F}_{6.0}$.

The mineral, previously named zajacite-(Ce), is known from only one natural occurrence, a hypersolvus granite from the Strange Lake Zr-Y-REE-Nb-Be deposit, Quebec-Labrador. The space group was identified as $P\bar{3}$ (Jambor et al. 1996) and later $P6_3/m$ (Sciberras et al. 2011).

The gagarinite-(Ce) in our experiments crystallized in $P\bar{6}$, with $a = 6.1465(2)$, $c = 3.75950(10)$, R_1=1.37%. We observed 26% twinning by a twin centre.

Previous studies assumed full occupancy of the *A* site. To charge balance the substitution $2^{A}\mathrm{REE}^{3+} \rightarrow {}^{A}\mathrm{Ca}^{2+} + {}^{A}\mathrm{REE}^{3+} + {}^{B}\mathrm{Na}^{+}$, the amount of extra Na^{+} must equal Ca^{2+} in the final formula, giving $\mathrm{Na}_x(\mathrm{Ca}_x\mathrm{REE}_{2-x})\mathrm{F}_6$. Gagarinite-(Ce) from the experiment shows surplus Na over Ca with a ratio close to 2:1. A vacancy in the REE site is necessary, equal to 1/3 of the redundant Na to remain in charge balance. If the Na content exceeds 1 in the formula unit, Na has to substitute for REE in the cation site. Thus, the overall substitution mechanism is:
$(2x-y)\mathrm{REE}^{3+} \rightarrow y\ {}^{B}\mathrm{Na}^{+} + (x-y)\ {}^{A}\mathrm{Na}^{+} + y\ {}^{A}\mathrm{Ca}^{2+} + (x-y)/3\ {}^{A}\square$, where □ stands for vacancy and $x > y$.

We gratefully acknowledge funding by NCN Harmonia grant no. 2017/26/M/ST10/00407.

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Oligocene burial effects on the magnetic fabric of the Huty Fm in the Orava-Podhale Paleogene Basins

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We investigated Anisotropy of Magnetic Susceptibility (AMS) and Anisotropy of Anhysteretic Remanent Magnetization (AARM) fabrics to reconstruct the tectonic evolution of post-thrusting Huty Fm sediments in the Central Western Carpathians. Petromagnetic methods supported by paleotemperature analysis enabled recognition of the origin of the magnetic fabric. The rock magnetic result shows that the AMS fabric is mainly controlled by phyllosilicates. In the majority of sites, the orientation of magnetic lineation points to an approximately NW-SE compression, coinciding with the uplift-related Miocene shortening direction. AARM is governed mainly by secondary magnetite. Its origin is most probably related to illite/smectite transformation at elevated temperatures during the maximal burial in the Late Oligocene. The magnetic lineation in AARM diagrams is presumably controlled by the preexisting phyllosilicate matrix and/or the stress field during crystallization of the secondary magnetite.

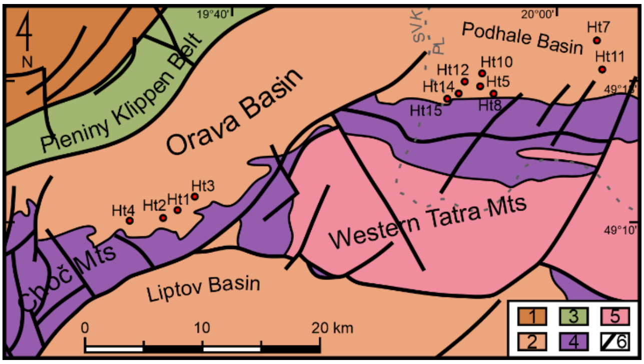

Fig. 1. Simplified geological map of the study area with marked sampling sites (after Lexa et al. 2000). Map explanations: 1 – Outer Carpathians, 2 – Central Carpathian Paleogene Basin, 3 – Pieniny Klippen Belt, 4 – Mesozoic sediments of Central Western Carpathians, 5 – crystalline basement of the Tatra Mts, 6 – major faults.

