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Abstracts

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The mineral system approach applied to magmatic Ni–Cu–PGE sulfide deposits revisited

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The mineral system approach interprets the formation of ore deposits in terms of source, pathway, and sink processes, with the aim of improving ore exploration. Magmatic Ni–Cu–PGE sulfide deposits, form by the segregation and accumulation of immiscible sulfide melts from mafic or ultramafic magmas. The mineral system approach for these deposits mainly investigates (i) mantle melting processes, (ii) magma ascent and crystallization through the lower to the upper crust, and (iii) sulfide segregation and accumulation at upper crustal levels. Here we revisit these processes in the light of recent studies, with a particular attention to experimental studies dealing with physical and chemical mechanisms controlling sulfide saturation, sulfide melt mobility and metal enrichment. In particular, we discuss how an optimum in the degree of mantle melting leads to the highest sulfur and metal enrichment of the primary magma. Then we examine the processes of sulfur incorporation into the magma from an external sedimentary source. Experimental studies reveal several possible mechanisms of magma-sediment interaction that allow early sulfide saturation and lead to sulfide melt segregation and accumulation. Finally, we present how the occurrence of a fluid phase in the magma affects sulfide melt mobility by means of the formation of sulfide-fluid compound drops that may float within the magma. This close association of the sulfide melt with the fluid phase can also favor the metal enrichment of the sulfide melt, due to sulfur degassing to the fluid phase and concentration of chalcophile elements in the sulfide melt. We use the magmatic Cu-Ni-PGE sulfide deposits of the Central Lapland Greenstone Belt in Finland and the Noril'sk region in Siberia as case studies to illustrate the role played by the discussed processes in ore formation.

Rhenium transport and fractionation by hydrothermal fluids in porphyry Cu-Au-Mo-W systems

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Most of the world's rhenium (~90%) is obtained from MoS_2 (molybdenite) of porphyry Cu deposits. Among porphyry systems, the highest Re contents in MoS_2 were observed in Cu and Cu-Au porphyries with smaller concentrations in Cu-Mo, Mo and W-Mo deposits (Barton et al., 2020). The goal of this study is to determine the mechanisms that lead to the fractionations of metals in porphyry ore deposits.

We combined thermodynamic modeling with solubility experiments in H_2O-salt-sulfur systems to assess the role of salt and sulfur in the behavior of these metals in hydrothermal fluids. Our analysis shows that the presence of salts and sulfur may have the following impacts on metals transport: a) soft metals (Au) form complexes with Cl- and S-bearing ligands; b) hard metals (W, Mo) form oxyanions and their ion pairs with Na and K; c) Re is a borderline metal, similar to Cu, that exhibits characteristics of both hard and soft acids depending on its oxidation state and coordination environment. By analogy with Au and Cu^+, Re should be transported by Cl- and S-type complexes in its reduced oxidation state (+4).

We are investigating the solubility of major ore minerals ($CuFeS_2$, MoS_2, ReS_2 and Au) in H_2O-KCl-H_2S supercritical fluids in the presence of mineral buffers of pH, fS_2 and fO_2. These data will allow a revision of the available speciation models for those metals in hydrothermal fluids.

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In situ experimental studies of As enrichment and transport in magmatic-hydrothermal fluids

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Arsenic is ubiquitous in all kinds of gold deposits and an indicator for Au, Ag, Cu and Zn crustal deposits. Understanding the enrichment of As and its association with critical metals requires better constraints of its extraction from magma during degassing and transport mechanism to shallower settings, as well as on the dissolution-precipitation of As-bearing minerals at relevant conditions.

While arsenic solubility/speciation data is available at shallow crustal conditions (e.g. Pokrovski et al., 2002a), information at relevant magmatic-hydrothermal conditions is scarce, and fluid/melt partition coefficients only indirectly available from fluid inclusion studies (e.g. Simon et al., 2007).

We apply *in situ* XAS and XRF techniques coupled with the FAME hydrothermal autoclave at BM16 (FAME-UHD) beamline of the ESRF to determine arsenic fluid/melt partition coefficients and speciation at magmatic-hydrothermal conditions, and the solubility of realgar (As_4S_4) in saline hydrothermal fluids.

We aim to constrain the effects of temperature, pressure, and ligands (S and Cl) on the distribution and speciation of As during magma degassing to estimate the As budget of magmatic volatiles. A comparison of our results on realgar with previous *ex situ* solubility studies (e.g. Pokrovski et al., 2002b) provides new insights into the role of S and Cl in the transportation of As in hydrothermal fluids.

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The system $Na_2O+CO_2+H_2O±SiO_2$: Experimental study on phase relations and the solubility of pyrochlore at high pressures and temperatures

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The system $Na_2O+CO_2+H_2O$ is a relatively simple model for fenitising fluids and natrocarbonatites. Little is known about the phase diagrams at high pressures and temperatures, and on the solubility of pyrochlore, the predominant Nb ore mineral in carbonatites, in alkali carbonate fluids. Here, we used a hydrothermal diamond-anvil cell to gain information on phase relations for the bulk compositions $H_{20}CO_{13}Na_2$ (Figure), $H_{20}CO_{13}Na_2$+quartz, $H_2CO_4Na_2$, and HCO_3Na by visual observation and in situ Raman spectroscopy.

Decompression at high temperatures resulted in unmixing of two aqueous fluids, a dilute solution and the other rich in silica species (Q^0, Q^2, Q^3, Q^4) and carbonate. For $H_2CO_4Na_2$, the natrite liquidus was observed at 794 °C, ~460 MPa in the presence of aqueous fluid, and showed a positive dP/dT slope. For HCO_3Na, it was located at 787 °C, ~100 MPa, in the presence of two aqueous fluids. In contrast to HCO_3Na, heating of $H_{20}CO_{13}Na_2$ did not generate detectable CO_2^0.

Based on integrated intensities of Nb–O, Si–O, and C–O stretching bands, the Nb concentration released from pyrochlore at 600 °C was by two orders of magnitude higher if quartz was present. In a quartz-free run at 600 °C, 623 MPa, the aqueous sodium carbonate liquid reacted with pyrochlore contained about 60 ppm Nb. At 600 °C, 1456 MPa, it contained about 1% Nb if quartz and pyrochlore were present. The Raman band from Nb–O stretching vibrations resembles that observed in alkali silicate glasses, in which it is from Q^2 species (NbO_6–SiO_4 chains).

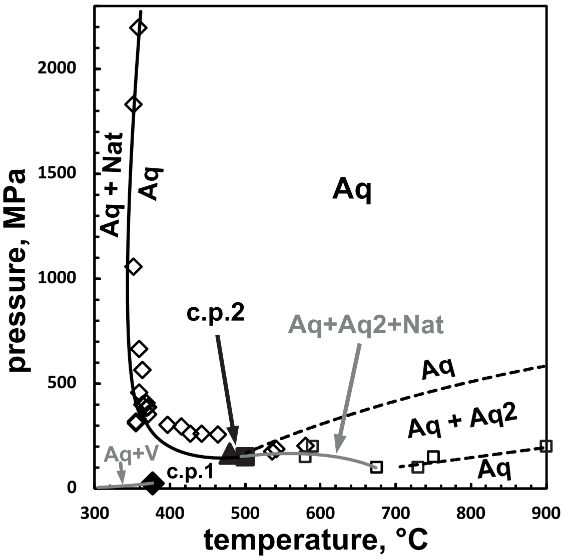

Figure. *P-T* diagram, bulk composition $H_{20}CO_{13}Na_2$. Nat – natrite Na_2CO_3, Aq – aqueous fluid, V – vapor, c.p. – critical point, diamonds – this study, squares – Koster van Groos (1990), triangle – Ravich (1974)

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Germanium/silicon differentiation at hydrothermal conditions

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Gaining insight into the distribution of rare but critical metals at the atomic level is a scientifically important, yet technically challenging aspect of comprehending ore formation and exploration. Germanium is one such economically critical metal that resembles silicon (Si) from a geochemical perspective due to their similar ionic radii and electron configurations, as both elements are in the IVA group of the periodic table. Consequently, in the crustal environment, Ge tends to mimic the geochemical behaviors of Si and even substitute Si in the lattice sites of minerals. Since silicon is evenly distributed throughout the Earth's crust, germanium follows this pattern and so, we rarely observe a Ge deposit, although its crustal concentration is 1.5 ppm, similar to that of W, Mo, and Sn with relatively extensive ore deposits. However, there are a few exceptions, such as coal and zinc deposits, where the concentration of Ge is high enough for economical extraction. Moreover, it is now known that Ge is more abundant in epigenetic sedimentary-hosted Zn deposits compared to other high-temperature Zn deposit types.

Previous experimental works suggested that under the geochemical conditions relevant to ore genesis, Ge(OH)4 and Si(OH)4 are the most abundant species for Ge and Si in the aqueous phase; however, complexation with F- and S2- is also expected, where the affinity for those elements is high. In this regard, we explored the differentiation of Ge from Si utilizing thermodynamic integration based on ab initio molecular dynamics simulation at a supercritical condition (673K) similar to a hydrothermal solution with a magmatic origin and a subcritical temperature (423K) similar to an epigenetic condition.

Our findings indicate that silicon will be preferentially enriched in the aqueous phase, while germanium will be found in the gas phase. Furthermore, the calculated free energies of the reactions at those temperatures suggest that the Si/Ge differentiation is more pronounced at lower temperatures. This aligns with field observations indicating that germanium is enriched in low-temperature deposits, such as coal mines and epigenetic zinc deposits.

