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#### Theme: Research

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# Rare earth element bearing phosphate chemistry: Developing a tool for iron sulfide-copper-gold exploration

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Exploration techniques to combat the declining rates and increasing cost of base metal discovery are needed to meet the transition to a green energy future, including methods to increase the effective size of detectable deposit footprints, particularly in regions where thick sedimentary cover buries prospective basement rocks.

The chemistry of rare earth element (REE)-bearing phosphate resistate minerals (monazite, rhabdophane) are used to indicate proximity to a mineralised system or as a potential indicator of permissiveness where resistate minerals are entrained in the cover material above mineral systems.

The Jericho and Kulthor iron sulfide-copper-gold (ISCG) deposits in the Cloncurry District, Queensland, are used as case studies. At Kulthor, hydrothermal REE-bearing phosphates associated with mineralisation are characterised by elevated light REE (except Ce) and S and depleted Ca, Th and U concentrations compared to samples with no direct association with mineralisation. Hydrothermal REE-phosphates associated with mineralisation at Jericho preserve elevated Ca, S and Eu, and depleted Th and U compared to barren metamorphic REE-phosphates. Monazite (REEPO4) is the principle REE-bearing phosphate mineral at Kulthor, while rhabdophane (REEPO4 · nH<sub>2</sub>O), a hydrated, low temperature mineral, is the main REE-bearing phosphate found within mineralisation at Jericho. Molar ratios of Ca/Th and S/Th can be used to distinguish between grains associated with mineralisation and grains that are outside of the mineralised zone at both ISCG deposits. Moreover, ongoing investigations suggest that these ratios can serve as discriminative indicators for distinguishing REE-phosphates linked to ISCG mineralization from those associated with iron oxide-copper-gold (IOCG) deposits.

## Trace element compositions of micro inclusions extracted from mixed LA ICPMS signals

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Micro-inclusions in minerals carry valuable information on co-crystallising assemblages in magmatic rocks or on the conditions of formation of the host minerals in alteration assemblages. They are often too small to obtain confident analyses by LA ICPMS but are frequently ablated accidentally when analysing host minerals for mineral chemistry or geochronology. Currently they are mostly excluded from the integration intervals at data reduction stage, but such mixed analyses have potential to extract trace element compositions of micro-inclusions keeping in mind that care should be taken due to differences in matrix effects between the host mineral and microinclusions, differences in elements that can be used as internal standards for quantification, and other similar issues.

We present examples of the extracted compositions of micro-inclusions from two different environments – magmatic and hydrothermal. The first example is the trace element compositions of apatite inclusions in zircons. Co-crystallising apatite and titanite can potentially influence the extents of Ce and Eu anomalies displayed by zircon, and therefore influence estimates of magma oxidation calculated based on zircon compositions and used to estimate prospectivity of magmas to produce porphyry Cu deposits. Therefore, studying compositions of co-crystallising minerals should improve targeting outcomes. The second example is the compositions of rutile and titanite inclusions in chlorite and epidote. The latter two alteration minerals are often used for vectoring and fertility studies during exploration for porphyry Cu deposits with Ti being one of the elements used for vectoring. Therefore, Ti bearing inclusions can affect the vectoring conclusions and are thus excluded from integrations intervals, but their compositions could carry vectoring information as well.

We explore an approach used to deconvolute mixed signals during analysis of framboidal pyrites and an approach that involves utilising individual readings within the LA ICPMS signal to project towards the major element composition of micro-inclusion and to quantify their trace element compositions. We compare our results with the compositions measured independently using EPMA and LA ICPMS on inclusions that were large enough for confident analyses.

# Sulfide and Fe-Ti-P liquid immiscibility in the Ni-Cu-Co Ovoid deposit of the Voisey's Bay complex, Labrador, Canada

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Hydrous silicate rims are developed at the interface between the sulfide matrix and the silicate framework of magmatic breccias within the Mesoproterozoic Voisey's Bay complex. These sulfide-matrix breccias developed through the percolation of dense sulfide melt, leading to the displacement of the silicate melt within partially molten silicate-matrix breccias. Multiple lines of evidence support a magmatic origin of the hornblende-biotite rims, which was largely coeval with the emplacement of the sulfide melt in the magmatic breccias. The formation of the reactive hornblende-biotite required the addition of alkalies and water that could not have entirely been sourced from either the sulfide melt or the silicate framework. Through the integration of compositional maps with major and trace element analyses of the main accessory minerals, we propose that the critical components required for the development of the hydrous silicate rims in sulfide-matrix breccias originated from an immiscible Fe-Ti-P melt. Distinct textural and compositional features of apatite, hercynite, ilmenite and magnetite support the presence of small amounts of Fe-Ti-P melt in the sulfide melt. This Fe-Ti-P melt likely formed through melt immiscibility in the early stages of the development of the Voisey's Bay complex, and was transported in the magma conduits together with the sulfide melt. The recognition of specific trace-element signatures in apatite and oxides tracing the evolution of a mineralized system, reinforces the potential of detrital minerals as effective targeting tool in the exploration for new Ni-Cu-Co magmatic deposits.

#### Ore to metal: tracking critical minerals in the Olympic Dam Cu-U-Au-Ag mining-processing-refining operation, South Australia

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Mining-smelting-refining operations at Olympic Dam produce copper cathodes, U3O8 concentrate, gold and silver bullion. Ores from the >10 billion tonne deposit also hosts trace concentrations of several elements that fall within the definition of critical minerals: Co, Ni, Sb, Bi, Te, and rare earth elements (REE). Characterization studies using cutting-edge analytical approaches have established the distribution of these components in ore, concentrate, flotation tailings and through smelting and electrorefining. An appreciation of the chemical and physical states of each element in ore, through flotation circuits, and smelter/refinery operations is essential if critical mineral opportunities are to be realized in the future.

Olympic Dam ores are hematite-dominant breccias and contain >120 minerals although most are minor. Cobalt occurs in pyrite, carrollite and subordinate cobaltite; Cu-(Fe)-sulphides are insignificant carriers of Co and Ni. Despite their low concentrations in mill feed, the deposit represents a global-scale Se and Te anomaly. Pb-, Bi- and Ag-selenides and tellurides occur as nm- and  $\mu$ m-sized inclusions within Cu-(Fe)-sulphides.

REE minerals are bastnäsite, synchysite, florencite, monazite, xenotime, and Ca-Sr-REE-Al-phosphate-sulphates. REEs also occur at ppm- to wt.%-level in Fe-oxides, fluorapatite, and zircon. REE-fluorocarbonates and monazite are Ce-dominant, whereas xenotime, zircon, and uraninite are important HREE hosts. REE-minerals are typically fine-grained and display erratic distributions throughout the orebody but coarsen at deeper levels where allanite is also present.

REE-minerals are largely removed to tailings after flotation, alongside W (mostly contained in hematite), whereas Co, Ni, Sb, Bi, and Te report to copper concentrate. Much of the Co and Ni is sequestrated by fayalite, magnetite and delafossite within smelter slags. Residual REEs are noted in monazite and slag glasses.

After direct-to-blister smelting, Bi, Sb, Se, & Te occur as microinclusions with various compositions within Cu anodes. Interestingly, Cu-selenides in anode share comparable layered structures with secondary Cu-tellurides from bornite-chalcocite ore. After electrorefining, these elements, alongside Au/Ag which are subsequently recovered, attain wt% levels in anode slimes. Factors rendering recovery of Bi, Sb, Se, & Te from refinery wastes uneconomic at present include the co-presence of uranium decay chain radionuclides.

#### Understanding Hydrogeological Connectivity Between Great Artesian Basin Aquifers and Coal Seams: Geochemical and Reactive Transport Modeling Approach

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The Pilliga Sandstone is a major aquifer of the Great Artesian Basin (GAB) within the Coonamble Embayment sub-basin in New South Wales (Australia). The Pilliga Sandstone contains significant groundwater resources utilised for town water supplies, irrigation, and livestock. Underneath the GAB is the Permian-Triassic Gunnedah Basin, which hosts significant coal and coal seam gas resources. Previous studies demonstrated that the salinity within the Pilliga Sandstone increases between the superficial recharge areas towards deeper parts of the aquifer. However, there is persistent uncertainty on whether this increase is due to hydrogeochemical processes within the Pilliga Sandstone or if it results from connectivity with adjacent units (e.g., Gunnedah Basin strata or shallower GAB formations).

This research applies a combination of endmember mixing models and reactive transport modelling to understand the extent and nature of the hydrogeological connections between the Pilliga Sandstone aquifer and its over- and underlying formations. This will result in refined conceptual hydrogeological models, quantification of solute fluxes, and a better definition of the potential risks associated with aquifer interactions.

Using multiple data types such as (i) aqueous concentrations of major and trace elements (ii) dissolved gases (iii) mineral characterisation via XRD and XRF (iv) and isotope data for <sup>13</sup>C-DIC, <sup>7</sup>Li, <sup>11</sup>B,  $\delta^{18}O/2H$ , <sup>87</sup>Sr/<sup>86</sup>Sr, <sup>14</sup>C and <sup>36</sup>Cl, we evaluate multiple conceptual and numerical models and assess their ability to match the various observation data. The models will simulate hydrodynamic processes along multiple flow paths, coupled to the hypothesized geochemical reactions that define the hydrochemical and isotopic evolution along these flow paths. This is expected to allow for the selection of the most plausible conceptual hydrogeological model for the groundwater flow patterns within and adjacent to the Pilliga Sandstone aquifer.