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Bacteria enhance dissolution of Zn- and Pb-bearing rocks: Experimental simulation of bioweathering

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The Silesia-Cracow mining area is located at the south Poland and is well known for numerous occurrences of the Zn and Pb ore deposits. The last Zn and Pb mining operations took place in the Olkusz mining district in the eastern part of the Silesia-Cracow area. Although, the last Zn and Pb mine („Olkusz-Pomorzany”) was closed at the end of 2020, large amounts of mining wastes and tailings generated during historical- and recent mining activity still contain elevated amounts of Zn, Pb, Cd and As. Except for Zn-, and Pb-bearing sulphides, mining wastes are also composed of oxidated Zn-, and Pb-bearing rocks, well known as calamines. Different mineral- and chemical composition of disposed wastes create a different susceptibility to weathering. Awareness of microbial activity as an important factor of weathering processes is still increasing and could be considered in the future as a potential recycling method through the application of recovery processes. Bioleaching experiments focused on the leaching efficiency of Zn, Pb, Cd and As from Zn-, and Pb-bearing oxidated rocks mediated by *Acidithiobacillus thiooxidans* bacteria, native soil bacteria and root exudates. Two calamines (B - collected from the heaps of the calamine „Bolesław” open-pit, and OP - sampled from the weathering site of the „Olkusz-Pomorzany” mine) with different mineral (XRD, SEM-EDS, EPMA) and chemical (ICP-QQQ) composition were studied. Changes of mineral composition which occurred during the experiments were controlled using DSC-TG methods and Scanning electron microscopy. Experiments revealed the highest amounts of Zn (< 125 000 and < 14 000 $mg \cdot kg^{-1}$ for calamines OP and B, respectively), and Cd (< 817 and < 46.8 $mg \cdot kg^{-1}$ for OP and B, respectively) were leached by *A. thiooxidans* bacteria, whereas the highest amounts of released Pb (3840 $mg \cdot kg^{-1}$ for sample OP) were confirmed in the experiment with root exudates. During the experiments, only trace amounts of As were mobilized from both samples. The investigated calamines revealed significant differences in term of the leachability of Zn, Pb, Cd and As, with the mineral composition being found to be the main factor determining these differences.

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P-T conditions and chronology of the Variscan collision in the easternmost part of the Saxothuringian crust (Bohemian Massif, Fore-Sudetic Block, Poland)

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The Doboszowice Metamorphic Complex (DMC) is situated in the Fore-Sudetic Block within a collision zone between the Saxothuringian and Brunovistulian crustal domains of the European Variscides. The complex comprises the Chałupki paragneiss, intercalated with mica schist, intruded by the Doboszowice orthogneiss. The DMC bears an imprint of Variscan tectonometamorphic reworking previously estimated at a maximum 670-740°C and 8-10 kbars (e.g. Puziewicz et al. 1999).

To reconstruct the P–T history of the DMC, we have investigated three garnet-bearing samples (Chałupki paragneiss, mica schist and Doboszowice orthogneiss) using phase equilibrium modelling and Si content in white mica geothermobarometry. We documented the record of a well-preserved MP/HT metamorphism (M2) overprinting relics of a HP/LT event (M1). Our P–T estimations point to pressures of c. 13-19 kbar and 500-600°C for the M1 event while the M2 event took place at max c. 9 kbar and 660°C.

We supplemented our P–T data with Lu–Hf and Sm–Nd dating of garnet from the mica schist sample. Lu-Hf dating constrained the age of 347±3.6 Ma, while the Sm-Nd method provided the age of 337.3±6.6 Ma. We interpret the time difference recorded by the two clocks as related to different zonation styles. While Lu/Hf is strongly fractionated in the garnet core shifting the weight of the age towards the growth phase, Sm/Nd is more efficiently fractionated in the rim area shifting the weight of the age towards the metamorphic peak (Lapen et al. 2003). Consequently, the investigated garnet grew for c.10 Ma, documenting the duration of the M2 event related to collision between the Saxothuringian and Brunovistulian domains.

The study was financed by the NCN research grant UMO-2015/17/B/ST10/02212.

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Structure optimization and minimalization the effect of cross heating of samples during IR-laser argon extraction

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Introduction

The Institute of Geological Sciences PAN is equipped with a Nu-Instruments Noblesse noble gas mass spectrometer connected to two preparatory lines. For the first line, a double-vacuum crucible heated with a tantalum resistive spiral was constructed. In the second line, each sample is melted by a defocused 972 nm infrared laser with beam spot diameter of ca 4 mm.

Melting the samples by defocused laser beam allows measurements with low contributions of atmospheric argon to be performed; however, there are possible problems due to cross heating of neighboring samples. To analytically address this issue, cross heating of samples in various types of holders was studied using a non-contact optical pyrometer supported by K-Ar age dating tests on the GLO standard.

Results and discussion

A standard holder for the samples used for the laser heating process is usually made of copper. In this study, a total of six different holders were constructed, analyzed, and tested: standard copper, copper with cuts between sample holes, titanium, titanium with cuts, and two holders made of titanium rods with copper thermal shields at different distances between samples.