Tin Mobility in Hydrothermal-Magmatic Systems. In Situ Observations Using Hydrothermal Diamond Anvil Cells

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The mobility of tin (Sn) in magmatic-hydrothermal systems is a key factor in understanding the formation of tin deposits. Yet, the processes governing its partitioning between granitic melts and fluids remain poorly constrained. This study investigates the partitioning behavior of tin between a granitic melt and coexisting fluid, employing synchrotron-based in situ experiments in a hydrothermal diamond anvil cell (HDAC). Most experimental studies on Sn partitioning rely on quenched samples, where rapid cooling may alter phase equilibria and metal distribution (Duc-Tin et al, 2007; Hu et al., 2008; Keppler & Audétat, 2025). In contrast, in situ approaches provide direct observations of metal behavior at relevant P-T conditions, minimizing post-experimental modifications, although the direct data remain scarce (Schmidt, 2018).

Here, we address this gap of knowledge by utilizing the HDAC in conjunction with Synchrotron X-ray fluorescence (XRF) to directly probe the local distribution of tin between coexisting granitic melts and saline aqueous fluids at magmatic-hydrothermal conditions (< 890 °C and 10 kbar). These experiments reveal a higher affinity of tin for the silicate melt phase under oxidizing conditions, as well as the effect of temperature and salinity on the partition coefficients. Additionally, experiments investigating the solubility of Sn in aqueous fluids were performed in house. The implications of these results for the extraction of tin from magmatic intrusion and the tin budget of magmatic fluids in ore-forming environments will be discussed.

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Can baddeleyite (ZrO_2) be dated with CA-ID-TIMS with the same precision as zircon ($ZrSiO_4$)?

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Zircon ($ZrSiO_4$) is the most widely used mineral in geochronology because it produces precise and accurate ages. However, zircon is not universally applicable, as not all rocks contain zircon. For instance, carbonatites often lack zircon but frequently contain baddeleyite (ZrO_2), which can also be applied as a geochronometer. Methods like SHRIMP/SIMS and LA-ICP-MS offer fast and cost-effective ways to date baddeleyite and other minerals. Still, their precision is insufficient for resolving complex sequences of magmatic intrusions. The CA-ID-TIMS method, which uses a standard chemical abrasion (CA) process, was developed primarily for zircon and provides highly precise and accurate ages. Yet, its application to baddeleyite remains challenging.

In this study, we present experiments aimed at improving the precision of baddeleyite dating. Our analysis of baddeleyite from the Kovdor ultrabasic alkaline carbonatite complex (UACC) in Russia reveals that lead loss and common lead levels in leached grains depend on both the type of acid used and the duration of leaching. HCl leaching for 24 hours improved precision to <0.1% and reduced common lead concentrations to 5.4 pg, though residual lead loss persisted. Extending HCl leaching to 48 hours produced two ages that may reflect the true sample age. Leaching with HF proved more effective, achieving high precision with a 7-hour leaching time and reducing common lead to 4.3 pg. Extending HF leaching to 12 hours partially mitigated lead loss and yielded ages potentially representing the actual sample age. The study also discusses several changes we applied to the initial CA protocol.

We report baddeleyite age from Kovdor carbonatites as 379.28 ± 0.5 Ma. Further application of CA-ID-TIMS to baddeleyites from Vuorijärvi (Russia) and Palaborwa (South Africa) carbonatites highlights that optimal leaching duration is sample-dependent. The obtained ages have a precision of 0,1%, similar to the values of zircon. These findings demonstrate the potential of CA-ID-TIMS to achieve zircon-like precision for baddeleyite dating when appropriately optimized.

Non-matrix-matched *In situ* S isotope analyses by UV-fs LA-MC-ICP-MS and application to the sulfides from porphyry Cu mine Veliki Krivelj (East Serbia)

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This work evaluates the possibility of non-matrix matched standardization using an UV-fs laser ablation system coupled to a MC-ICP-MS instrument. A large chalcopyrite (Cpp) crystal and synthetically produced Ni-sulfide (PGE-A standard) were used as bracketing standards. Method was tested on a set of well characterized minerals: chalcopyrite (GC-1), pyrite (RPPY), galena (NWU-GN) and sphalerite (Sph-1) (Lv et al., 2022). All analyses lie on the terrestrial mass dependent fractionation line of the $\delta^{34}S$ and $\delta^{33}S$ with an internal precision of better than 0.08 ‰ (2s) and 0.2 ‰ (2s), respectively. An accuracy of better than 0.25 ‰ (2SD) for GC-1 and 0.6 ‰ (2SD) for Sph-1 and RPPY were achieved. Detailed analysis of NWU-GN revealed inhomogeneity of up to 2 ‰ in the $\delta^{34}S$ value within a grain or between small grains, possibly due to the smaller ablation diameter and the significantly smaller ablation rate during fs-LA.

This method was applied to a set of sulfides from the vertical profiles of the open pit Veliki Krivelj Cu deposit. Mineralisation is represented by chalcopyrite-pyrite–quartz veins in hydrothermaly altered andesites with rare polymetallic occurrences of galena (Gn) and sphalerite (Sph). Based on *in situ* measurements we were able to distinguish consistently heavier sulfur isotope composition for pyrite $\delta^{34}S$ = ~2 ‰, compare to the neutral or negative values for the coexisting Cpp, Gn or Sph. If occurring together Cpp showed heavier $\delta^{34}S$ compared to Gn and Sph. This indicates significant sulfur isotope fractionation between the minerals during hydrothermal fluid cooling and sulfide crystallization. Due to the secondary alteration, the noticeably lighter $\delta^{34}S$ values were collected in the sulfides from the shallower-, compared to the deeper parts of the ore deposit.

This instrumental setting with a non-matrix matched bracketing standard allows fast and precise measurements of S isotopes and changes in ore deposit formation or secondary processes can be monitored.

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High-Precision Sn isotope analysis using MC-ICP-MS/MS with Double Spike technique

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Tin (Sn) has ten naturally occurring stable isotopes, the highest number among the elements. This abundance provides significant advantages for research into cosmochemical processes (e.g., nucleosynthetic sources, accretion of volatiles to planetary) and geological processes (e.g., magmatic-hydrothermal transitions, ore deposit formation). Although accurate Sn isotope measurements have been reported over the past decade due to advancements in MC-ICP-MS techniques, greater precision, and accuracy in isotope ratio measurements are still needed to resolve the small variations due to fractionation effects and also correct for isotopic shifts caused by Sn loss during sample preparation. In this study, we set up double-spike Sn isotopic measurements using a Neoma MS/MS, equipped with a pre-cell mass filter (set with Wien B-field = 10 %, E-field = 46 V, Pre-filter slit = 100%) and collision cell (operated without reaction gas), and coupled with an Apex Omega desolvating system (Ar flow rate: ~2.2 L/min, without N2 gas).
The double spike (^{117}Sn-^{122}Sn) was added before dissolution at an optimal spike-to-sample ratio of 40:60 (Creech et al., 2017) to correct for Sn isotope fractionation during sample preparation and analysis. Tin was purified using 1.5mL TRU resin columns, effectively reducing isobaric interferences and matrix effects to negligible levels in ~0.4 to 0.7g granitic to mafic whole-rocks. A long-term precision of 0.013 ‰ on $\delta^{122}/^{118}$Sn (2SD, n = 34 over 4 months) was obtained for NIST SRM 3161a analyzed at 50 ng.g-1 with 120Sn beam intensity > 14 V. The average $\delta^{122}/^{118}$Sn of BCR-2, BHVO-2, JA-2, and AGV-2 geological reference materials are 0.315 ± 0.017 (2SD, n = 8), 0.353 ± 0.011 (2SD, n = 11), 0.169 ± 0.016 (2SD, n = 2), and 0.288 ± 0.023 (2SD, n = 3), respectively (all expressed in ‰ deviation from the measured NIST 3161a standard composition), which are consistent with values reported in previous studies (She et al., 2023; Wang et al., 2022).

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Thermodynamic model for aqueous species in the Na-Mg-K-Ca-Al-Si-Fe-C-O-H-Cl system for low-density hydrothermal fluids

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Thermodynamic properties of aqueous species are essential for the modeling and understanding of fluid-mineral equilibria occurring during magmatic devolatilization, metasomatic mass transfer, hydrothermal alteration, and ore deposit formation. The widely used Helgeson-Kirkham-Flowers electrostatic model (Shock et al., 1992) presents several drawbacks: (i) the Born theory is not applicable to uncharged species; (ii) predictions of thermodynamic properties of aqueous species are increasingly inaccurate at low pressures and do not approach correct physical limit; (iii) the electrostatic treatment does not explicitly account for volumetric effects of hydration. We develop a new thermodynamic dataset for aqueous species in the Na-Mg-K-Ca-Al-Si-Fe-C-O-H-Cl system applicable to hydrothermal fluids from low to intermediate density. We adopt a low-parameter functional form that captures the principal contributions to the Gibbs energy: intrinsic properties of solute in the ideal gas state (entropy, enthalpy, heat capacity), solute-solvent interactions accounted for by hardcore volume and volumetric compression in the hydration sphere. The thermodynamic parameters are calibrated for 42 aqueous species by fitting existing Gibbs energy data (Miron et al., 2017) in the range of 25-700 °C and 0.001-3.0 kbar. The new thermodynamic model improves modelling of fluid-mineral equilibria in shallow crustal magmatic and hydrothermal systems.