The results of the reactive transport modelling study will be complemented by other evidence, such as seismic data and airborne electromagnetic (AEM) data. This integrated approach provides increased confidence in the understanding of the potential hydrogeological connectivity between the Gunnedah Basin formations and the major GAB aquifers and ultimately underpin informed decision-making on groundwater management and resource development in the region.

### Sedimentary Geochemistry of sub-basins within the Batten Fault Zone, McArthur Basin

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The McArthur Basin covers much of the Northern Territory, Australia, and comprises multiple stacked siliciclastic and carbonate sedimentary sequences of Proterozoic age. Despite being labelled as 'the boring billion' due to the perceived stability of Earth systems, this period actually exhibits significant and geochemically traceable fluctuations in water chemistry. These rocks are also of interest for research purposes due to their hosting of economically significant hydrocarbon and mineral resources.

The Batten Fault Zone within the McArthur Basin is a broad structurally complex corridor with structural depocenters and sub-basins. This study uses litho-stratigraphy, geochronology, and sedimentary geochemistry over four of these sub-basins to correlate depositional sequences and highlight post-depositional alteration characteristics. Shale and carbonate geochemical data collected for this project focuses on the middle McArthur Group (ca. 1650-1630 Ma) stratigraphy, aiming to fill gaps in literature surrounding Earth systems and tectonic processes during this time of little preservation of life and productivity.

These rocks in the middle McArthur Group have predominantly been deposited under deep subtidal to slope conditions, and the combination of carbonate and siliciclastic samples sequence has produced Total Organic Carbon (TOC),  $\delta^{13}$ Corg, and  $\delta^{13}$ Ccarb profiles for sub-basins in the central and northern Batten Fault Zone. Notable trends observed in these profiles, such as the ~+2.0 ‰  $\delta^{13}$ Ccarb excursion transitioning from the Barney Creek Formation into the overlying Reward Dolostone, are valuable tools for local and regional stratigraphic correlation. Major and trace element data further enhances correlations between sub-basins while revealing geochemical changes associated with redox conditions, alteration processes, and paleoenvironmental factors during and after deposition. The combined data set will build a solid framework for the sedimentological, environmental, hydrological, and structural evolution of each sub-basin, which, in the scope of the "mineral systems framework" can then be used to examine models for Pb-Zn-Ag ore mineral formation processes in the McArthur Basin.

#### Enrichment of rare earth elements of the Qingxi deposit in South China: Genetic mechanism and formation preference

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Ion-adsorption type rare earth deposits are primarily located in the South China region. The Qingxi granite, situated in the southern part of Jiangxi province, is categorized as alkaline granite and is characterized by an enrichment of light rare earths in the upper part of its weathering crust. The rock-forming minerals albite, orthoclase, quartz, and biotite, which account for 98.8% of the mineral content, only provide 2.1% of the rare earths, while 97.9% of the rare earths come from rare earth accessory minerals such as apatite, zircon, rutile, fluorite, synchisite, monazite, titanite. In the weathering crust, rare earth elements are mainly present in states of ion exchange, residue, combination with iron-manganese oxides, and combination with carbonates. The differentiation between light and heavy rare earths is influenced by several factors including clay minerals, iron-manganese oxides, pH value, and water table. The upper part of the weathering crust is comparatively enriched in light rare earths, while the lower part is more enriched in heavy rare earths. The selective adsorption by clay minerals plays a crucial role in the differentiation between

light and heavy rare earths. During the formation of the weathering crust, rare earth elements from minerals, such as apatite, synchisite, titanite, are released and adsorbed onto clay minerals. Influenced by atmospheric precipitation, microorganisms, pH values, and clay minerals, a secondary enrichment occurs throughout the weathering layer.

# Using $\delta^{65}Cu$ to determine the fate of copper in stream waters draining porphyry mineralization: implications for exploration vectoring

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The fate of metals, such as Cu, in stream waters draining porphyry mineralization is often controlled by natural processes such as sorption, microbial processes and ligand availability. Isotopes of Cu offer one method of tracing these natural processes and understanding metal sources within often complicated mineralogical systems. To date, case studies of circum-neutral waters have typically reported adsorption of predominantly <sup>65</sup>Cu in aqueous dispersion halos. Here, we present isotopic data from waters draining from the Casino Cu-Au-Mo porphyry deposit (Yukon, Canada). The hydrogeochemistry of southern flowing drainages varies from circumneutral (>6.3) to natural acid rock drainage conditions (pH <3.5) with the formation of schwertmannite (Fe<sup>3+</sup>) hardpan. Isotopic systems of  $\delta^{65}$ Cu and  $\delta^{34}$ S indicate variation in the metal source in drainages, with distinction and indications of mixing between primary ( $\delta^{34}$ S <-2.0 ‰) and secondary  $(^{34}S > 5\%)$  mineral endmembers. Hydrogeochemical variation between drainages is also reflected on the stream beds, with mineral speciation varying between Fe mineral phases such as schwertmannite in ARD conditions, to white Al precipitates of alunite in circumneutral conditions. Copper fractionation into the dispersion halos of these streams contrasts between Fe(OH)3 precipitation in circum-neutral waters and the preferential adsorption of  $^{65}$ Cu, resulting in decreasing  $\delta^{65}$ Cu values, and either Cu co-precipitation with schwertmannite or intracellular assimilation or adsorption by microbes, both of which preferentially favour  $^{63}\text{Cu}$  and result in increasing  $\delta^{65}\text{Cu}$  values. Concentrations of metals and metalloids are significantly diluted as drainages confluence. However, pathfinder elements remain above regional natural background levels in thirdorder streams. Despite the abundance of surface water in many parts of Canada, stream water is an underutilised exploration sample medium. It is evident that hydrogeochemical prospecting using broad-scale stream water catchment analysis is a viable greenfield exploration methodology.

### Critical mineral exploration with the use of cassiterite trace element discrimination diagrams

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Cassiterite is a weathering-resistant mineral which can incorporate a variety of trace elements in its crystal structure. This can be used in mineral exploration to trace its origin. To differentiate cassiterite from various origins, new and published trace element data were collected from seven tin fields around the globe. Laser ablationinductively coupled plasma- mass spectrometry (LA-ICP-MS) was used to measure trace elements from twelve deposits in the Herberton Mineral Field, Australia. The results were combined with published data from six other tin fields, including the Andean Sn belt in South America; the Karagwe Ankole belt in Rwanda; and, from China, the Kangxiwa–Dahongliutan pegmatite field, the Youjiang basin, the Nanling belt and the Da Hinggan Range belt. The cassiterite-bearing deposits in the dataset were subdivided into four types: 1) greisen and veins; 2) skarns; 3) Li-Cs-Ta pegmatites; and 4) polymetallic veins. The trace element dataset was analysed using basic descriptive statistics, principal component analysis (PCA), and cluster analysis. Cassiterite grains from greisen and vein deposits are characterized by high concentrations of Ti (avg. 1751 ppm) and moderate concentrations of Al (avg. 97 ppm), whereas cassiterite grains from skarn deposits generally contain lower concentrations of Ti and Al. The cluster analysis allowed us to define compositional boundaries in the trace element dataset. These boundaries differentiate cassiterite grains from different sources or the four deposit types. We observed that greisenization reactions caused relative enrichment of Al and Ti in cassiterite. This is common in greisen and vein, and skarn deposits. Hence, the Ti vs. Al diagram can be used to differentiate cassiterite grains derived from greisen and vein, and skarn deposits. The Sb vs. V diagram was identified to be useful in differentiating cassiterite grains from polymetallic veins. Zirconium and Nb concentrations are useful in identifying cassiterite grains sourced from LCT pegmatite deposits. The discrimination diagrams developed in this study through cluster analyses indicated that cassiterite grains sourced from different deposit types can be differentiated based on their trace element geochemistry. Thus, cassiterite geochemistry (e.g., stream sampling) can be used in exploration to identify types of deposit present in a region and provide insight into mineralization processes.

#### Navigating Uncertainties of Remote Sensing Satellite Image Analysis in Exploration Geochemistry and Mineralogy

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The application of satellite imagery in mineral exploration considering geochemical and mineralogical analysis represents a significant technological advancement, offering a broad-scale and cost-effective means to identify potential mineral deposits across extensive and inaccessible terrains. However, this approach is affected by various forms of uncertainty that can compromise the accuracy and reliability of the data it produces. Technological constraints, particularly concerning spatial resolution limitations, pose a significant challenge in accurately capturing the detailed geological features necessary for precise mineral identification. The spectral resolution of satellite sensors further complicates this issue by limiting the differentiation between minerals with similar spectral signatures, leading to potential misinterpretations. Atmospheric conditions, including cloud cover and particulate matter, can adversely affect image quality, obscuring geological features and necessitating sophisticated correction techniques. Additionally, the angle and timing of satellite imagery acquisition introduce variability in illumination and shadow effects, complicating the interpretation of topographical and geological details. Temporal changes in the landscape, influenced by both natural processes and human activities, introduce another layer of uncertainty. To address these challenges, in this research, we delve into the primary sources of these uncertainties, encompassing the technological constraints of the ASTER-derived mineral maps, released by CSIRO in 2012 and new regional-scale mosaics derived from hyperspectral satellite imagery and compare them with geological maps and more detailed critical metals-related mapping information, for example, compiled by the Australian federal, state and territory geological surveys. We also investigate the impact of seasonal variations on scene statistics and resulting uncertainties when inferring mineralogical and geochemical patterns.