The research results allowed for the precise determination of heat distribution mechanisms in a heated set of samples, and the iterative optimization of both the shape of the holder and its material modification, as well as the implementation of additional elements. This allowed for the formulation of design guidelines for these types of containers and the construction of an optimal solution.

The experimental results also show that a decrease of thermal conductivity of the holder (from 400 W/mK for copper to 22 W/mK for titanium) leads to a substantial decrease of cross heating of neighboring samples. This indicates that the main mechanism of heat transfer between samples is by conduction. As additional cuts did not lead to any significant decrease of cross heating, either for copper or titanium holders, thermal radiation can also be an important contribution to heat transfer.

Holders made of titanium rods with thermal shields made of copper allow the minimization of thermal conductivity and radiation between samples. This enabled the heating the samples at maximal optical power of 18 W for 5 minutes without release of any radiogenic argon from neighboring GLO samples.

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Extended continental-margin development and deformation recorded by the Upper Gneiss Unit in the northern Scandinavian Caledonides

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The Scandinavian Caledonides comprise nappe stacks of far-travelled allochthons that record the opening and closure of the Iapetus Ocean, culminating with the collision of Baltica and Laurentia. In this study, we combined different geochronological methods to expand the knowledge about the metamorphic history of the Baltoscandian margin in the understudied Váivančohkka-Salmmečohkat region of the northern Scandinavian Caledonides. The work focused on rocks that belong to the upper gneiss unit, which constitutes a part of the Seve Nappe Complex (SNC) in the region. The unit comprises migmatitic paragneisses and garnet-mica schist containing metamafic bodies associated with leucogranitoids. U-Pb zircon and Th-U-total Pb monazite dating of the migmatitic paragneiss yielded consistent age of metamorphism ca 600 Ma. A similar U-Pb age of 604 ± 8 Ma was obtained for a zircon from a leucocratic vein transecting an amphibolite within the studied gneiss. Interestingly, no Caledonian ages were identified. Petrographic observations and calculated metamorphic P-T conditions indicate that the rocks belonging to the upper gneiss unit underwent upper-amphibolite facies metamorphism in a melt stability field at 8.0-10.5 kbar and 750-790°C.

Three rocks of the studied unit, two paragneisses and a leucogranite, were chosen for in-situ ^{40}Ar/^{39}Ar geochronology to further investigate possible Caledonian tectonism of the unit. The collective datasets are interpreted to record 1) top-to-E deformation of the upper gneiss unit at ca 459 Ma during cooling through ^{40}Ar biotite closure temperatures followed by 2) top-to-E reworking of the unit at ca 434 Ma corresponding to metamorphism of the leucogranite with white mica replacement of biotite. These two events are interpreted as exhumation followed by initial stages of continental collision and closely resemble the deformation histories of other northern SNC terranes.

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Evaluation of the gaseous pollutants yields produced during the self-heating process of coal waste simulated by dry and hydrous pyrolysis

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Introduction

Organic material dispersed within coal wastes deposited in dumps may undergo self-heating in oxygen-depleted conditions associated with emissions of pollutants (mainly gaseous). Siltstone and claystone from the Janina Mine (J1, J2) (R_r ca. 0.5%) and from the Marcel Mine (M1, M2) (R_r ca. 0.9%) were collected. The Rock-Eval data indicate 1.8, 27.3, 2.3 and 24.1 wt. % TOC, respectively and presence of the gas-prone kerogen in all samples. Pyrolysis experiments were conducted in closed reactors without (DP) and with water (HP) in temperatures 250, 360 and 400°C for 72 h. The molecular composition of generated gases (i.a. HCs (C_1-C_8), CO, CO_2, H_2, H_2S, organic S-compounds) was determined and the yield of each gas was converted to mg/g TOCo (of the original sample). The effect of the degree of organic matter dispersion (TOC content), type of pyrolysis (DP v. HP), organic matter (OM) maturity and process temperature on the yields of each gas was evaluated.

Results and Discussion

The total yield of generated hydrocarbons strongly relates to the temperature of the process: from below 1 mg HC/g TOCo for all samples and experiments at 250°C to over 20 mg HC/g TOCo for J1 sample at 400°C. Usually, more HCs is generated in DP than in HP conditions, regardless of the TOC content and maturity of the OM. The yields of produced CO_2 increase with the increasing temperature of pyrolysis and are related strongly to TOC content in the waste – the TOC-poor rocks produce much higher yields of this gas than TOC-rich ones. Very high yields of CO_2 from the M1 sample are related to the presence of siderite in this rock. CO yields are highest for DP conducted for J1 sample and decrease as the process temperature increases. The presence of water and process temperature increase generally reduce production of this gas, but boost the generation of H_2 and S-compounds (dominated by H_2S).