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Control factors on metal mobility deduced from initial (isotope) geochemical data of hydrothermal vent fluids in different geological settings

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Hydrothermal vent systems on the seafloor host large quantities of metal-rich sulphide deposits. Various factors influence the mobilization, transport, and deposition of metal sulphide in hydrothermal vents. These include the composition of the host-rock, pressure and temperature conditions, phase separation and magmatic degassing. The hydrothermal vent fluids from key sites along the northern Mid-Atlantic Ridge (Rainbow, Broken Spur, Menez Gwen sampled during cruise M190) and the Mediterranean Sea (offshore Milos, cruise M192) were analysed for their major and minor chemistry and additionally analysed for lithium (Li), boron (B) and Sr (Strontium) signature.

Initial results from Rainbow, Broken Spur (M190, 3000m – 2800m depth) and Southeast of Milos (M192, 180m depth) show higher chloride with decreased magnesium values than surrounding seawater, indicating phase-separation and a brine phase ascending at these sites, whilst Menez Gwen (M190, 800m depth) and Northwest of Milos (M192, 180m depth) show lower chloride and lower magnesium than surrounding seawater, indicating a vapor-phase ascending from these sites. Li concentration in all the end-member hydrothermal vent fluids is higher than seawater, with δ^7Li values around 5‰ for Rainbow, Broken Spur, and Menez Gwen, but lower for Milos. Sr is enriched in case of Rainbow, Menez Gwen, and Milos, but depleted in Broken Spur. The ^{87}Sr/^{86}Sr ratio ranges from 0.7039 to 0.7050, except for Milos, which has a higher ratio (0.7101). B enrichment varies across vent sites, Milos has higher B concentrations, while Rainbow is depleted in B. δ^{11}B values range from 15‰ to 23‰ for Rainbow, Broken Spur, and Menez Gwen, with Milos showing lower values. These isotopic variations suggest significant interaction with water and rock but also indicate other processes like mineral precipitation, phase separation, and magmatic gas addition.

The sampled areas at the Mid-Atlantic Ridge (M190) and the Mediterranean Sea (M192) provided optimal conditions for our collaborative project to investigate the controlling factors of metal mobilization. Further high-temperature and high-pressure experiments are planned for the next phase of our project.

New Insights into SMS Deposits: How Microbial Activity and Oxygen Levels Shape Metal Preservation

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Seafloor massive sulfide (SMS) deposits form on the modern ocean seafloor at active hydrothermal vent systems through mixing of mineral-rich, hydrothermal fluids with ambient oxygenated seawater. Once hydrothermal activity ceases, oxygenated seawater infiltrates these deposits, fostering to abiotic oxidative weathering. Microbial activity considerably accelerates this transformation, driving sulfide mineral breakdown, thus enhancing metal transport. Under conditions, restricting oxygen entrainment, low-oxygen zones form below the surface, shielding SMS deposits from oxidative weathering, potentially extending their preservation. SMS deposits are valuable sources of metals governing the interest of their lifespan. In this study, we explore the impact of microbial activity on SMS transformation and mineral dissolution under oxic and low-oxygen conditions. We incubated sulfide minerals, i.e. pyrite and chalcopyrite for four years on the seafloor at active and inactive vent sites along the Indian Ridge. These sulfide minerals were then used for metagenomics, microscopy, microbial enrichment experiments, physiological studies, and geochemistry to identify the key microbial agents driving mineral transformation and metal release. Scanning electron microscopy (SEM) reveals diverse mineral structures, such as twisted stalks and nanowires, suggesting various Fe-oxidizing microbes as well as those involved in extracellular electron transfer. Preliminary metagenomic analyses provide insights into the presence of genes associated with iron oxidation and reduction. Laboratory cultivation experiments mimicked different temperature, oxygen, and pH conditions of hydrothermal vent fluids admixed to distinct degrees with ambient seawater and suggest faster microbially mediated mineral dissolution under oxic conditions and of pyrite as opposed to chalcopyrite. By assessing turnover rates of mineral transformations, we aim to predict how microbial activity affects SMS deposit longevity under varying oxygen conditions.

Accessory Phases in the Archean Kidd Creek VMS Deposit – Fingerprints to unravel a complex deposit history

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Volcanogenic massive sulphide (VMS) deposits contain exploitable metal contents of high economic importance and are actively mined globally. One of the world´s largest VMS deposits is the Kidd Creek deposit in the Archean Abitibi Greenstone Belt, Canada. Three main orebodies comprise a Cu-Zn-Ag mineralization hosted by felsic rhyolite rocks within the bimodal Kidd-Munro-assemblage. The deposit host rocks underwent a complex history including syn- and post-mineralization hydrothermal alteration and metasomatism at greenschist-facies metamorphic conditions (Hannington et al., 1999; Koopman et al., 1999).

Previous studies on the ore and host rock mineralogy revealed the presence of accessory phases throughout the lithologic succession such as REE-bearing phosphates (florencite, monazite, xenotime), TiO_2-polymorphs and zircons (Hannington et al., 1999; Koopman et al., 1999; Schandl et al., 1999). These phases can preserve distinct trace elemental and REE patterns indicative of hydrothermal and metamorphic processes (Volante et al., 2024), and bear the potential to be used as tracers to distinguish between the different alteration processes.

Conducting petrographic studies of Kidd Creek samples, several accessory minerals were identified in the altered hanging wall and footwall rhyolites as well as mineralization hosting rocks. Their relationships to the ore minerals as well as to other alteration phases are evaluated and combined with geochemical analyses. Distinct chemical patterns should indicate their origin and their role in the deposit alteration history. The results obtained in Kidd Creek will be compared to other Devonian VMS deposits from the Iberian Pyrite Belt, Portugal.

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Koopman, E., et al. (1999) Econ. Geol.Monograph 10: 267-296
Schandl, E. S., et al. (1999) Econ. Geol.Monograph 86(7): 1546-1553
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The Enriched Anatectic Source of Granite-Related Lithium Deposits

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Lithium is a high-demand, critical metal that is primarily sourced from rare-metal granites and pegmatites (RMGPs). In order to meet the rising demand of lithium for modern-day technologies, it is imperative to better understand the petrogenetic model of granite-related ore deposits. The enrichment of rare-metals in felsic melts has been historically associated with high-degree fractional crystallization; however, recent studies have demonstrated that this mechanism alone is unlikely to produce melts that are consistent with economic-grade deposits (>5000 ppm; e.g., Koopmans et al., 2023). Alternatively, lithium may become enriched during the partial melting of crustal rocks; however, the anatectic source of RMGPs remains poorly explored. In order to test the anatectic origin of RMGPs, partial melting experiments were performed on enriched metasedimentary rocks (100-800 ppm lithium) in a piston-cylinder apparatus at 750-800°C and 400-1000 MPa. The experiments produced felsic melts with up to 2200 ppm lithium which is comparable to weakly enriched RMGPs. To further explore the enrichment of lithium during crustal anatexis, trace element modelling was performed using newly constrained mineral-melt partition coefficients. Experimental and modelled results demonstrate that RMGPs are unlikely to be sourced from conventional metasedimentary deposits (<200 ppm lithium). Instead, RMGPs are interpreted to form by the partial melting of enriched crustal rocks (300-500 ppm lithium), followed by the moderate fractional crystallization of the extracted melts. Alternatively, the partial melting of unconventional metasedimentary deposits (~1000 ppm lithium) can produce felsic melts that crystallize to form economic-grade RMGPs (>5000 ppm lithium).

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Enrichment and mobilization of tin during metamorphism in Erzgebirge

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Melting of siliciclastic sedimentary rocks with low tin (Sn) concentrations (~5-10 ppm Sn) require extreme fractionation to generate Sn-granites, compared to their enriched counterparts. Therefore, primary Sn deposits are commonly associated with highly fractionated, reduced granites derived from melting of evolved crustal rocks. In this study, we present an example of tin enrichment (typically 50 to 200 ppm Sn) in sediments during prograde metamorphism. In the Bockau area, quartz phyllites and mica schists host minor strata-bound Sn mineralization with local concentrations reaching up to 5000 ppm. Cassiterite (SnO_2), the primary tin mineral, occur as inclusions within prograde biotite in the schists. Tin, further released during retrogression of biotite, precipitated to form a second generation of cassiterite. Cassiterite U-Pb ages older than post-orogenic granitic intrusion and younger than the deposition of the protoliths, i.e., feldspar-free Ordovician shales (Romer et al., 2022) implies that Sn was added during prograde metamorphism. Our study focuses on the mobility of elements during the two metamorphic phases i.e., prograde metamorphism and chloritization of biotite to elucidate tin enrichment and mobilization. Comparison of protoliths (Romer and Hahne, 2010) with non-retrogressed schists reveals a significant increase in Si, Fe, and Sn during prograde metamorphism. During retrogression K, Rb and Ba were lost as biotite was altered to chlorite. Lighter elements, such as Li and B also showed a marked increase during metamorphism indicating their high mobility.

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Revisiting redox-driven pathways of tin cycle from source to economic deposit

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Recent years have seen tin largely overlooked as a pivotal critical metal driving the technological revolution and the green energy transition. Its demand is soaring as it powers a diverse array of modern applications, arousing renewed interest in the scientific community. Tin ore deposits are the result of a complex interplay of crustal processes and intensive parameters to enrich tin by a factor of more than 1000 compared to the average crustal ppm level. The model for magmatic-hydrothermal tin ore formation, established for more than three decades, dictates that reducing conditions and redox reactions play a crucial role for tin transport and concentration because of the greater solubility of SnII in reduced granitic magmas and fluids. Yet, no study has systematically documented the tin oxidation state in crustal rocks involved in tin-ore formation, which was mainly due to analytical challenges. This study shows that X-ray Absorption Near Edge Structure (XANES) spectroscopy allow direct assessment of the tin oxidation state at concentrations as low as 30 ppm. Here, we report the oxidation state of tin for a wide range of reference materials and natural rock samples, often for the first time. Our findings that SnIV is dominant in crustal metamorphic, magmatic and hydrothermal rocks suggest that redox conditions play a smaller role in economic tin-ore formation than previously postulated, with redox reactions being significant, but not essential, during granitic magma generation and crystallization. Moreover, tin can serve as a new redox indicator to help solving major questions such as redox conditions in the continental crust or Earth's redox evolution.