#### Temporal variations in biogeochemical contents of plants may adversely affect the search for mineral deposits

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Biogeochemistry is gaining increasing attention from explorers searching for mineral deposits because of its ability to detect buried mineralisation. Traditional geochemical methods such as soil sampling struggle to be useful in depositional environments, but deeprooted plants can bring elements to their leaves and other organs from this underground source and may be more effective as sample media. Biogeochemical data are difficult to interpret and has hindered its general adoption by exploration companies. However, a simplistic approach to data interpretation may lead to poor discovery rates. Many previous temporal studies have revealed variation between plants but generally they have been conducted over a short time frame. Here, results are presented for elements from 23 plants monitored over nearly seven years at a gold mineralised area in South Australia.

The Barns Gold Prospect (southern Gawler Craton) is situated in farmland that has been cleared of native vegetation except in areas of unproductive thicker sand cover. Mineralisation is buried beneath seif dunes and deep weathering. Amphibolite-grade, granulite facies, Archaean Sleaford Complex (2.45 Ga) dominate the eastern part of the Prospect, while the Tunkillia Suite rocks (1.69 Ga) occur in the west. Primary Au mineralisation occurs within an envelope of hydrothermal alteration with numerous, narrow Au-bearing veins dominated by quartz, pyrite and sericite, with traces of chalcopyrite, galena, sphalerite and native Au.

Some 23 designated plants were sampled and analysed up to 15 times between August 2006 and February 2013. Variations in biogeochemical content appear to be associated with rainfall for several non-essential elements e.g. Au, U and Al while other plant-essential trace elements showed little variation e.g. Ca, Zn, and Cu. Elements showing generally high concentrations in a single sampling campaign may distort data interpretation and downgrade weak anomalies in a subsequent campaign where concentrations may be lower; thus, lower element concentrations may be merely caused by environmental factors rather than the true tenor of mineralisation. Biogeochemistry, if properly applied, may provide an additional means to explore for mineral deposits in a sustainable and relatively non-invasive way.

### Critical metal incorporation in hydrothermal minerals: experiments and simulations

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Many critical metal resources are recovered as by-products of mining for other principal elements. For example, Germanium (Ge), Indium (In) and Gallium (Ga) that are widely used in electronic and optoelectronic devices are recovered as by-products from refining zinc ores. One of the scientific challenges to maximise the values from by-products of mining major commodities is understanding the distribution and speciation of trace elements in the complex ores, and the formation of their ore deposits. This knowledge not only helps predict the resource potential of critical minerals as by -products, but also helps improve extraction and ore processing techniques to lower both the recovery cost and the environmental impacts. To address this challenge, we conducted hydrothermal experiments and employed molecular simulations to understand better the process of germanium in sulfide mineral, and rare earth elements in sulfide minerals, during dynamic mineral formation processes aims to simulate conditions typical of sediment-hosted Pb-Zn deposits.

In the first series of hydrothermal experiments, we synthesised major minerals (sphalerite,

galena, dolomite, anhydrite and barite) of Zn-Pb ores at 200 °C and similar solution compositions as ore fluid of sediment-hosted Zn-Pb deposits. The synthesised minerals resemble the minerals observed in natural ore deposits and modern seafloor hydrothermal systems, and the results are consistent with the prediction from thermodynamic modelling, revealing the role of carbonate in buffering pH and thus facilitating Zn-Pb mineralisation. In subsequent studies, we introduced Ge, Eu, and Ce in the starting solutions. The mineral products after the experiment were characterised using micro-analytical techniques, including electron probe microanalysis (EPMA), electron backscattered diffraction (EBSD) and synchrotron X-ray fluorescence elemental and oxidation state mapping. Our experimental and simulation results reveal that Ge(IV) is readily incorporated into sphalerite with or without coupled substitution by other cations (e.g., Cu(I)). In contrast, the rare earth elements Ce and Eu are incorporated in anhydrite with mixed valent states. Our results shed light on understanding the mechanisms of the incorporation of trace elements in host minerals. These studies provide molecular-level insights for understanding the processes of forming and extracting critical metals in sulfide and sulfate ores.

# Modelling cobalt speciation, mobility, and ore-formation in hydrothermal fluids

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The industrial demand of cobalt (Co) is predicted to skyrocket in the next decades because of its usage in Li-ion rechargeable batteries. A large proportion of Co deposits have been formed from hydrothermal processes, such as low-temperature sediment-hosted and hightemperature vein-type mineralisations. These types include the world-class Co deposits in the Central African Copperbelt or Bou Azzer in Morocco.

Cobalt forms strong complexes with Cl<sup>-</sup> in aqueous fluids: therefore, Co is mainly leached and mobilised by highly oxidised and saline hydrothermal fluids. Reliable thermodynamic properties for Co chloride complexes are thus pivotal for understanding and numerical modelling of ore formation of hydrothermal Co deposits. However, previous experimental studies produced contradicting information on the stability of Co chloride complexes at elevated temperature, in particular for high-order chloride complexes (e.g., CoCl4<sup>2-</sup>). This study aims to solve the controversy and provide molecular-level insight into those Co chloride species from ab initio molecular dynamics (MD) perspectives. The MD simulations indicate a decrease in the coordination number of aqueous  $Co^{2+}$  from octahedral to tetrahedral with increasing temperature or chloride concentration and are thereby consistent with previous in-situ XAS studies. The predicted speciation and geometry of Co-Cl complexes from MD simulations show good agreement with the XAS results. The confirmation of Co-Cl speciation and free energy surface of Co-Cl complexation from MD will, therefore, extend the available thermodynamic data for modelling cobalt speciation in hydrothermal fluids. Further studies using thermodynamic integration in MD will provide new stability constants for those Co chloride complexes.

Geochemical modelling shows that cobalt-bearing minerals such as catierite, linnaeite, and saflorite mainly precipitate in the presence of reduced sulphur and arsenic species. This is caused by decreasing fO2 and/or increasing pH, which can be achieved through various processes such as fluid boiling, fluid mixing, or fluid-rock interaction.

#### Towards low-cost quantitative mineralogy across the resource cycle

#### Mark Pirlo, ALS

Objectively quantifying the mineralogy of a rock or soil has traditionally faced several challenges. These have acted as barriers to widespread, routine, and effective use in many parts of the resource cycle. Visual logging of samples by geoscientists can suffer from consistency and subjectivity, as well as being impractical in some situations. Petrographic and microanalysis techniques including scanning electron microscope options are time consuming, expensive and their relatively limited field of view may not adequately represent a system. X-ray diffraction can assess homogenised and composited material yet can often be restricted by time and expense issues. Consequently, it is rare to have systematic quantitative mineralogy available across a project, and importantly, at different stages of a project.

While infra-red spectroscopy has a long history of delivering data that is useful to geoscientists working across the resource cycle, it has faced limitations in terms of a restricted number of minerals, and by not being conventionally quantified. Recent work has taken advantage of the spectral ranges and resolution offered by Fourier Transform Infra-Red (FTIR) spectroscopy. FTIR data have been considered along with independently quantified mineralogy in a machine learning system. By considering an extensive number of natural geological materials that are both geochemically and mineralogically diverse, a model capable of quantifying mineralogy on new samples has been developed. With an initial focus on common rock and soil-forming minerals, the model is actively developing to improve determinations and expand applicability in terms of stoichiometry and abundance.

Availability of a rapid, objective, quantitative and cost-effective option for mineralogy is expected to drive subsequent innovations across mineral exploration, geometallurgy, mineral deposit knowledge and mine closure geoscience. This could provide value in its own right, or through effective proxies for some key parameters. Applications might include clay mineralogy for geotechnical and geometallurgical investigations, proxies for hardness affecting comminution, feldspar type and abundance for interpreting hydrothermal alteration, regolith mapping and leveling generative geochemical data.

Ultimately, objective, and quantified mineralogy, available at relatively low cost is expected to provide data that can complement traditional geochemical data to better understand mineral systems.

#### Geochemical Fingerprinting of Australian-sourced Lithium Minerals

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Environmental footprint disclosure is an important factor for evaluating new policies and regulations that aim at harmonizing the effective production of critical minerals on one side, and net-zero emissions and other sustainability goals on the other. Greenhouse gas emissions disclosure is already an essential reporting requirement under several sustainability reporting standards world-wide. However, increased competition for limited resources may lead to decreased transparency in critical mineral supply chains, and 'Greenwashing' may undermine credible efforts to meet environmental goals.

In this contribution we present a comprehensive physical and geochemical characterisation of Australian-sourced lithium minerals to identify and validate the provenance of battery chemicals through the supply chain, initially focusing on the lithium source mineral spodumene and thereof derived chemicals LiOH and Li2CO3. We discuss how far geochemical 'fingerprints', comprising a combination of elemental and isotopic characteristics, can faithfully tie a test sample to the collected information about its origin and/or its environmental impact, including the complex transformation processes that occur during ore refining. The in-situ methods and protocols developed in this study will enable the regulatory instance to detect blending and product alteration of lithium ore concentrates with high confidence.

This project is part of the Future Battery Industries Collaborative Research Centre (FBICRC) hosted at Curtin University. However, the analytical workflow developed here for the Australian Li supply chain may serve as a template for application to provenance testing of other critical minerals such as e.g., Co, Ni and REE-bearing ores.