Conclusions

The presented results helped to understand and evaluate the emission of gaseous pollutants during pyrolysis of the stored coal wastes induced by self-heating. The highest yields of pollutants (HCs, CO_2, H_2 and S-compounds) per g of TOCo are noted for TOC-poor rocks, but considering the low TOC content in these rocks, self-heating of TOC-rich waste is a major source of gaseous emissions from thermally active dumps.

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27th Meeting of the Petrology Group of the Mineralogical Society of Poland

FIELD TRIP GUIDE

Thermal image of the slope of the burning Anna coal-waste dump, 23.10.2022

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The Anna-Pszów coal-waste dump - a multilayered case of contamination

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Introduction

The Anna dump stores coal waste from the Anna (later Rydułtowy-Anna) Mine opened in 1856 in the town of Pszów (Rybnik Region, Upper Silesia Coal Basin). At the beginning, the mine exploited the Anna and Albin fields (600 and 700 coal seams, respectively). Exploitation lasted up to the closure of the mine in 2012 (Frużyński 2012).

The dump originally comprised a single cone covering an area of 0.43 km^2, with the oldest part (~ 0.20 km^2) reaching a height of ca 50 m. Planned dump capacity was $>3 \times 10^6$ m^3 (Barosz, 2003). During storage, a part of the waste was exploited for road building. This enabled access of oxygen to the dump and intensified self-heating. Landsat images show intensive thermal activity in 2001, 2004 and 2010, further evidenced by partially molten rock fragments commonly found on the dump (Fabiańska et al. 2019). Due to the intensity of the thermal processes, further exploitation was abandoned. Additional oxygenation caused by off-road driving activity on the dump served to destroy its slopes. In 2015, the main cone was flattened. However, a second cone built at that time began to self-heat in ca 2019. Toxic fumes and odors became a problem in nearby Pszów (Misz-Kennan et al. 2013). In response, in 2020, the dump top was covered with a clay layer ca 50 cm thick to dampen the smell and diminish the self-heating. Currently, the dump is in a state of moderate self-heating, with hot spots, tar smell, cracks in the dump top and slopes, gas vents, and crusts of efflorescing minerals reflecting the process.

Results and discussion

The coal waste in the Anna dump were extensively investigated by remote sensing, petrographic-, geochemical- and mineralogical methods to characterize its composition, changes caused by self-heating and emissions to the environment.

Elevated temperatures within the self-heating dump significantly affected the geochemistry- and petrography of the coal waste. Petrographicaly,, signs of alteration such as irregular cracks, devolatilization pores, oxidation rims, and plasticization are typical. Measured vitrinite reflectance values of < 7.36% contrast with 0.95% for material not affected thermally. However, most R_r values are much lower at ca 1.3%. The range of R_r values reflects the highly varying conditions of the heating both at present and in the past.

The Anna dump should be deemed a significant source of contaminations for its vicinity. Despite waning thermal activity revealed by remote sensing methods (Nádudvari et al. 2021), gas sampled from active vents (t~80°C) contained, apart from atmospheric components, light aliphatic hydrocarbons from methane (0.14% vol., on average) to *n*-hexane (0.0005% vol., on average), high levels of CO_2 (4% vol. on average), H_2, NO_2, NH_3, SO_2, and polar organic compounds such as thiophene, acetic acid, acetaldehyde, and dimethyl sulphide. Chlorinated compounds include vinyl chloride dichloromethane (Fabiańska et al. 2019; Kruszewski et al. 2020). Thermal activity is also reflected by the presence of pyrolytic bitumen composed mostly of *n*-alkanes showing a Gaussian distribution, pentacyclic triterpanes, phenols and polycyclic aromatic hydrocarbons (PAHs) with 2-3 ring structures predominating (Nádudvari et al. 2021; Wojnowski 2022).