Unraveling the tin isotope composition of granitic ore deposits

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Tin is an element of significant economic importance. Understanding the formation of tin deposits where cassiterite (SnO_2) is the predominant ore mineral, is crucial for efficient mining and ensuring sustainable tin utilization. Since, the crystallization of cassiterite is accompanied by redox change from mainly Sn^{2+} in silicate melts (or fluids) to Sn^{4+} in SnO_2 (Linnen et al., 1996; Yao et al., 2018) and heavier tin isotopes are preferentially bonded to Sn^{4+} (Yao et al., 2018), studying tin isotope compositions may help track the relative effect of melt and/or fluid on tin enrichment and cassiterite crystallization.

This study aims at improving our understanding of the tin isotopic behavior in granitic systems and greisen ore deposits in order to constrain the crystallization conditions of cassiterites. As a case study, we compare the isotopic evolution of cassiterites from the rare metal granite system of Argemela (Portugal), where tin transport and concentration are mainly melt-driven, with the greisen system of Sadisdorf (eastern Erzgebirge, Germany), resulting mainly from fluid-driven processes.

Tin isotope analyses were conducted *in situ* using femtosecond laser ablation multi-collector ICP-MS, enabling to measure the tin isotope composition of individual zones corresponding to different crystallization stages of the cassiterite grains. This method provides information on the transport medium involved and the conditions during the evolution of the ore-forming processes.

Preliminary results show that cassiterite crystals of Sadisdorf show relatively heavier isotopic ratios ($\delta^{124/117}Sn$ = +0.17 to +1.43 ±0.06‰) as compared to those from Argemela with a more magmatic signature (most $\delta^{124/117}Sn$ ratios between -0.34 ±0.08‰ and +0.57 ±0.11‰), in agreement with tin transport by oxidizing fluids. Differences in crystallization environments are also supported by differences in cassiterite compositions, which are Nb-Ta-bearing in Argemela and W-Ti-bearing in Sadisdorf.

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The contributions of subducted sediments to the formation of magmatic-hydrothermal deposits

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The association between porphyry deposits and subduction zones is well established. However, the ultimate primary source of metals such as Cu, Mo, Zn and W is still poorly constrained. One potential source may be the subducted marine sediment. The NaCl content of the fluids released from the dehydrating slab may help to mobilize the metals by chloride complexing. In this project, we studied the partitioning of Cu, Mo, Zn and W between fluids of variable salinity (0 – 15 wt.% NaCl) and subducted sediments between 600–700°C and 2.5–3.5 GPa. The diamond trap method was used for experiments in end-loaded piston cylinder presses. The trace element concentration in both fluids and minerals was determined by laser ablation ICP-MS. We found that Cu and Zn remain virtually immobile in the absence of Cl. Experiments with 0 wt.% NaCl show fluid/mineral partition coefficients below 1. However, with increasing salinity both elements start partitioning into the fluid phase ($D^{fluid/mineral}$ = 1–80). On the contrary, Mo and W show consistently high solubility with little dependence on salinity ($D^{fluid/mineral}$ = 3-96). This is probably because both metals are hard acids, and they are more likely to form hydroxy complexes rather then chloride complexes. Notably, only rutile, which was very rare or absent in the run products, has the capacity to strongly retain Mo and W ($D^{fluid/rutile} < 0.1$). Generally, our data show that the mobilization of Mo from a subducted sediment by aqueous fluid is very efficient, in particular compared to a MORB source, which would contain more rutile. Since Mo may be greatly enriched in some marine sediments formed under reducing conditions, a link between subducted Mo-rich black shales and porphyry molybdenum deposits may be plausible. Cu and Zn mobilized by saline fluids from a subducted sediment may also contribute to metal enrichment, but likely to a lesser extent.

Timing and alteration footprint of the Pb-Zn-Ag epithermal vein system of the Freiberg District, Saxony, Germany

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The Freiberg Pb-Zn-Ag District is a prime example of a precious and base metal epithermal deposit in Europe. The mineralogy and mineral paragenesis of the vein infill have been the focus of extensive studies over the past decade (Swinkels et al., 2021; Bauer et al., 2019; Burisch et al. 2019), leading to its classification as a low sulfidation epithermal system. However, further research is required to characterize the hydrothermal alteration footprint as well as the age of the epithermal vein system, which remain poorly documented. We present detailed petrographic and mineral chemical data of hydrothermally altered gneiss from vein selvages. This is combined with Ar-Ar age data of micas occurring in the unaltered host rock, altered host rock and as vein infill. Preliminary results suggest the presence of a complex interplay of sericitic and silicic alteration; typical of epithermal mineral systems. Geochronology of coarse crystalline muscovite from within mineralized veins and fine crystalline sericite from the alteration halo yield ages ranging from 316.7±3.2 to 306.8±3.1 Ma. These ages are slightly older than previous ages (276±16 Ma, Rb-Sr on sphalerite, Ostendorf, 2019), but in excellent agreement with a well-known pulse of highly evolved felsic magmatism in the region (Breitkreuz, 2021; Tichomirowa, 2022). This study provides further evidence for the complex relationship between geodynamic evolution, felsic magmatism and the formation of hydrothermal ore deposits in the Erzgebirge region.

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Intermediate sulfidation system at the Armanis polymetallic deposit, northern Armenia

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The Armanis Au and base metal deposit (Cu, Zn, Pb, ±Ag, ±Au) is located in the Lesser Caucasus, which forms part of the central segment of the Tethyan metallogenic belt (Moritz et al., 2016) and is spatially associated with the Amasia-Sevan-Akera ophiolite belt, which forms the suture zone between the Somkheto-Karabakh belt and the Gondwana-derived South Armenian block. On the deposit scale, the large post-Eocene 'Urasar' reverse fault, striking NW-SE, is highly linked to fluid ascent from deeper levels. This trans-lithospheric fault structure thrusted ophiolites from Lower Cretaceous onto the mid-Eocene volcanic host rocks of the Armanis veins. The deposit consists of SW-NE and SE-NW trending, steeply dipping ore veins hosted in andesitic to tuffitic rocks, structurally controlled by strike-slip and thrust faults. Quartz is the main gangue mineral, with basaltic sills locally overprinting vein geometry, emphasizing the importance of geochemistry to decipher the ore-forming event. Armanis exhibits three ore types: (1) Cu-Fe ±Zn, ±Pb, ±Ag assemblages with chalcopyrite and pyrite, plus minor sphalerite, galena, and acanthite. Pyrite shows idio- to hypidiomorphic crystals with sizes up to 1000 µm, whereas the chalcopyrite exhibits predominantly more massive textures. (2) Fe-Zn ±Pb veins dominated by pyrite of the same size as in (1) and finer-grained vesicular sphalerite. (3) base metal-rich Cu-Zn ±Pb veins also with massive chalcopyrite and large (up to 2000 µm) sphalerite crystals. All stages contain small idio- to xenomorphic galena crystals with decreasing amounts from type (1) to type (3). Microprobe data already suggested a declining temperature regime from ore type (1) to (3), e.g. evidenced by high Co, Ni, Cu values and low Au, Ag values in pyrite (1) and vise-versa in pyrite (2) or high Se contents in chalcopyrite in (1) pointing towards higher temperatures compared to higher Au and Te in (3) which are commonly found in a more distal and colder regime. However, to understand the multiple mineralization phases, we used LA-ICP-MS analyses, which provide more detailed insights into element distribution. The Armanis veins can be generally characterized as an intermediate sulfidation (IS) epithermal deposit of Oligocene age. Compressive stress was dominant during ore formation. This work has significant implications for further exploration of the area, as the compressive subtype of IS veins can be associated to a porphyry Cu-Mo deposit at depth (Wang et al., 2019).

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Metamorphism of pyrite during the Himalayan orogeny: implications for orogenic gold genesis

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In the metamorphic devolatilization model for orogenic gold, Au and trace element release into metamorphic fluids is linked to breakdown of pyrite to pyrrhotite during prograde metamorphism of sedimentary rocks. Through the investigation of metasedimentary rocks up the metamorphic gradient of the Himalayas, the youngest and loftiest orogen on the planet, we evaluate this idea. We describe the metamorphic evolution of texture and trace element chemistry of sulfides as well as bulk rock Au contents of carbonaceous metapelites of Mandhali Formation, inner Lesser Himalayas, Uttarakhand, India. Our findings from chlorite-muscovite (372 °C) and muscovite ± biotite zone (505 – 520 °C) show that in a prograde path, up to 90% of Au, 75% of As and majority of other trace elements are released from pyrite due to metamorphism prior to its progressive breakdown to pyrrhotite. The corresponding depletion of bulk Au contents, together with pyrite > pyrrhotite-nature and complete chlorite consumption in the muscovite ± biotite zone phyllites shows that Au has been mobilized from the metapelites and hence suggest (1) a complete pyrite to pyrrhotite transition is not a pre-requisite for Au mobilization in metamorphic belts, (2) the presence of a potential carbonaceous sedimentary gold reservoir in the inner lesser Himalayas.