### The role of indicator minerals in greenfields exploration in the Madura Province, Western Australia

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The Madura Province in Western Australia is an underexplored greenfields area that lies adjacent to the Albany-Fraser Orogen and bound by the Rodona and Mundrabilla tectonic shear zones. The Proterozoic basement rocks are buried beneath 200-800 m of Cretaceous clastics of the Bight Basin and Eocene limestones of the Eucla Basin. Thick cover, absence of basement outcrops, and the low likelihood of metal dispersion from the basement through the cover contribute to the challenges in mineral exploration. However, sampling across the Cretaceous-Eocene and Cretaceous-basement unconformities for indicator minerals analysis has revealed the presence of numerous grains of detrital pyrite, pyrrhotite, chalcopyrite, pentlandite, sphalerite, cobaltite, galena, and Bi-Se tellurides. These findings are indicative of the presence of prospective sulfide-rich rocks in the region. In addition, diagenetic/hydrothermal pyrite, sphalerite, and galena are observed in the Cretaceous siliciclastics of the Madura and Loongana formations. The composition and abundance of detrital pentlandite and chalcopyrite vary spatially across the Cretaceous-Eocene unconformity. The trace element compositions indicate that chalcopyrite and sphalerite are likely derived from epithermal or skarn deposits. Chalcopyrite is rich in Ag, Bi, Pb, Se, and Zn compared to the basement rocks in the region. Sphalerite is rich in Ga, Ge, Se, As, In, Sn, Sb, Pb, Tl, Ni, Co, Bi, and Mo compared to another generation of sphalerite, which consists of micro-spheroidal aggregates that possibly indicate the involvement of sulfate-reducing bacteria in the precipitation of ZnS. The presence of detrital sulfides correlates with elevated concentrations of Cu and Co in the vicinity of the Cretaceous - Eocene unconformity. In general, chalcopyrite and pentlandite exhibit limited resistance to mechanical weathering and transportation. These grains have single or composite fabrics and are subangular to angular in shape, which suggests they may have been transported over short distances from nearby copper mineralization. The elevated proportions of detrital sulfides at the Cretaceous - Eocene unconformity imply proximal basement paleohighs as the main sources of detrital sulfides. Therefore, targeting unconformities for indicator mineral analysis and mapping the relevant paleotopography could serve as an effective exploration strategy to vector toward mineralization and reduce the costs associated with basement drilling.

# Incorporation mechanisms of phosphorus in goethite: insights from nano-scale investigations on Australian Iron Ores

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The large volumes of high-P (>0.07 wt.%) iron ores in Westen Australia (WA) are currently considered as uneconomical because of the highly deleterious nature of P in the steelmaking process. Unlocking the economic potential of high-P iron ores will benefit from the development of cost-effective methods for the removal of P from goethite, the dominant P bearing mineral. This requires a better understanding of P speciation and incorporation mechanisms into goethite (single atom or coupled substitution, surface complexation followed by incorporation).

The characterisation of P distribution in P-doped synthetic goethite and in representative high-P goethitic ores from WA provides new insights on the intimate association between phosphorus and goethite. STEM-EDS mapping of P- and P-Al-doped synthetic goethite and lepidocrocite demonstrate that (i) P is readily incorporated into goethite up to about 0.25 mol%, but not into lepidocrocite, and (ii) the Al-to-Fe substitution facilitates the uptake of phosphorus in goethite. These findings are consistent with ab-initio modelling of P incorporation into goethite, which suggests that the most stable configuration involves P-Al co-substituting for Fe in the lattice.

SEM-EDS, micro-XRF and LA-ICP-MS mapping of P-rich iron ore samples hosted in the Brockman and Marra Mamba iron-formations highlights the preferential enrichment of phosphorus in late-stage ochreous and vitreous goethite, or in brown goethite formed after carbonates. ToF-SIMS trace chemical mapping of selected high-phosphorus zones provides an assessment of the heterogeneity of phosphorus distribution at the micron and sub-micron scale. Higher-resolution TEM (<5 nm) and ToF-SIMS (<50 nm) maps were also obtained on FIB-SEM-prepared slices to further investigate phosphorus, aluminium and silicon association with goethite crystallography.

### Uranium ore deposits and redox reactions: insights from U, Mo and TI isotopes

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Uranium mobility undergoes significant fluctuations under varying redox conditions, infl uencing its behaviour in both surficial and underground environments. In oxidizing environments, such as surface waters (streams, upper layers of lake waters), uranium typically exists in its hexavalent state (U(VI)), characterized by high solubility and mobility. Under these conditions, uranium can readily form aqueous complexes(most common are oxyanions),facilitating its dispersion through water bodies and enhancing its potential for long-range transport. Conversely, in reducing environments, such as anoxic sediments or water, uranium tends to undergo reduction to its tetravalent state (U(IV)), which results in decreased solubility and increased tendency for immobilization by precipitation as insoluble phases (i.e. uraninite, UO2).

Developing a proxy for changes of redox conditions in uranium-rich environments (i.e., uranium ore deposits, nuclear waste repositories) is thus of prime importance for environmental monitoring or mineral exploration purposes.

Since the advent of MC-ICPMS techniques, a constantly increasing number of studies on isotopes of transition metals related to redox-related processes have been published, spanning from microbial-mediated meta reduction in soils to the analysis of sediments formed during significant anoxic episodes, or the mobilization of uranium in roll-front deposits.

In this study, we examine the fluctuations in isotopic signatures of several redox-sensitive elements—uranium ( $\delta^{238}$ U,  $\delta^{234}$ U), molybdenum ( $\delta^{97}$ Mo), and thallium ( $\epsilon^{205}$ Tl)—across various types of uranium ore deposits. Our objective is to assess the in fluence of temperature, ore chemistry, mineral composition, and redox conditions on isotopic fractionation.

The isotopic compositions of  $\delta^{97}$ Mo and  $\epsilon^{205}$ Tl exhibit a wide range of values, spanning from -17 to +6‰ for  $\delta^{97}$ Mo and from -17 to +9  $\epsilon$ -units for  $\epsilon^{205}$ Tl, encompassing the full spectrum of isotope values observed in natural systems. In lower temperature environments, such as unconformity-related deposits, these variations demonstrate strong correlations with uranium isotopes ( $\delta^{238}$ U) and align with expected fractionation patterns resulting from redox-controlled processes. Contrarywise, in deposits formed at higher temperature (magmatic or intrusive), the presence of sulfide minerals significantly infl uences the concentration and isotopic fractionation of molybdenum. Concurrently, thallium isotopes variations can possibly be attributed to a Nuclear Volume Effect, suggesting a connection with changes in redox conditions.

### Enhancing Mineral Carbonation Through Molecular Simulations on Diopside Surfaces

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The increasing carbon dioxide level in the atmosphere in the past century has caused dire effects on the environment. Mineral carbonation offers a promising approach to remove  $CO_2$ 

from the atmosphere by reacting with rocks enriched with  $Ca^{2+}$ ,  $Mg^{2+}$ , and  $Fe^{2+}$  to form stable carbonate minerals. However, in nature these processes typically occur at extremely slow rates. Therefore, it is crucial to develop technologies that can rapidly accelerate these processes for effective CO<sub>2</sub> removal and storage. The slow dissolution of  $Mg^{2+}$  and  $Ca^{2+}$ from the silicate minerals has been pinpointed as one of the significant limiting reactions for carbon mineralisation. Recently, experimental and engineering studies have demonstrated the potential of using  $Ca^{2+}$  and  $Mg^{2+}$ -rich mafic-ultramafic rocks to store  $CO_2$ . Yet, the reaction mechanisms during the mineral carbonation processes at various fluid compositions and temperature-pressure conditions are poorly understood. Molecular modelling techniques provide a molecular-level understanding of key chemical processes. Ab Initio Molecular Dynamics (AIMD) simulations enable us to explore the mineral-water interface accurately, which, however, costs high computational resources. In this study, we applied a recently developed method called Machine Learning Molecular Dynamics (MLMD) to enable a much longer time scale to investigate the reaction mechanism but at reduced costs within the accuracy of AIMD. Here, the mineral diopside (CaMgSi2O6), one of the most abundant mafic minerals found in the Earth's Crust, was chosen as the studied silicate because of its enrichment in both  $Mg^{2+}$  and  $Ca^{2+}$ . Molecular modelling will include looking at the diopside surface and seeing the optimal parameters (e.g. temperature, water, etc.) to dissociate these cations so they can be used for carbonation. This molecular study can help further enhance this reaction by pinpointing what is happening at an atomic level, and thus how to improve the reaction.