The composition of efflorescing minerals blooming at fissure vents is simple compared to that of other neighboring burning dumps, e.g., Szarlota or Radlin (Kruszewski et al. 2020; Parafiniuk & Kruszewski 2009; Kosałka 2020). However, their phase compositions change in time due to changes in exhalating gases coming out of hot spots/burning places. Their amounts and composition depend on the composition of the coal wastes that are on fire, the stage of the fire and its intensity. At the initial stage of fire, salammoniac (NH_4Cl) dominates, and then gypsum ($CaSO_4 \cdot 2H_2O$) and elemental sulphur (S_8) form. On-going fire favors gypsum and sulphur which become, almost exclusively, the only minerals observed in the vents. Subordinately, sulphates such as alunogen, epsomite, hexahydrite and tschermigite start to crystallise (Kruszewski et al., 2020). Recently, Al, Mg, Mn, Fe and K sulphates dominate as epsomite $Mg(SO_4)\cdot(H_2O)_7$, pickeringite $(Mg_{0.93}Mn_{0.07})Al_2(SO_4)_4\cdot 22(H_2O)$, alunogen $Al_2(SO_4)_3\cdot 17H_2O$, hexahydrite $Mg(SO_4)\cdot 6(H_2O)$ and jarosite $KFe^{3+}{}_3(OH)_6(SO_4)_2$, create a white- and yellow halo/aureole around and above the active vent. Gypsum and elemental sulphur are subordinate, and salammoniac is absent.

Water in a stream flowing from under the dump that shows signs of life (plants, water insects) and in a lake fed from the stream in its lower course, contains a wide range of organic compounds of coal-waste origin. Compounds leached from the waste include *n*-alkanes, steranes, pentacyclic triterpanes, 2-4 ring polycyclic aromatic hydrocarbons (PAHs) and their alkyl derivatives. Sums of PAHs concentrations of 5.82 and 2.14 ng/L characterize the stream and lake, respectively; intermediate values compare to those of other water reservoirs close to coal-waste dumps (Fabiańska et al. 2020). Phenols deriving from vitrinite thermal destruction, are indicative of the impact of self-heating on the water quality. Concentrations of organic phosphates, sourced from lubricants of heavy-duty machinery working during dumping and fire-fighting, measure at 289.74 and 26.47 ng/L in the stream- and lake water, respectively. Ca contents that are ten times lower in lake water, point to contaminant removal due to sedimentation.

Inorganic ions investigated include NH_4^+, HCO_3^-, F^-, Cl^-, Br^-, NO_2^-, NO_3^-, PO_4^{3-}, SO_4^{2-} ions and Al, B, Ba, Ca, Cd, Cr, Cu, Fe, K, Li, Mg, Mn, Na, P, Pb, S, Si, Sr, and Zn (Lewińska-Preis et al. 2021). Concentration levels for all ions and elements exceed the maximum allowable for industrial water (Journal of Laws 2017 and 2018, Poland).

Conclusions

The results indicate that the Anna dump should be considered a significant source of contaminations for its neighborhood, and as such, constantly monitored. Compounds that formed in the past, in periods of more intense thermal activity, can potentially migrate to the dump surroundings and present a serious environmental hazard in soil and water. Recent thermal activity leads to the emission of gaseous pollutants.

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Szarlota - the largest and hottest coal-waste dump in the Upper Silesian Coal Basin

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The Szarlota coal-waste dump is located in Rydułtowy town, a settlement with a long industrial history located in the Rybnik Industrial District. This dump is considered to be the largest in Poland and the second largest in the whole of Europe, a little smaller than the Anna I dump in Alsdorf, Germany. Polygonal in shape, the Szarlota dump covers an area of 37 hectares and has a volume of 13.3 million m^3. From its base, the dump is ca 134 meters high, with the summit reaching 406 m a.s.l. However, its size varies as dumping continues even as, in the southern part of the dump, older burnt rocks are exploited. At the beginning, its structure comprised two cones, No. 1 rising to 406.9 m a.s.l. and No. 2 rising to 367.9 m a.s.l. The No. 2 cone has been flattened and covered with new material. It is due to be liquidated by 2024. The lower north-western part of the dump is densely overgrown with trees and shrubs (mostly blackberries) or sparse grass, whereas other parts are mostly barren (Hyla 2011; Helios & Lorenc 2016). In 2007, the local community decided that cone No. 1 could be a great promotion of the town. The authorities announced a competition for a name, and from several proposals, the name "Szarlota" was chosen, referring to the historical name of the first Rydułtowy mine - Charlotte.