Typical and atypical orogenic gold deposits from Paleoproterozoic Finland: assessing fluid chemistries by hydrothermal alteration styles

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During the last decades genetic models have been developed to describe the formation of orogenic Au deposits. These deposits are usually only economically enriched in Au. Some deposits, however, show additional exploitable enrichments in base and critical metals, mainly Cu, Co, Ni ± Sb, U and REE and are defined as orogenic Au deposits with atypical metal association (Eilu, 2015; Hector et al., 2023). These enrichments in base and critical metals are not fully explained by the current genetic models (i.e. metamorphic devolatilisation, subcrustal fluids, magmatic-hydrothermal model) and the mechanisms leading to different metal endowments are still unclear.

The Paleoproterozoic Pohjanmaa Belt (PoB) of western Finland hosts both typical and atypical orogenic gold deposits, including the second largest orogenic gold mine of Finland (Laivakangas Au deposit, 44t Au resource, owner: Laiva Gold)(Eilu, 2015). Both subtypes of orogenic gold deposits are found along the same structure and are hosted by similar wall rocks, yet showing diversities in their metal association. The coexistence of typical and atypical deposits along the same structure questions the mechanisms leading to varying local metal associations (e.g. different fluid chemistries, different fluid sources or different precipitation mechanisms). The Pohjanmaa volcano-sedimentary schist belt is a type locality to investigate the genesis of atypical orogenic Au-Cu-Co-Ni deposits and establish a genetic deposit model including both type of deposits. Four orogenic Au deposits are investigated during this project, two are typical orogenic Au (Laivakangas and Huhta) and two represent atypical orogenic Au deposits (Jouhineva and Kurula).

Orogenic Au mineralization found in these deposits are the result of two main auriferous events, a first As-Au (Co, Ni) event close to peak metamorphism at amphibolite facies conditions and a later Cu (Au)-rich sulfide event on the retrograde metamorphic path at greenschist-facies conditions (Hector et al., 2023). The nature of the metamorphosed source rocks seems to play a major role in controlling the base metal content in orogenic Au deposits (Patten et al., 2023). Nevertheless, the parameters controlling the enrichment in Co, Ni ± Sb, U and REE are yet not well constrained (Hector et al., 2023; Patten et al., 2023) and the characteristics and nature of the fluids responsible for varying metal endowments in the two subtypes of orogenic Au deposits remains not sufficiently understood. By combining fluid inclusion analysis and measuring geochemical changes in hydrothermal alteration haloes, this project explores the origin and nature of the mineralizing fluids and precipitation mechanisms leading to the differences in metal enrichments.

First petrographic studies underline the interpretations for the mineralizing history of the deposits made by (Hector et al., 2023). While the deposits show similar mineralization history between each other, they don’t show the same metal associations because of varying intensity of each mineralizing event, leading to different base metal contents.

With a first focus on samples from the Laivakangas and Kurula deposits, primary results from systematic study of hydrothermal alteration patterns in proximity to the mineralizing veins show that previous epidotization and chloritization, pre-dating the sulfide (Cu-Au) mineralization event, may act as important prerequisites for the subsequent sulfidation and formation of mainly chalcopyrite and pyrite. The decomposition of epidote and chlorite may deliver necessary Fe (MacKenzie et al., 2007), resulting in the formation of existing Fe-sulfides. The strong correlation of epidote with chalcopyrite (±pyrite) and chlorite with pyrite supports this hypothesis. Decomposition of muscovite may supply Fe for chalcopyrite formation as well, as these minerals show an apparent intergrowth. Sericitization in the vein selvedges is ubiquitous and plagioclases were almost completely replaced by sericite, though the intensity of replacement is decreasing towards the unmineralized host rock.

Cathodoluminescence (CL) studies allows to investigate the growth sequence between gangue minerals in reactivated hydrothermal veins, consisting mainly of quartz, feldspars and to a lesser extent calcite. The feldspars are represented by k-feldspar (mainly microcline) and plagioclase and they seem to be older than the mineralizing quartz veins. Calcite seems to be younger and is only rarely present.

The next steps to better constrain the nature of the mineralizing fluids are a systematic investigation of hydrothermal alteration and analysis of halogen ratios from mineral separates. Systematic whole rock geochemical analysis from the vein selvedges towards less weathered host rock will highlight chemical changes caused by hydrothermal alteration, providing insights in the fluid composition. Halogen ratios (Cl, Br, F, I) in mineral separates of hydrothermal alteration products (actinolite, tourmaline, biotite, sericite, chlorite, scheelite) will yield information about fluid sources and allow to understand the parameters controlling metal associations in typical and atypical orogenic gold deposits.

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Progress on modelling of Chromium enrichment in the mantle and crust (CHROME)

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Economically viable chromium is predominantly sourced from chromite, a mineral belonging to the spinel group, which is most commonly found in ultramafic, mantle-derived rocks. The primary goal of the CHROME project is to develop numerical models that provide insights into the geological conditions responsible for the formation of ophiolite-hosted, podiform chromite deposits. Our approach includes three major directions, namely: i) the thermodynamic calibration of phase equilibria including Cr-bearing phases, ii) the modelling of the flow of Cr-enriched melts in the mantle, and iii) understanding the mechanisms of Cr-deposit formation. We will investigate the interplay between the chemical reactive flow of the melt and the mechanical segregation of spinel to identify the predominant mechanisms of Cr-deposit formation in the mantle.

Here, we present the current progress of our research in accordance with the three major directions outlined above. First, we present our current approach for the thermodynamic framework needed for solution-model calibration. Our new approach allows the efficient calculation of phase equilibria (using MAGEMin; Riel et al., 2022) by the reformulation of complex solution phases, which results in more efficient and more stable calculations (Riel et al., *in review*). This approach will be used in the recalibration of Cr-bearing solution models in agreement with recent experimental findings. In addition, we have developed new models for multiphase flow that focus on the distribution of trace elements (including Cr) in the mantle phases. Compared to previous work, these models allow the consideration of fluid/melt flow in regions with discontinuous mechanical and hydraulic properties (Boisserée et al., *in review*). This study will provide the framework for the investigation of element mobility in geologically stratified layers. Finally, we will present preliminary results from small-scale 2D thermo-mechanical convection models of magma pocket emplacement. These models will be used to quantify and test the scenario of Cr-deposit formation via the mechanical segregation of spinel during melt flow.

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Riel, N., Kaus, B., Green, E., and Berlie, N. (2022): MAGEMin, an Efficient Gibbs Energy Minimizer: Application to Igneous Systems. Geochemistry, Geophysics, Geosystems, https://doi.org/10.1029/2022GC010427

Riel, N., **Kaus, B.,** de Montserrat, A., **Moulas, E**., Green, E., and Dominguez, H. (2025). An unconstrained formulation for complex solution phase minimization. Geoscientific Model Development, in review, https://gmd.copernicus.org/preprints/gmd-2024-197/

Sulfide-Silicate emulsion textures in orthomagmatic sulfide deposits

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Emulsion textures are rare intergrowths of silicates and sulfides, with both fractions showing clear evidence of magmatic origin. Despite their rarity, they are found globally in lower crustal Ni-Cu deposits such as Nova-Bollinger, Savannah, and Voisey's Bay (Barnes et al., 2018), predominantly at the infiltration fronts of ore bodies. Additionally, emulsion textures are hosted in smaller, upper crustal sulfide occurrences, such as the Sora quarry and the Sohland mine in eastern Germany (Jaroka et al., 2021).

Emulsion textures are interpreted as the lithified products of mingling between two immiscible melts: a denser, less viscous sulfide melt and a lighter, more viscous silicate melt (Staude et al., 2017). Depending on the ratios of the melts, they occur as "droplet emulsions" (e.g., disseminated sulfide droplets in silicate melt or vice versa) or "bicontinuous emulsions," with the latter showing an approximately 50/50 ratio (Raisch et al., in press). This mingling must be rapidly "frozen" before phase separation occurs, during which the silicate melt floats above the denser sulfide melt. This final separated stage is well-preserved at Nova-Bollinger, where pegmatoidal silicate pockets are located on top of the ore body (Raisch et al., in press).

Additional features of emulsion textures include silicate megacrysts up to 10 cm in size, suggesting a magmatic origin for the silicate phase, and oxide rims, potentially indicating a third immiscible melt (Barnes et al., 2024).

Understanding these textures sheds light on the kinetics of magmatic sulfide ore formation, including sulfide melt percolation and accumulation in (ultra)mafic magma (Naldrett, 2011) or sulfide infiltration into country rock via anatexis (Staude et al., 2017). Furthermore, their petrology may help to distinguish between these processes (Raisch et al., in press).

Barnes, S.J., Staude, S., Le Vaillant, M., Piña, R., Lightfoot, P.C., 2018: Sulfide-silicate textures in magmatic Ni-Cu-PGE sulfide ore deposits: Massive, semi-massive and sulfide-matrix breccia ores. Ore. Geol. Rev. 101, 629-651.
Jaroka, T., Staude, S., Seifert, T., Pfänder, J. A., Bauer, M. E., Krause, J., Schulz, B., 2021: Mineralogical and geochemical constraints on the origin of the Sohland-Rožany Ni-Cu-(PGE) sulfide mineralization (Lausitz Block, Bohemian Massif, Germany/Czech Republic). Ore. Geol. Rev. 133, 104055.
Staude, S., Barnes, S.J., Le Vaillant, M., 2017: Thermomechanical erosion of ore-hosting embayments beneath komatiite lava channels: textural evidence from Kambalda, Western Australia. Ore. Geol. Rev. 90, 446-464.
Naldrett, A. J., 2011: Fundamentals of magmatic sulfide deposits. Rev. Econ. Geol. 17, 1-50
Raisch, D., Staude, S., Markl, G., (in press): Revisiting semi-massive sulfides: Textures of sulfide-silicate interactions in magmatic sulfide deposits. Ore. Geol. Rev.