### Rare Earth Element potential and related mineral systems in the Curnamona Province, South Australia

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The global transition to sustainable energy production and green technologies is fuelling the demand for critical minerals, and of those, demand for rare earth elements (REE) is expected to grow by  $\sim 30 - 40\%$  for Nd and Pr, and between 77 - 81% for Tb and Dy by 2050. The demand for these elements currently outstrips the predicted supply, in particular for Tb and Dy, thus additional sources of REEs are required to de-risk the global supply. The Paleoproterozoic to Mesoproterozoic Curnamona Province in the eastern part of South Australia carries great potential for REE discoveries, with some occurrences reporting values over 2 wt.% total REE (Mount Victoria) as well as significant outcrops of coarse-grained monazite, with rock assays of up to 10.69 wt.% total REE (Boolcoomatta GK1 prospect). Initial prospectivity analysis using legacy data shows that there are two main mineral systems associated with REEs, these include the U-REE and Cu-Au?-REE mineralisation styles that are common in the southern (Olary Domain) and central (Mulyungarie Domain) respectively. These two mineral systems are believed to be closely linked to the intrusions of the Mesoproterozoic Ninnerie Supersuite based on their close spatial relationship. However, in many instances, REE mineralisation is hosted in mica-rich shear zones, with many mica-rich shear zones in the southern Curnamona Province thought to be related to the Cambrian Delamerian Orogeny. Consequently, the timing of the REE mineralisation in the Curnamona Province is currently poorly understood. In this study we use U-Pb geochronology of the zircon, rutile and monazite and whole rock geochemistry to decipher the origin of the REE mineralisation in the Curnamona Province, and to constrain the timing of the mineralisation and its relationship to the main orogenic and intrusive events in the province. Furthermore, whole rock and mineral (rutile, monazite and zircon) geochemistry is used to trace the origin of rare earth elements and to characterise barren vs. mineralised bedrock, thus developing new geochemical proxies to aid REE exploration in the Curnamona Province.

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# Comparative Analysis of PCA and UMAP in geochemical characterization of Mary River Banded Iron Formations, Nunavut, Canada

Adibi, Mahsa; Acosta-Gongora, Pedro & Saumur, Benoit M.

Principal Component Analysis (PCA) and Uniform Manifold Approximation and Projection (UMAP) are widely utilized techniques for dimension reduction and visualization, particularly in the context of geochemical analysis. In our investigation of the geochemical composition of Mary River Banded Iron Formations (BIF), PCA revealed significant correlations between Fe-W±Sb, which exhibited an anticorrelation with Ti-Al-Mg. These insights helped to understand the complex relationships between key elements within the BIF samples and potential mineralization. Conversely, UMAP proved more adept at distinguishing subtle variations related to metamorphic grades and hydrothermal alteration. UMAP decouples more efficiently samples exhibiting higher metamorphic grades (upper amphibolite to granulite facies) and hydrothermal alteration, from those with lower metamorphic grades (greenschist facies). In general Co, Ni, and Nb are enriched in rocks representing higher metamorphic facies and hydrothermal alteration, whereas Ti, Mg, and K are more conspicuous in rocks overprinted by greenschist facies. Our preliminary results underscore the effectiveness of UMAP in finding complex, non-linear relationships within the dataset, particularly those associated with geological processes such as metamorphism and hydrothermal alteration. Our comparative analysis emphasizes the complementary nature of PCA and UMAP to interpret the geochemical footprint of rock samples. While PCA highlights linear relationships and major trends, UMAP offers a richer visualization, revealing nonlinear patterns and intricate structures within the data. Integration of both techniques can enhance our understanding of the geological and metallogenic processes shaping the formation of BIF and associated ores. This advancement in knowledge contributes to a deeper understanding of Earth's geological history and mineralization processes.

#### Mineral Deposit Characterisation from Drill Core to Microscale

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Queensland is home to many traditional and new economic mineral resources, however its key mineral systems require further characterisation. The GSQ New Economy Minerals Initiative program aims to build up a comprehensive systematic physical and virtual reference collection of samples and associated geological data characterising signatures and footprints of the major mineral systems and their key deposit types and styles in NW and NE Queensland. The workflow developed by GSQ is a systematic multi-analytical approach to cover a wide range of scales, from core to macro and microscale, that is implemented in several stages, including:

• Acquisition of drill core and samples representative of ore and mineralisation from major deposit types of the state.

• Continuous core scanning using hyperspectral (HyLogger) and X-ray core scanning instruments (Minalyzer and/or TruScan).

• A systematic collection of multi-element whole-rock and mineral chemistry data.

Recent efforts have focused on integrating *in-situ* micro-analytical datasets and imaging techniques to provide a comprehensive understanding of geochemical data within its mineralogical context, including data integration across different scales (macro to micro). This includes micro-analytical techniques, such as SEM, Micro-XRF, TIMA, EPMA, and LA-ICP-MS that are required to characterise host rocks, alteration halos and importantly the endowment of both base-metals and critical metals. Elemental and mineral phase maps generated by our in-house Bruker  $\mu$ XRF Tornado scanner, in conjunction with TIMA analytical techniques, provide invaluable insights into the elemental distribution, modal composition, textural relationships of mineral phases, and their paragenesis. Results from the Tornado and TIMA instrument prove highly beneficial for rapid and precise mineral targeting during subsequent *in-situ* analytical work such as geochronology and isotope geochemistry.

The combination of these cutting-edge analytical techniques propels our understanding of intricate geochemical and isotopic signatures, as well as the variability in critical element abundances and distributions, within individual deposits and across diverse deposit types. This ongoing effort collects and provides pre-competitive geochemical and mineral data to the exploration industry, thereby facilitating mineral exploration in Queensland for both traditional and critical mineral commodities.

#### Investigating Atmospheric and Oceanographic Changes in the Western Pacific and Indonesian Throughflow During the Mid-Pleistocene Transition

Sebastian Bland, ANU

One of the most significant unresolved mysteries in paleoceanography and paleoclimatology is the climate transition of the middle Pleistocene. This global phenomenon recorded in the benthic  $\delta^{18}$ O of deep-sea sediments highlights a shift from 41 ka glacial cycles in the early Pleistocene to higher amplitude ~100 ka cyclicity in the late Pleistocene. Despite increased attention towards understanding the mid Pleistocene transition, there is still a sparsity of prior research studying this event and its associated effects in the Indo-Pacific region. Therefore, this study aims to contextualise regional changes and provide a piece to the global puzzle. Here we set out to assess the impacts of atmospheric and oceanographic processes in the Pacific Ocean and Indonesian Throughflow on global climate change through the middle Pleistocene (1,200 - 400 ka). Fossilised marine micro-plankton, foraminifera, preserve transient ocean properties in their shell, enabling paleoceanographers to characterise past ocean properties. Specifically identified species G. ruber and G. sacculiter inhabit different depths in the water column. Independent isotopic analysis and characterisation of changes can allow for reconstructions of the ocean mixed layer depth and, by extension, atmospheric processes such as wind speed. By analysing these properties and geographical area we hope to elucidate the causes and dynamics of the mid-Pleistocene climate transition.

#### Pyrite chemistry from key mineral prospects in the Delamerian

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The Cambrian-Ordovician Delamerian Orogen formed during the transition from a passive margin setting during the rifting of Rodinia, to an active subduction margin along the eastern margin of Gondwana. It is spatially and temporally extensive, covering five states in central and eastern Australia, and extended to Antarctica. The area is largely underexplored, however resource potential has been demonstrated through the presence of numerous mineralising systems, particularly along the eastern margin. These mineralising systems include porphyry-epithermal, volcanic hosted massive sulfide (VHMS), orogenic gold and mafic-ultramafic copper-nickel-platinum group element (Cu-Ni-PGE) mineral systems.

Trace element analysis of pyrite via Laser Ablation Inductively Coupled Plasma Mass Spectrometry(LA-ICP-MS) can be used to reconstruct the conditions of pyrite formation in complex mineral systems. This project assesses the pyrite from the key prospects of multiple types of mineral systems across the Delamerian in South Australia, Victoria and New South Wales. Pyrite samples have been collected from various porphyry Cu-Au, VHMS, orogenic gold and orthomagmatic Ni-Cu-PGE prospects to gain a better understanding of these systems in the Delamerian. Additionally, samples from several metallogenetically undefined mineral prospects in Delamerian have been analysed to compare their metallogenic characteristics with those known systems. These results will provide a new understanding of the mineral potential of the Delamerian Orogen, aiding mineral exploration in the region.

# Advancing Mineral Exploration through Optimized Semantic Segmentation Scaling

#### Yuanzhi Cai, CSIRO Mineral Resources

The application of remote sensing technologies has significantly enhanced mineral exploration, offering novel avenues for detecting the subtle yet crucial geochemical footprints of mineral deposits. This study centers on optimizing semantic segmentation models, pivotal for the analysis of remote sensing imagery, to refine the detection and characterization of these geochemical indicators. By investigating the optimal scaling factor for semantic segmentation across three diverse remote sensing datasets—UAVid, LoveDA, and Potsdam—this research underscores the importance of scale adjustment in boosting the models' performance, which is directly beneficial for mineral exploration tasks.

Semantic segmentation models are essential for accurately processing remote sensing images, which are integral in identifying geochemical patterns indicative of mineral deposits. Random scaling is a widely employed training technique to mitigate overfitting in semantic segmentation models, enabling models to handle images with varying scaling factors. However, existing deep learning frameworks for remote sensing images adopt a default scaling factor of 1.0 for single-scale testing. This raises the question of whether this scaling factor is optimal for single-scale testing. Addressing this, our analysis across six semantic segmentation models revealed dataset-specific optimal scaling factors: 0.75 for UAVid, 1.0 for LoveDA, and 1.25 for Potsdam. These findings highlight the critical role of customized scaling in enhancing the accuracy of identifying geochemical footprints and mineral chemistry for exploration purposes.

The improvement in segmentation accuracy facilitated by optimal scaling adjustments is instrumental for more effectively identifying mineral deposit footprints and other indicators. Higher segmentation precision ensures that the subtle differences between geochemical markers, often overlooked by less refined models, are accurately captured. This capability enhances our ability to detect and analyze mineral deposits, paving the way for more targeted and efficient exploration strategies.