The dump stores coal waste mainly derived from the Rydułtowy-Anna Coal Mine, comprising sandstones and coaly claystones. The exploitation of coal measures there began in 1806 in the "Charlotte" mine, first in Czernica town and later, after depletion of the seam, in nearby Rydułtowy. In 1968, the mine was joined with the Ignacy Mine and, in 2004, with the Anna under the name Rydułtowy-Anna Mine. More than 200 years of coal waste mined there was deposited mostly in two dumps - the Anna in Pszów town and Szarlota dump (Kosałka 2020). The Szarlota dump started to collect waste rocks in the 1900s. The type of transport and storing caused material segregation according to grain size, with larger fragments rolling down and gathering at the slope foot, the gravel fraction at the central part, and the finest at the dump top. This promoted dump oxygenation and led to self-heating (Helios & Lorenc 2016). The Szarlota dump has been thermally active since the 1960s at least. This is confirmed by thermal maps that show that both parts of the dump, the cone and the flat part, have been in a state of continuos burning since 1993. Internal fire has caused landslides in some parts of the dump and caverns under the dump surface, making it unsafe to move about on it. Recently, in the southern side of cone No 1. the fire has been waning (Nádudvari 2014; Nádudvari et al. 2021). The most intense smoldering of the coal waste that occurred in the southwestern part of the dump produced burnt clinker and paralavas that are excavated for road building purposes. The approximate length of the burning side from north to south was ~600 m, and the width ~200-400 m (Nádudvari 2014). In 2017, intense burning of the flat part of the dump forced its partial deconstruction and rebuilding and the digging of deep trenches to prevent the fire from spreading.

Several projects have been carried out to define the extent of any changes in the coal waste caused by the heating, the types and concentrations of compounds emitted into the environment and the measures taken to prevent and/or extinguish the fires.

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GEOsfera: Triassic geoproduct in Jaworzno, Poland

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Every year, geoparks (and so-called geoproducts) play a big role in local communities. They should protect local geological heritage, promote the economic well-being of the people who live there, and educate people by using their qualities. An excellent example of such object is GEOsfera in Jaworzno, which is located in S Poland (Fig. 1).

Fig. 1. GEOsfera localization in Jaworzno, Poland

GEOsfera is placed in a closed Triassic quarry, which was used for cement production. The main sedimentary rock is represented by the Middle Triassic limestone (the Muschelkalk; Ger. "shell-bearing limestone"; *Fr. calcaire coquillier*), which locally is rich in fossils, trace fossils and sedimentological textures (e.g. Niedźwiedzki et al. 2020a&b; Surmik et al. 2021).

Formally, GEOsfera was estabilished on the first of July 2013 by an official act signed by the major of the Jaworzno city. The present shape of GEOsfera is represented by different exhibitions, educational activities with local communities, and cooperation with industry and the university, which grows every year.

The local, geological potential is used mostly for education. Numerous bones of marine reptiles (*Nothosaurus sp.*), nautilouids, crinoids, brachiopods, bivalves, fish, mega ripple marks (formed after tsunami) was base for local design and concept of GEOsfera (Fig. 2). Moreover, theses paleontological values as well as presence of unique plants and animals were used to establish the University of Silesia in Katowice field research station with its official name BIOGEO (BIO- biology, GEO- geology).

The scientific activities of GEOsfera is mainly visible by periodically organized paleontological excavations for students. Because of these works, numerous fossils led to the reconstruction of the Triassic biocenosis of this area. Part of the specimens from various collections were used to create numerous publications.

Fig. 2. An examples of Triassic geodiversity in GEOsfera: A) crinoids (remnants are commonly hosted by local limestones; FOV 35 cm), B) detailed model of *Nothosaurus sp*. (1.7 m long) in the didactic diorama, and C) outside models of other vertebras (each ~1.2 m long)

Fig. 3. An example of didactic path, which includes palaeogeographical reconstructions and the past ecosystems information

The exhibitions are the base for educational proposes. GEOsfera conducts an extensive educational program for pupils at all levels. The most common forms of education are: 1) scientific workshops: practical classes are held for a maximum of 60 participants in four groups simultaneously. Participants can choose classes such as: rock type identification, fossil characterization, laboratory in chemistry, and determination of the absolute age of rocks; 2) field workshops: participants can use basic geological knowledge and tools to recognize rock types, learn field orientation, and characterise geological outcrops; 3) lectures: two hours long lectures on the field of geological sciences, geography, evolution of life, and ecology are provided by the GEOsfera staff, as well as invited guests (Fig. 3).

GEOsfera in Jaworzno is an excellent example that shows how geological and biological potential can become a local brand combining economics, science and education. GEOsfera in Jaworzno may become the first “Polish Lyme Regis”.

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