Petrogenesis and ore-forming processes of the ultramafic Kylmäkoski Ni-Cu-(Co) magmatic sulfide deposit, SW Finland

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The 1.89 Ga ultramafic Kylmäkoski intrusion, located in the Vammala Ni Belt in southwest Finland, is an example of a magmatic Ni-Cu-(Co) deposit related to a subduction zone setting (Peltonen, 1995b). This study uses petrographical and textural observations combined with in situ major and trace element, whole-rock, and $\delta^{34}S$ analyses to determine how melt evolution and the physiochemical conditions in the magma chamber influenced the process and timing of sulfide saturation.

Geochemical results suggest that assimilation of external sulfur from sedimentary rocks, such as graphitic black schists, is probably not the main mechanism for the attainment of sulfide saturation. This is indicated by mantle-like $\delta^{34}S$ isotope values (-0.91 to 0.08 ‰) in the ore minerals and low concentrations of elements typically found in black schists, such as As, Sb, Mo, Sn, and Pb (Samalens et al., 2017b). A large spread in forsterite contents of olivine (66 to 78 mol%) suggest that the melt experienced fractionation in the magma chamber. Fractional crystallization of the silicate melt is an effective mechanism to increase the S budget due to its incompatible nature during silicate fractionation (Ripley et al., 2013). This process, coupled with the crystallization of magnetite that led to a decrease in f_{O2} in the alkaline melt (ΔFMQ +2.35±0.43), resulted in late-stage sulfide segregation. The dense sulfide liquid settled down in the magma chamber and infiltrated the intercumulus spaces between the partially crystallized cumulates, leading to a distinct poikilitic texture of the sulfides.

We conclude, due to the similar redox state of the Paleoproterozoic Kylmäkoski melts and modern arc magmas (Richards, 2015) that assimilation of sedimentary rocks, acting as an external S source, may not generally be necessary to form economic magmatic sulfide deposits at convergent plate boundaries.

Peltonen, P. (1995b): Petrogenesis of ultramafic rocks in the Vammala Nickel Belt: implications for crustal evolution of the early Proterozoic Svecofennian arc terrane. *Mineralogy and Petrology,* 52, pp. 1-24.

Richards, JP. (2015): The oxidation state, and sulfur and Cu contents of arc magmas: implications for metallogeny. *Lithos,* 233, pp. 27-45.

Ripley, EM., and Li, C. (2013): Sulfide saturation in mafic magmas: Is external sulfur required for magmatic Ni-Cu-(PGE) ore genesis?. *Economic Geology,* 108.1, pp. 45-58.

Samalens, N., Barnes, SJ., and Sawyer, EW. (2017b): The role of black shales as a source of sulfur and semimetals in magmaticnickel-copper deposits: example from the Partridge River Intrusion, Duluth Complex, Minnesota, USA. *Ore Geology Reviews,* 81, pp. 173-187.

Timing and nature of HFSE enrichment and mineralization in alkaline peridotite-melilitolite-foidolite-carbonatite complexes – a melt inclusion study from Gardiner (Greenland) and Kovdor (Russia)

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Some carbonatites are associated with alkaline ultramafic rocks, foidolites, and melilitolites. Such rock suites are of economic interest due to their common enrichment in critical and strategic elements like Ti, P, HFSE, or REEs. Key examples for such systems are the Gardiner (Greenland) and Kovdor (Russia) complexes. Previous work has focused on the source of melts for these complexes by interpreting daughter mineral assemblages in olivine-hosted melt-inclusion from ultramafic rocks (Nielsen et al., 1997; Veksler et al., 1998). These studies concluded that both complexes share similar parental melts.

Recently, it was shown that peridotitic and melilitolitic rocks from Gardiner represent early magmatic cumulates, whereas some of the dunites and melilitolites at Kovdor lack typical cumulate textures, contain unusual phases, such as calcite, apatite and baddeleyite. Together with unexpected mineral compositions (e.g., low Ni concentration in Olivin), a metasomatic origin for these rocks seems likely (Gudelius et al., 2023)

The enrichment of HFSE and the timing of ore formation during the lifetime of these two complexes remain under debate. Carbonatites at Kovdor are HFSE-mineralized, with only minor HFSE-phases in the associated silicate rocks. In contrast, melilitolites from Gardiner show ore-grade enrichment of perovskite, while the associated carbonatites are barren. To reconcile the different processes during the formation of these systems, homogenization temperatures of melt inclusions and their chemistry across all major rock units (dunites, pyroxenites, ijolites and melilitolites, carbonatites) are needed. Particularly, differences in melt inclusions between metasomatic- and cumulate-type rocks at Kovdor are crucial to constrain the behavior of REEs and HFSE during these contrasting modes of formation. This will shed light on the nature of these rocks at variable evolutionary stages and the subsequent enrichment processes.

Gudelius, D., Marks, M. W., Markl, G., Nielsen, T. F., Kolb, J., and Walter, B. (2023): The origin of ultramafic complexes with melilitolites and carbonatites: a petrological comparison of the Gardiner (E Greenland) and Kovdor (Russia) intrusions. Journal of Petrology, 64(6).
Nielsen, T. F. D., Solovova I. P., and Veksler I. V. (1997): Parental melts of melilitolite and origin of alkaline carbonatite: evidence from crystallised melt inclusions, Gardiner complex. Contributions to Mineralogy and Petrology, 126.4.
Veksler, I. V., Nielsen, T. F. D., and Sokolov S. V. (1998): Mineralogy of crystallized melt inclusions from Gardiner and Kovdor ultramafic alkaline complexes: implications for carbonatite genesis. Journal of Petrology, 39.11-12.

Approach to Constraining Depth-Controlled Fluid-Mediated Metal Distribution in Alkaline-Carbonatite Magmatic Systems

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Intrusive alkaline rock and carbonatite complexes are of high societal importance, since the complexes are major sources of critical metals like Nb, Ta, REEs, Zr, Hf, or Ti and play a major role as we approach the critical metal reliant green energy transition (Hou et al., 2015; Goodenough et al., 2018; Smith et al., 2018).

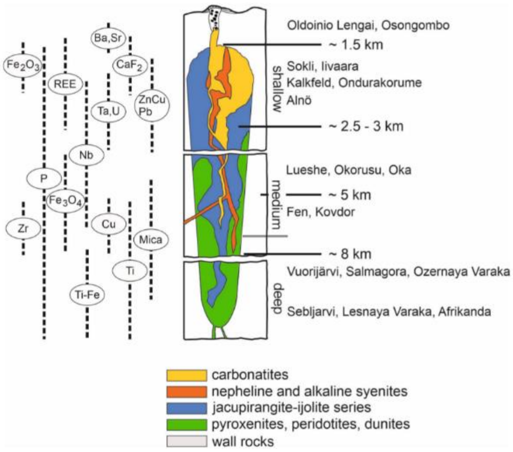

Fig. 1: Sketch of Vertical Zonation shown in alkaline and carbonatite intrusive complexes, modified after (Frolov, 1971; Arzamastsev et al., 2000).

Despite the economic importance of ultramafic alkaline and carbonatite complexes, their formation is contested. On one side, the vertical and lateral zonation often observed in these complexes is considered to represent different magmatic processes at different depths (Fig 1) (Woolley and Kjarsgaard, 2008). However, it has also been suggested that they are metasomatic, and that zonation is caused by ascending low-viscosity carbonatite melts reacting with crustal silicic country rocks (Vasyukova and Williams-Jones, 2022). Unfortunately, many publications about inclusions in alkaline and carbonatite rocks lack information pertaining to the abundance of rare metals and halogens present. Since mineralization reactions are impacted by multiple types of fluids in alkaline complexes, it is important to determine the capacity of the fluids to transport and fractionate rare metals and other elements, to separate them, relate the fluids to the different levels, and constrain the cause of the zonation process (Walter et al., 2021). To construct a representative dataset from fluid and melt inclusions, the sample collection must be comprehensive, with depth data, and well characterized petrological evolution with formation stages and compositional variability. We will present some of our initial findings including sample selection, petrographic findings, testing use of Raman to calculate volume proportions of melt inclusions, along with a brief overlook of future plans and other methods.

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Frolov, A.A., (1971), Vertical zonation in deposition of ore, as in ultrabasic-alkaline rocks and carbonatites: International Geology Review, v. 13, p. 685–695.

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Hou, Z., Liu, Y., Tian, S., Yang, Z., and Xie, Y., (2015), Formation of carbonatite-related giant rare-earth-element deposits by the recycling of marine sediments: Scientific Reports, v. 5, p. 10231.

Smith, M., Kynicky, J., Xu, C., Song, W., Spratt, J., Jeffries, T., Brtnicky, M., Kopriva, A., and Cangelosi, D., (2018), The origin of secondary heavy rare earth element enrichment in carbonatites: Constraints from the evolution of the Huanglongpu district, China: Lithos, v. 308–309, p. 65–82.

Vasyukova, O.V., and Williams-Jones, A.E., (2022), Carbonatite metasomatism, the key to unlocking the carbonatite-phoscorite-ultramafic rock paradox: Chemical Geology, v. 602, p. 120888.

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Woolley, A.R., and Kjarsgaard, B.A., (2008), Paragenetic Types Of Carbonatite As Indicated By The Diversity And Relative Abundances Of Associated Silicate Rocks: Evidence From A Global Database: The Canadian Mineralogist, v. 46, p. 741–752.