Conclusively, this study not only furthers the technological frontier of semantic segmentation in remote sensing for mineral exploration but also establishes a significant link to geochemistry. By optimizing the interaction between scale factors and model accuracy, we lay the groundwork for future research aimed at integrating geochemical insights into remote sensing methodologies, ultimately enhancing the precision and effectiveness of mineral exploration efforts.

### Quantification of artificially sorbed radionuclides as a proxy for geo-sequestration in geological disposal

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Geological disposal is a widely accepted method for the long-term management of intermediate (ILW) and high-level (HLW) radioactive waste, and chiefly relies on the principles of containment and isolation. With a significant global stockpile of ILW and HLW awaiting disposal and ongoing developments in nuclear power technologies, further research is required to also develop improved methods to characterize the natural rocks in their ability to contain any potential radionuclides that may escape engineered barriers. Near or total absence of fluid flow and strong sorption of radionuclides to rocks surrounding the disposal facility are key attributes that minimize the migration of radionuclides.

In the framework of developing generic rock characterization capability relevant to geological disposal, the Hiltaba Suite granite intrusion in the Gawler Craton (South Australia) has been selected to test novel ways of determining RN sorption to granite minerals. The Hiltaba Suite granite has previously undergone comprehensive physical rock characterization to develop an integrated workflow suitable for site characterization for geological disposal. These previous tests confirmed conditions of low porosity and low permeability contribute to the containment potential of the rock body, however, the mineralogy and its degree of alteration varies with depth, suggesting a variety of potential sorption mechanisms and capacity across the 1200-m long borehole section (down to 1900 m). Testing the sorption affinity of minerals at such depths requires an understanding of temperature effects. Sorption of RN will be quantified by using the 'batch' test approach, which involves placing crushed rock samples in contact with a radionuclide doped solution. Performing similar experimentation using thin sections of core allows the spatial distribution of the minerals to remain intact and allows the identification of mineral boundary sorption sites. Quantification of sorbed radionuclides is often determined through measuring the activity of the sample as few tools possess the scale to view micron scale sorption. Gel autoradiography facilitates high resolution mapping of alpha emitting RN in complex mineral substrates. This method will be used to spatially locate, at the micron scale, where RN have undergone a preferential sorption to specific minerals, identifying key minerals for subsequent tests with varying sorption conditions.

#### A regolith lead isoscape of Australia

Dr Candan Desem, University of Melbourne, Adj Prof Patrice de Caritat, Curtin University, Geoscience Australia, Prof Jon Woodhead, University of Melbourne, Dr Roland Maas, University of Melbourne, Dr Graham Carr, Commonwealth Scientific and Industrial Research Organisation

We present the first national-scale lead (Pb) isotope maps of Australia based on surface regolith for five isotope ratios, <sup>206</sup>Pb/<sup>204</sup>Pb, <sup>207</sup>Pb/<sup>204</sup>Pb, <sup>208</sup>Pb/<sup>204</sup>Pb, <sup>207</sup>Pb/<sup>206</sup>Pb, and <sup>208</sup>Pb/<sup>206</sup>Pb, determined by single collector Sector Field-Inductively Coupled Plasma-Mass Spectrometry after an ammonium acetate leach followed by aqua regia digestion. The dataset is underpinned principally by the National Geochemical Survey of Australia (NGSA) archived floodplain sediment samples. We analysed 1219 'top coarse' (0–10 cm depth, <2 mm grain size) samples, collected near the outlet of 1119 large catchments covering 5.647 million km<sup>2</sup> (~75 % of Australia). The samples consist of mixtures of the dominant soils and rocks weathering in their respective catchments (and possibly those upstream) and are therefore assumed to form a reasonable representation of the average isotopic signature of those catchments. This assumption was tested in one of the NGSA catchments, within which 12 similar 'top coarse' samples were also taken; results show that the Pb isotope ratios of the NGSA catchment outlet sediment sample are close to the average of the 12 sub-catchment, upstream samples.

National minimum, median and maximum values reported were 15.558, 18.844 and 30.635 for <sup>206</sup>Pb/<sup>204</sup>Pb; 14.358, 15.687 and 18.012 for <sup>207</sup>Pb/<sup>204</sup>Pb; 33.558, 38.989 and 48.873 for <sup>208</sup>Pb/<sup>204</sup>Pb; 0.5880, 0.8318 and 0.9847 for <sup>207</sup>Pb/<sup>206</sup>Pb; and 1.4149, 2.0665 and 2.3002 for <sup>208</sup>Pb/<sup>206</sup>Pb. The new dataset was compared with published bedrock and ore Pb isotope data, and found to dependably represent crustal elements of various ages from Archean to Phanerozoic. This suggests that floodplain sediment samples are a suitable proxy for basement and basin geology at this scale, despite various degrees of transport, mixing, and weathering experienced in the regolith environment, locally over protracted periods of time. An example of atmospheric Pb contamination around Port Pirie, South Australia, where a Pb smelter has operated since the 1890s, is shown to illustrate potential environmental applications of this new dataset. Other applications may include elucidating detail of Australian crustal evolution and mineralisation-related investigations. The new regolith Pb isotope dataset for Australia is publicly available from the Geoscience Australia data portal.

# Cu isotope Insights into Ore Formation Processes, Spatial Variations and Exploration Potential of Iron-Oxide Copper Gold Deposits

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In the mining industry, stable isotopes, including copper (Cu), are increasingly utilized to trace metal sources and understand ore formation processes. Thus far, previous studies have focussed on Cu porphyry systems while Iron-Oxide Copper Gold deposits (IOCG) have not been the subject of a major study, probably due to their complexity and the potential for large data scatter. However, there are significant gaps remaining in the current knowledge of how Cu isotopes vary across distinct zones of mineralization and its applications on IOCG environments. Out of all the reported transition metal isotope data, copper isotopes reveal the greatest range of fractionation ( $\delta^{65}$ Cu ranges from -16.5 to 10.0  $\pm$  c. 0.05). Cu isotope fractionation is greatest at the low temperature ore deposits and conversely, higher temperature ore deposit mineralization processes do not cause significant fractionation. Therefore, identification of Cu isotopic differences in metal sulfides reflects high versus low temperature ore sources and secondary lower temperature processes of Cu by fluids will be recorded by their isotope signatures. Thus, copper isotopes serve as a promising paleoredox proxy to understand ore forming processes by oxidation-reduction processes in magmatic and hydrothermal activities of metal sulfides precipitation.

Here we present a systematic study of Cu isotope ratios from a variety of individual sulphides and native copper through different mineralised zones within the IOCG deposit of Olympic Dam. Preliminary data on native copper from Olympic Dam show evidence of low temperature remobilisation of copper. Through a comprehensive analysis of Cu isotopes, this research will reveal how the metal isotopes vary across distinct zones of mineralisation, track the potential source(s) and direction of fluids in an IOCG deposit. Finally, this research will develop an application in ore deposit exploration methods as a vectoring tool in IOCG deposit, which could enhance future exploration efforts.

#### **Opening Pandora's box: diurnal metal cycling in stream waters**

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As the 'greening' of economies continues, so will the reliance on an exploration pipeline of high-quality metal deposits. In areas of remote northern Canada, one of the main barriers to the expansion of greenfield exploration is sample acquisition, with pioneerstyle exploration often requiring expensive travel support and slower survey times. Hydrogeochemistry, coupling ultra-low detection limits for most trace elements at relatively low cost, with the abundance of surface water, which is a powerful surveying tool for exploration and environmental assessment. However, surface water geochemistry can be significantly impacted by diurnal (or 'diel') cycling, which represents regular (24-hour) patterns of variation in light and temperature, as well as seasonal climatic changes. Here we present data (physiochemical, trace element, and isotopic) from contrasting environments and climatic regimes across Canada, including (i) the subarctic climate of the Dawson Range (Yukon); (ii) Arctic tundra on Axel Heiberg Island (Nunavut); and (iii) the humid continental climate around the Onaping River (Ontario). Samples collected over 24 hours highlight the extent of metal and metalloid cycling and the continental amplitude across the varying climatic and photochemical settings in Canada. As seen elsewhere, persistent and predictable variation in physiochemistry (temperature, pH, dissolved oxygen) is observed at all sites. Climatic disruptions to these cycles include increased run-off during precipitation, resulting in dilution, and seasonal melt flushes, increasing stream flow and water-atmosphere interaction and exchange. Variations in common pathfinder metals and metalloids are presented and further investigation into the possible key controls on metal cycling, including light-driven microbial activity (metabolism. photosynthesis. and respiration), and changes in sorption and precipitation reactions resulting from temperature-driven changes in physicochemistry.

### Applied Isotopic and Elemental Geochemistry to Understand the Proterozoic Evolution of the South Nicholson Basin

Li, Ruoheng, Collins, Alan S., Subarkah, Darwinaji., Blades, Morgan L., Imbrogno, Dana, Virgo, Georgina, Menpes, Sandra, Lawley, Christine

The Benmara region of the northern South Nicholson Basin lies south of the highly mineralised Batten Fault Zone (McArthur Basin), it borders the Murphy inlier and lies directly east of the newly defined Brunette Downs Rift Corridor. Here we present new research focussing on the exploration potential of this part of the northern South Nicholson Basin using data from a newly drilled ca. 1km deep core, which samples a series of Proterozoic sedimentary and volcanic rocks. We applied a comprehensive suite of exploration techniques, including sedimentary logging, chemostratigraphy, isotopic stratigraphy, and in-situ Rb–Sr laser dating, alongside seismic interpretation, to better understand the stratigraphy in the region, to help link the sequences of the greater McArthur Basin to those of the Isa Superbasin and to further help de-risk the region for exploration for sedimentary- hosted mineral deposits.

### In situ Rb-Sr dating of basement in the helium-rich Jacko Bore 1 (Mt Kitty 1) well, Amadeus Basin, Australia

Cecilia Loyola, University of Adelaide

The Jacko Bore 1 well, located in the Amadeus Basin, represents the highest reported concentrations of helium on Earth, reaching 9% helium. Helium is contained within fractures present in granitic basement at the base of the well, which is sealed by thick evaporites of the Tonian-aged Bitter Springs Group. Helium is generated through radioactive decay of uranium and thorium-rich minerals in the granite, where it initially remains trapped within mineral matrices. Migration of He<sup>4</sup>out of the basement source can be through a combination of long-term diffusion, in conjunction with interconnected fluid-filled fracture migration pathways.

The objective of this study is to determine the generation and/or most recent reactivation timing of fracture migration pathways within the granitic basement by the analysis of fractures in sidewall cores.

We employ a novel in situ rubidium-strontium (Rb-Sr) geochronology technique, complemented by simultaneous trace-element concentration data collection using laser ablation tandem mass spectrometry (LA-ICP-MS/MS). Isochrons were constructed for the different mineral facies using IsoplotR, utilizing the <sup>87</sup>Rb decay constant. The analysis of orthoclase and muscovite from the granite samples returned an age of ~1100 Ma, while the white micas contained within the fractures yielded an age of ~ 580 million years. The older age is consistent with widespread Pitjantjatjara SupersuitegraniticmagmatismintheregionassociatedwiththeMusgraveorogeny, to which the basement granites are interpreted to relate. The younger age coincides with early stages of the Petermann Orogeny, which tectonically reworked the southern portion of the Amadeus Basin, including the Jacko Bore region, and uplifted the adjoining Musgrave Province.

By constraining possible time frames for helium migration from the basement source rock into fractures and shallower stratigraphy, this may help reduce uncertainty for helium exploration in the play. Into the future, it could also potentially assist with fracture network characterisation for production modelling and well planning purposes.

Overall, the results of this study illustrate the potential of novel in-situ Rb–Sr geochronology to date both primary crystalline facies and subsequent tectonic events affecting the basement.

<u>Footnote:</u> MT Kitty 1 was re-named Jacko Bore 1 in2023 at the request of Traditional Owners.

### In situ Rb-Sr dating of early Palaeozoic glauconites from the Amadeus Basin, Australia

Cecilia Loyola, University of Adelaide

Sedimentary systems face challenges in obtaining reliable in situ authigenic age constraints. We have enhanced in situ Rb-Sr dating on rubidium-rich minerals, offering age constraints with a quick, efficient process and minimal sample preparation. This method relies on the radioactive decay  $of^{87}$ Rb to<sup>87</sup>Srthroughnegativebetadecay(electronemission), featuring a half-life of  $49.61 \pm 0.16$ Ga. Traditional rubidium-strontium dating typically involves the separation and acid digestion of mineral phases and/or bulk rocks, hindering high-resolution and microscale geochronology applications.

Our study presents the outcomes of the novel in-situ (laser-based) rubidiumstrontium dating applied to glauconite, in Early Palaeozoic marine sedimentary rocks from the Amadeus Basin. The investigated units include the Arumbera Sandstone, Todd River Dolostone, Tempe Formation, Pacoota Sandstone, and Goyder Formation. The stratigraphic ages of the examined samples span from the latest late Ediacaran(ca.550Ma) to early Ordovician (ca.505Ma).

This study employs a novel in-situ rubidium–strontium geochronology technique, complemented by simultaneous trace-element concentration data collection using laser ablation tandem mass spectrometry (LA-ICP-MS/MS. Before analysis, the micro-scale mineralogy and petrography of the samples were characterized through backscatter electron images and mineral maps.

Isochrons were constructed with IsoplotR using the<sup>87</sup>Rb decay constant. The analysis of the authigenic phases of the Arumbera Sandstone returned an age of ca. 426 Ma, the Todd River Dolostone ca.436Ma, Tempe Formation ca. 445Ma, Goyder Formation ca. 376 Ma and Pacoota sandstoneca.387 Ma.

Although the ages are younger than expected, we ascribe these younger-thanexpected depositional ages to post-depositional diagenetic overprint from Rodingan movements (~440– 430 Ma) and the Pertnjara-Brewer events (ca. 395–375 Ma). On average, the Rb–Sr ages coincide with the period of maximum burial, as defined by previous works done using proxies such as vitrinite reflectance, and rock eval.

Overall, the results from this study illustrate the potential of novel in-

situRb–Srgeochronologyto date post-depositional events, which can be done quickly, efficiently, and with minimum sample preparation. The data from the authigenic glauconites can yield the timing and history of subsequent diagenetic and post-depositional events.

#### Bioproductivity and detrital influx variations control the organic matter enrichment in the Velkerri Formation, McArthur Basin, Australia

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The Velkerri Formation (Mesoproterozoic in age) in the McArthur Basin was deposited during an evolutionary transformation in Earth's history. The middle member of this formation, known as the Amungee Member, has three cyclic organo-facies with dominated organic-rich shales, and they are separated by organic-lean intervals. Organic-rich intervals include A-B-and- C-organofacies from the bottom to the top of the member, and two lean intervals including Between A-B and B-C intervals are distinguished. This study represents some organic and non-organic geochemical data such as total organic carbon (TOC), organic carbon isotope  $(^{13}C)$ , and elemental analysis for the Amungee Mb. of the formation in two boreholes of the Beetaloo subbasin including Altree-2 and Marmbulligan-1. TOC shows the highest values in B-and-C-organofacies in both wells, while that of two lean intervals is the minimum. Intervals with higher OM contents represent heavier  $\delta^{13}C_{org}$ , which point out higher primary productivity and associated fractionation of C isotopes, while more negative  $\delta^{13}C_{org}$  values were detected through intervals with lower TOC content. The exception is the dataset from the A-Shale member in Marmbulligan-1, which shows an opposite trend and a negative correlation between TOC and  $\delta^{13}C_{org}$  values. Interestingly, Zr and Ti variations, as detrital influx proxies, show less enrichment compared to the upper continental crust values (UCC) in intervals with higher TOC contents, while they become closer to the UCC average values in low TOC contents intervals (e.g., Between A-B and B-C intervals). This means that the rate of detrital influx into the basin was higher during the deposition of the last intervals, resulting in more dilution and less accumulated OM in sediments. In the B-C interval, the constant increasing trend in TOC simultaneously with no significant changes in  $\delta^{13}$ Corg suggests that siliciclastic influx has played the most important role in less OM accumulation here.

### Exploring Geochemical Data from the CSIRO Mafic-Ultramafic Ni-PGE Mineralisation Data Compilation Through the AusGeochem Platform

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AusGeochem is an open-access cloud-based platform and analysis tool for the geosciences, currently being developed by the AuScope Geochemistry Network (AGN) in collaboration with geoscience data solution company Lithodat Pty Ltd. Increasing production and availability of geochronological and geochemical data both in Australia and globally has highlighted the need for community analytical and reporting standards to allow end users to successfully interact with and evaluate quality of large data sets drawn from multiple sources. In response to this community-identified need for improved geoscience data architecture and collaboration between research institutions, the AGN initiated the AusGeochem project. AusGeochem allows researchers to easily store, disseminate and interrogate a variety of geochemical and geochronological data in line with FAIR (Findable, Accessible, Interoperable and Reusable) data principles, and aims to serve as an active part of the research pathway. The platform has recently released a new capability focusing on major, minor and trace element geochemical data at a range of analytical scales from wholerock to in situ mineral or single-grain analyses. Within the user environment, users can explore geochemical data produced by researchers and institutions from around the globe using a number of flexible live plotting capabilities, such as versatile biplots or ternary diagrams, spiderplots, whole-rock geochemical discrimination plots and geochemical interpolation maps. These additions provide powerful tools for simultaneously interrogating geochemistry data obtained by a multitude of institutions from large data sets on regional to global scales in real time.

To demonstrate the power of this new functionality within the AusGeochem platform, the AGN has collaborated with CSIRO to host a significant legacy collection of data from ma fic-ultramafic rocks and associated magmatic Ni-PGE mineralisation from Archean cratons and Proterozoic orogenic belts of Western Australia. Curated by Steve Barnes, this data set is explored using tools within AusGeochem to highlight regions of potential mineral prospectivity and geochemical anomalies. This case study illustrates the power of geochemical data interoperability and synthesis within a platform providing dynamic interrogation tools for furthering research and discovery.

## Enhancing gold exploration by improving detection limits for gold in groundwater

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This study was conducted as part of the MinEx CRC under the National Drilling Initiative, with the aim of enhancing gold exploration by improving the analytical methods used for detecting ultra-trace levels of gold in groundwater. These results are applicable throughout Australia and globally.