Carbon and Rare Earth Element Speciation in Late-Stage Carbonatite Fluids: Insights from Molecular Dynamics

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Carbonatites are among the most significant sources of light rare earth elements worldwide. Hydrothermal activity and other processes alter the original composition of carbonatitic melts after primary mineralization and deposition. Several aspects of carbonatitic melt and fluid evolution remain to be explored and understood. This project aims to shed light on the behavior of oxidized carbon species at the melt-fluid interface (see Figure) in late-stage magmatic-hydrothermal carbonatite systems. Temperatures in this stage range from approximately 700 to 1000 K. Due to the complexity of experimental approaches, we employed ab initio molecular dynamics (AIMD) simulations to create a melt-vapor interface in the H_2O–CO_2–Na_2CO_3–NaCl system at 1000 K. Our model system represents a brine-melt and hydrothermal fluid with densities of 1.08 and 0.25 g/cm³, respectively. Understanding CO_2 and CO_3^{2-} speciation at the molecular level will provide key insights into the following reactions

$$H_2O + Na_2CO_3 \rightleftarrows NaOH + NaHCO_3$$

$$NaHCO_3 \rightleftarrows NaOH + CO_2$$

Thus far, CO_2 molecules form through the dissociation of Na_2CO_3 and $NaHCO_3$ in the melt, ultimately migrating into the vapor phase. Plotting the partial radial distribution functions of C–O as a function of the coordination numbers of CO_2 and CO_3^{2-} illustrates the formation of CO_2 in our model system. An additional goal is to introduce rare earth elements (REE) into our brine-melt model system (H_2O–Na_2CO_3–NaCl). As a first step, we incorporated lanthanum under different environmental conditions to establish distinct coordination environments within the brine-melt. These serve as a foundation for the next phase of our investigation. To further explore the free energy surface (FES) of the system, we employ enhanced sampling techniques such as metadynamics in combination with AIMD calculations. The FES is described by the function

$$F(s) = -T \lim_{t \to \infty} \ln N(s,t)$$

Here, *s* represents collective variables such as coordination numbers or interatomic distances, while *N(s,t)* denotes a histogram of *s* obtained from unbiased AIMD calculations. In metadynamics, external history-dependent potentials are applied as small Gaussian functions to the unbiased AIMD simulations, gradually filling the free energy surface (FES) by disfavoring previously visited configurations, represented by the equation

$$V(s,t) = \Delta T ln(1 + \frac{\omega N(s,t)}{\Delta T})$$

ΔT is a temperature and ω describes the initial bias deposition rate. In the current phase we carefully test, select and combine CVs to ensure accurate results.

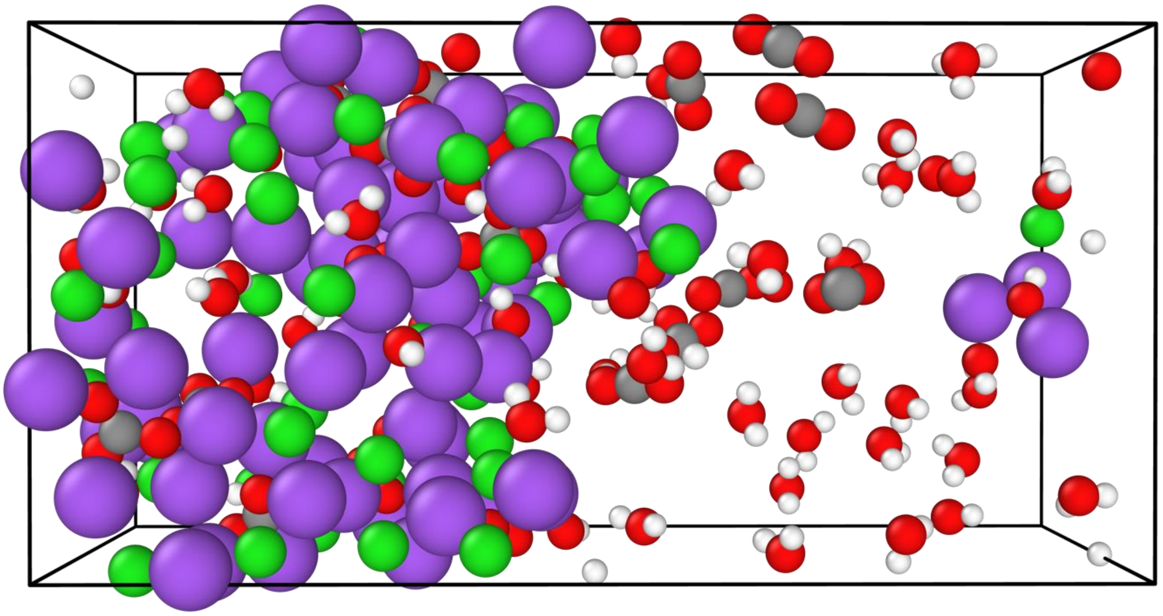

Figure: Snapshot of the simulation box of the melt-vapor interface. Left side: brine-melt phase. Right side: vapor phase. Red - Oxygen; white - Hydrogen; grey - Carbon; green - Chlorine; purple - sodium. This figure was generated using OVITO (Stukowski, 2010)

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Boron deportment in Mamatwan-type mangano-lutite ores from the Kalahari Manganese Field, Northern Cape Province, South Africa

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The Kalahari Manganese Field (KMF) of the Northern Cape Province of South Africa hosts more than 70% of all known minable manganese ores globally. Current mining operations in the KMF yield more than 30% of global supply. More than 90% of the Mn resource in the KMF is best described as mangano-lutite, e.g., a finely laminated and microcrystalline sedimentary rock containing 30 to 40 wt. % Mn. Across the KMF, this mangano-lutite occurs in three well-defined intercalated sedimentary units in gradational contact with Superior-type banded iron formations of the 2.42 Ga Hotazel Formation. The latter forms part of the undeformed and virtually unmetamorphosed volcano-sedimentary succession of the Postmasburg Group, Transvaal Supergroup. Despite its economic relevance as the world's single-most important source of manganese, mangano-lutites remain poorly studied. There is a striking lack of quantitative mineralogical data and a complete lack of published elemental deportment studies available. Arguably, this is due to the exceptionally fine-grained nature of the mangano-lutite. This contribution illustrates how modern analytical methods can be combined to provide reliable deportment data. Boron is studied here as a well-known penalty element occuring in concentrations of up to several hundreds of ppm in the mangano-lutite. A new workflow for very fine-grained ores characterization using SEM-based automated mineralogy, quantitative XRD and whole rock geochemistry has been developed for this purpose. The results reveal surprising differences in mineral assemblages and their associated boron content among various textural zones of the three ore bodies in the Hotazel Formation. We find that boron deportment is controlled by the distribution of braunite (Si-bearing Mn-oxide mineral) but also by silicate minerals that occur in minor / trace amounts. The results document the opportunity to produce Mn ore products with low vs. moderate to high boron content from the mangano-lutite.

Tracing sulfide precipitation pathways in small and large deposits in Zn-Pb sediment-hosted McArthur Basin, Australia

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This study describes a workflow for analysing the multiple sulfur isotope composition of paragenetically constrained sulfides in Proterozoic Clastic Dominant (CD) sediment-hosted Zn-Pb deposits. This pioneering dataset will be used to investigate different stages of diagenetic (pyrite) and hydrothermal (pyrite, sphalerite) sulfide formation in the world class Zn province of McArthur Basin, Australia. The sulfide paragenesis in the large Teena and small Myrtle deposits preserves two different stages of pyrite and sphalerite. The first pyrite stage is characterized by fine-grained diagenetic pyrite (py1). The first generation of light color sphalerite (sp1) is the most volumetrically significant, and is finely disseminated in the host rock and associated with a second stage of coarse pyrite (py2). A minor second generation of medium grained red-brown sphalerite (sp2) is disseminated in the clastic matrix. The different end-member styles of sulfides are being characterized and will be chemically extracted from the host rock matrix in preparation for isotopic analysis. The isotopic dataset will potentially help differentiate between different pathways of diagenetic sulfate reduction (organoclastic vs. anaerobic methane oxidation) and potentially thermochemical sulfate reduction, which remain challenging to distinguish in ancient rocks when using conventional methods. This may also help determine which pathways dominate in larger (e.g. Teena) compared to smaller (e.g. Myrtle) CD-type deposits.

Reactive transport modelling of ore formation in sedimentary basins: non-isothermal compressible fluid flow

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Sediment-hosted ore deposits are major resources for base metals like Zn, Pb and Cu. These deposits form by basin-scale flow of hydrothermal fluids through permeable aquifers and fault structures, incorporating metals from source rocks and transporting them to a deposition site where metals precipitate as sulfide minerals due to fluid reduction and/or fluid mixing. Metal enrichment in hydrothermal systems requires favorable combinations of chemical and physical processes on different temporal and spatial scales. Numerical models can help to identify first-order controls on ore formation and quantify the potential to generate world-class deposits. The aim of this project is to further develop and apply a reactive transport model for the formation of Zn-Pb deposits in sedimentary basins, using fluid flow modelling (CSMP++) coupled with geochemical modelling (GEMS3). The fully coupled numerical model will be able to 1) capture the interplay between the chemical and physical processes relevant for metal mobilization, transport and precipitation, and 2) constrain the temporal and spatial scales required for metal enrichment to economic grades. Geodynamic modeling results of continental rifting and basin formation (Glerum et al. 2024) will eventually inform the model setup to incorporate geodynamic controls as well.

The subproject presented here focusses on the numerical representation of non-isothermal compressible fluid flow with CSMP++ within the coupled reactive transport model. In a first step, we developed simplified hydrothermal systems as 1D- and 2D-simulations with basin-scale heat flux and fluid flow based on idealized benchmark simulations (Weis et al., 2014). First tests used existing proxies for the temperature- and salinity-dependent solubility of Cu, Pb and Zn in the ore fluid from Stoltnow et al. (2023). In a second step, we added the full chemistry calculations by coupling with GEMS3 (Yapparova et al., 2017). In this meeting, we will present preliminary simulations of our work towards unraveling the major controls on sediment-hosted ore deposits.

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Geochemical modelling of sediment-hosted Pb-Zn deposits

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Sediment-hosted ore deposits are major resources for base metals like Zn, Pb, Cu and many other metals and critical metals. Based on the type of the host rock, they include two main types of ore deposits: the clastic-dominated (CD-Type, formerly SEDEX) and Mississippi-Valley-Type (MVT) deposits. These deposits are formed by flow of oxidized fluids through permeable aquifers and fault structures, which dissolve metals from source rock and transport them to a locally confined deposition site, where metals are precipitated as sulfide minerals due to fluid reduction and/or fluid mixing.

Understanding the first-order controls on chemical enrichment in hydrothermal systems of these deposits is challenging. This is because geological observations are usually limited to the scale of the deposit itself. As a result, larger-scale aspects, like the potential source rocks for the metals and the pathways of the fluids, remain largely speculative due to their inaccessibility.

Numerical modeling has the potential to offer valuable constraints and resolve the complexities related to ore formation and the efficiency of hydrothermal systems. To achieve this, the study combined comprehensive thermodynamic databases with ore fluid chemistry data from published sources. This included using microthermometry data for the homogenization temperature to understand the entrapment temperature and geochemistry of fluid inclusion from Laser ablation data especially the metal and total sulfur content. The research focused on well-known deposit types, such as CD-type deposits in the Selwyn Basin, Canada, and MVT deposits in the Ozark region, USA.

This research utilizes the GEMS3 and GEMSFITS suites for geochemical modeling and creating consistent thermodynamic datasets. These tools effectively manage complex fluid and rock compositions under hydrothermal conditions, providing insights into metal sources, fluid mobilization and transport, and elucidating the differences and genetic relationships in mineralization between CD-Type and MVT deposits.

From hydrothermal fluids to mineral deposits: development of a new internally-consistent geochemical-thermodynamic model of Pb-Zn-Ag-Au-As-Sb systems

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Hydrothermal ore deposits represent significant metal enrichments in the Earth's crust, formed through efficient extraction of metals from source rocks, their transport by hydrothermal fluids and their subsequent precipitation under favorable geochemical conditions. Fluid-mineral interactions play a central role in the formation of world-class ore deposits, including magmatic-hydrothermal porphyry Cu-Au-Mo, epithermal Ag-Au-As-Sb and sediment-hosted Pb-Zn deposits. Understanding the fundamental processes that control metal solubility, speciation and precipitation in these systems requires robust geochemical-thermodynamic modeling.

The development of accurate thermodynamic datasets is critical for simulating the complex interactions between hydrothermal fluids and minerals. However, many existing datasets suffer from inconsistencies, limiting the predictive capability of current ore-forming models. To address this gap, this work presents a new internally-consistent geochemical-thermodynamic model for the hydrothermal transport of Pb-Zn-Ag-Au-As-Sb, significantly expanding the recently developed thermodynamic dataset for the Na-K-Ca-Mg-Al-Si-C-Cl-O-H system (Miron, 2016). By incorporating a large body of experimentally derived solubility and spectroscopic data, this dataset provides improved constraints on the standard Gibbs energy of aqueous species, allowing for more precise modeling of metal extraction, transport and deposition in hydrothermal environments.

The new thermodynamic framework is applied to simulate first-order geochemical processes that control the formation of sediment-hosted exhalative (SEDEX) and carbonate-hosted Pb-Zn deposits (Mississippi-Valley-Type, MVT), as well as epithermal Ag-Au-As-Sb systems. The modeling addresses key questions related to the formation of globally important ore deposit types, namely the relative role of reduced acidic vs. oxidized brines in metal mobilization in sediment-hosted Pb-Zn systems, the link between exhalative and carbonate-hosted Pb-Zn deposits and the impact of arsenic (As) and antimony (Sb) on the hydrothermal transport of Pb, Zn, Ag and Au. The modeling approach, using the GEM-Selektor v.3 and GEMSFITS software (https://gems.web.psi.ch), integrates thermodynamic equilibrium calculations with solubility and speciation data to provide new insights into ore formation processes.

This work represents a major advancement in geochemical modeling of hydrothermal metal transport, offering a more consistent and accurate thermodynamic framework for simulating the extraction, transport and precipitation of economically important metals. The results contribute to a better understanding of ore-forming fluid evolution and provide a valuable tool for interpreting natural hydrothermal systems, with direct implications for both fundamental geoscience research and mineral exploration.

The talk will focus on new results on the geochemical-thermodynamic modeling of hydrothermal Pb-Zn systems.

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The role of organic matter on Kupferschiefer mineralization

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Late Permian Kupferschiefer in north-central Europe is one of the world's most significant sediment-hosted stratabound copper (SSC) deposit. Mineralization of economically relevant metal concentrations is restricted to the southern margin of the Southern Permian Basin (SPB), where metals such as copper or silver have been mined for centuries (Borg et al., 2012; Paul, 2006).

Previous studies indicate a pronounced thermal overprint of organic matter in mineralized rocks, indicating a significant role of organic material in Kupferschiefer mineralization. These investigations primarily focused on bulk parameters (e.g., non-polar hydrocarbons and biomarkers) using conventional analytical methods (e.g., gas chromatography mass spectrometry, GC-MS). However, by concentrating only on specific parameters, subtle changes in organic composition may remain undetected. Consequently, the exact mechanisms governing organic matter transformations during mineralization remain unresolved (Bechtel et al., 2002; Bechtel and Gratzer, 2001; Püttmann et al., 1991; Sun and Püttmann, 2001, 2000).

Poetz et al. (2020) expanded these approaches by integrating high-resolution mass spectrometry (Fourier transform ion cyclotron resonance mass spectrometry, FT-ICR-MS) with conventional analytical techniques to characterize high-molecular-weight compounds containing heteroatoms like nitrogen, sulfur and oxygen (NSO compounds) and to investigate their transformations during mineralization. However, this study did not reveal significant differences in NSO compound composition between Cu mineralized rocks and Zn-Pb mineralized rocks (Poetz et al., 2022).

Building on this foundation, the present study aims to further elucidate the role of organic matter in Kupferschiefer mineralization by analyzing samples with varying degrees of mineralization and thermal overprint. To achieve this, bulk parameters obtained through conventional analytical methods (GC-MS, GC-IRMS, ICP-MS, and Rock-Eval pyrolysis) are combined with FT-ICR-MS data, providing a more comprehensive understanding of organic matter dynamics during mineralization.

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Vanadium isotopes as a novel redox tracer: insights from modern anoxic basins and ancient shale-hosted V deposits

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Shale-hosted deposits of vanadium (V) are ideal candidates to meet the projected future demand for this critical metal due to their relatively high grade and abundance, but their precise formation mechanism remains highly debated and this impedes exploration efforts. A central focus of this project is measuring the V isotope composition ($\delta^{51}V$) of shale-hosted V deposits that may reveal the local redox conditions at the time of deposition in three localities: the Selwyn Basin in north-western Canada, the Yangtze Platform in southern China and the Alum Shale Formation in northern Europe. However, interpretations of metal isotope signatures may be complicated by local and basin-specific effects. Therefore, to better understand and calibrate our approach to $\delta^{51}V$ measured in ancient settings, we utilise sediment $\delta^{51}V$ from the two of the largest modern anoxic basins globally, the Black Sea and the Baltic Sea. In both modern restricted basins, we find there is a trend towards higher $\delta^{51}V$ which may be attributed to recent marine deoxygenation. Moreover, sedimentary $\delta^{51}V$ appear highly sensitive to local hydroclimatic shifts, for instance, as expressed in a large negative V isotope excursion over the Little Ice Age in the Black Sea. In this presentation, we will evaluate if findings from modern analogues can improve our understanding of paleo-redox conditions during the formation of shale-hosted V deposits in the Selwyn Basin.

Ernst-August mine water monitoring: multi-sensor system for floating exploration of cavities

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Water will play a greater role in the future than ever before, which is why natural water reservoirs are being explored around the world to meet the ever-increasing demand for water. The Harz Mountains, with their numerous old mining infrastructures and the "Upper Harz Water Management", have great potential for water storage [1]. It is essential that the water quality is not degraded, that the hydraulic system and its stability are properly understood, and that the monumental landscape above and below ground is preserved. The research project Ernst-August Mine Water Monitoring (EAGruMo) evaluates the potential of the Ernst-August adit as a water storage in a network of three sub-projects.

The project focuses on the youngest, longest and deepest water drainage adit of the Upper Harz mining industry, which was excavated between 1851 and 1864. The Ernst-August adit, which has been an UNESCO World Heritage Site since 2010, connects and drains the mines of the Harz mining districts at a maximum depth of 204 lachtern (392 m) at the Caroline mine over a distance of around 40 km. The outlet of the drainage system is located in the Gittelde karst area [2].

This article presents the first results of the sub-project "Development of a mobile multi-sensor system (MSS) for spatial and water quality exploration". The concept and design of the MSS is based on a semi-autonomous floating platform as a carrier system for various sensors. Laser scanners are used above and below the waterline for spatial exploration and the associated recording of the geometry of the mine workings. Fused with the collected image data and positional information, the movement of the MSS is used to create a 3D point cloud as the base for modeling the mine. This model is supplemented by the water quality parameters recorded by the MSS. The MSS shows great potential for the exploration of water-bearing mines.

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