Gold exploration has been increasingly focused on rocks buried beneath sedimentary cover. The cover limits the utility of traditional soil samples to provide geochemical gold anomalies associated with buried deposits. Groundwater provides an alternative and complimentary method to explore for gold. Due to the mobile nature of groundwater, gold anomalies can form large haloes around buried deposits, which can be useful for identifying mineralisation at a regional scale. However, gold concentrations in groundwater are often near the limit of analytical techniques, especially in saline groundwaters, common in Australia. To address this, gold can be bonded to an adsorbent material in a pre-concentration step. This offers the potential to increase the limit of detection by an order of magnitude.

Different adsorbents possess varying characteristics that influence their ability to adsorb the different species of gold present in groundwater. To test these four Purolite adsorbent materials, (Puromet MTS9850, Purosorb PAD600, Purogold MTA-1930 and Puromet MTS 9140) were tested with three gold complexes (Na-Aurothiomalate, Au-Thiosulfate, and Au(III)Cl3). The adsorbent capabilities were tested after 30 minutes, 60 minutes, 24 hours, and 5 days. Textural analysis of the Purolites was performed using SEM and Micro-CT imagery. It was found that the Purolite resin with the Cl functional group (Purogold MTA-1930) exhibited the best adsorbent capabilities for gold in groundwater due to its high-efficiency gold precipitation from all gold complexes and the homogeneous nature of the gold precipitated on the Purolite surface. These results suggest this adsorbent should be used when undertaking gold exploration using groundwater.

### Copper exploration through the Kalahari transported cover in NW Botswana

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The basement rocks of northwestern Botswana are obscured by c. 25-90 m of Kalahari sand, presenting a significant challenge for mineral exploration. The top of the sand cover is oxidized and ferruginous, while the base is calcareous and siliceous, which unconformably overlies a slightly weathered basement. Various techniques, including optical and scanning electron microscopy, total and partial extraction, and laser ablation ICP-MS analysis of cores, heavy minerals, and soil size fractions, have been used to detect mineralogical and geochemical footprints of metal dispersion through the cover. Cover materials with 2 km spacing were sampled across the basement-cover interface, which showed an abundance of weathered rock fragments indicative of the mechanical dispersion of basement rocks. The critical indicator mineral near the interface is almandine-spessartine garnet containing pyrrhotite and chalcopyrite inclusions. The weathering of garnet and its sulfide inclusions concentrated Fe and Mn oxides in a paleoredox front within aeolian sand. Relics of cuprite and chalcocite are preserved in Feoxides. Copper, Ni, Co, Zn, and As were extracted from Fe and Mn oxides in the paleoredox zone by 0.1M and 0.25M hydroxylamine hydrochloride and weak agua regia. Extraction of elements from <2, 2-75, 75-250, 250-2000, and >2000 µm soil fractions by mild aqua regia shows that Cu, Mo, and Co are concentrated in the 75-250 µm fraction, whereas Pb, Zn, Ag, Se, and Te are concentrated in the  $<2 \mu m$  fraction. Partial extraction analyses using water, Na-acetate, Na-pyrophosphate, and hydroxylamine hydrochloride were performed on the <250 µm fraction of samples collected at various depths within the cover. Napyrophosphate extracted Cu, Ag, Co, Zn, As, Bi, Cd, Se, Sb, W, and Te from these samples, indicating their association with organic materials.

Our research shows that the interface sampling and use of redox samples are recommended to detect the geochemical signature of copper mineralization. Specifically, Napyrophosphate extraction is suitable to concentrate ore and pathfinder elements for efficient undercover targeting, and the 75-250  $\mu$ m soil fraction should be analyzed by aqua regia. Soil sampling should be targeted below the top 50 cm to avoid false anomalies formed by scavenging of metals by Mn oxides.

## Diagenetic Constraints on Glauconite Rb–Sr Ages: In-Situ LA-I CP-MS/MS, Geochronology, Micropetrography, and Elements—A Case Study from the Mid-Cambrian Georgina Basin, Australia

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While glauconite has traditionally played a crucial role in dating depositional ages within sedimentary strata using methods such as K-Ar, Rb-Sr, K-Ca, and <sup>40</sup>Ar-<sup>39</sup>Ar dating, conventional approaches involving chemical elemental separation are time-consuming and limit the amount of data realistically obtainable. Frequently, reported glauconite ages are observed to be younger than depositional ages. These are commonly assumed to result from burial diagenetic alteration. In this study, we introduce an innovative approach using laser ablation inductively coupled tandem quadrupole mass spectrometry (LA-ICP-MS/MS) for Rb-Sr dating of glauconite, complemented by petrographic analyses, high-resolution imaging, as well as quantitative major and trace element characterisation. The goal is to investigate the potential diagenetic overprinting of Rb-Sr ages in shallow marine ramp carbonate-hosted glauconite within mid-Cambrian sequences (ca. 505 Ma) from the Georgina Basin in Australia. Our observed younger ages can be categorised into approximately 450-410 Ma (Age Group 1, AG1) and around 400-350 Ma (Age Group 2, AG2). These closely correspond to two episodes of the Alice Springs Orogeny, specifically the Rodingan and Pertnjara-Brewer events. Early dissolution and illitization were the primary factors driving the first-stage alteration of glauconite (AG1), while de-illitization and dolomitization played key roles in the second-stage alteration (AG2). Apatite, dolomite, and calcite were prevalent inclusions within glauconite, impacting the overprinted ages, with AG1 glauconite being richer in impurities. Additionally, quartz and pyrite inclusions were observed in the glauconite, although they didn't significantly influence the rejuvenated ages. We conclude that orogenesis was crucial in promoting burial fluid-rock interaction, leading to the dissolution of glauconite with subsequent illitization. This was followed by de illitization, accompanied by phosphatization, calcification, and dolomitization. These cumulative processes collectively re-equilibrated the Rb–Sr system within glauconite, ultimately resulting in the observed younger ages. Our study's refined age calibration method (NIST 610 + MDC) for LA-ICP- MS/MS data processing yielded ages 2-3% younger than those obtained through the traditional approach, showing enhanced precision with lower uncertainties.

#### Mineralogical and geochemical signatures of intrusionrelated versus orogenic gold deposits, Western Lachlan Orogen, Victoria

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Southeast Australia's largest and richest known orogenic gold deposits lie in the Bendigo and Stawell Zones of central Victoria. The Lachlan Orocline Model suggests the Tabberabbera Zone of eastern Victoria is a possible along-strike extension to the Bendigo Zone with a change in the tectonic environment raising potential implications for orogenic gold endowment in northeast Victoria. In the Tabberabbera Zone, some gold deposits interpreted as orogenic-type coincide with gravity lows and/or Devonian granitic plutons and are the same age suggesting they may be intrusion-related. Distinguishing these systems has broader implications for exploration throughout the Western Lachlan Orogen, where abundant granitic intrusions remain poorly studied.

This study focuses on several gold prospects spatially associated with the Beechworth Granite, the Yackandandah Granite, the Dead Bird Suite in the Tabberabbera Zone and the Strathbogie Granite in the northern part of the Melbourne Zone. A classic orogenic gold deposit of the Bendigo zone (Gill Reef) is also studied for comparison. Their mineralogy and geochemical signatures are investigated using automated mineralogy, micro XRF MAIA mapper, cathodoluminescence and apatite U-Pb geochronology.

Preliminary results indicate that Golden Mountain, south of the Strathbogie Granite may be intrusion-related based on the occurrence of minor gold in the granite identified using the MAIA mapper. The mineralisation assemblage for all deposits typically includes galena, sphalerite, chalcopyrite, arsenopyrite (except for Golden Mountain), and rare Ni-Co arsenide. Distinct Bi +/- Te occurrence is only found in gold deposits hosted in the hornfels of the Beechworth and Yackandandah granites. These two granites interpreted as I-type are oxidised while the S-type Strathbogie granite is more reduced.

Cathodoluminescence on quartz reveals multiple episodes of silica-rich fluids with the latest crosscut veinlets associated with stylolites and arsenopyrite-gold mineralisation. These stylolites indicate a significant pressure-dissolution event that may have contributed to gold enrichment. Large apatites are associated with gold mineralisation and are also found in stylolitic veins at Gill Reef. Geochronology of apatite will be used to date the mineralisation and assess how it relates to the emplacement age of the granitic rocks, enabling to constrain the timing and origin of gold mineralisation.

#### A complex web of detrital apatite to investigate the formation of the Castlemaine Group, Central Victoria

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Apatite is a common mineral in most rock types and sediments, that can preserve rare earth element (REE) profiles reflective of lithology and can be used for U-Pb age dating. When integrated with zircon geochemistry and geochronology, these features can offer insight into sediment provenance. The susceptibility of apatite to weathering renders it a reliable marker for initial sedimentation cycles, while zircon, which is more resilient to weathering, can accumulate in sediments through multiple cycles of sedimentation. This combined approach facilitates a nuanced understanding of sedimentary sources and their evolution over time.

This study investigates the use of apatite chemistry and geochronology to constrain source regions and sedimentation cycles related to the deposition of detritus. The Ordovician sediments of the Castlemaine Group from the Lachlan Fold Belt, South-Eastern Australia are used as a case study as they have potential sources nearby in Australia and further afield in Antarctica. The combined REE, Sr and Y geochemistry and U-Pb geochronology of detrital apatite grains was obtained by LA-ICP-MS and used to classify source lithology (igneous, metamorphic, mixed origin) and grain age. Comparison of apatite chemistry to pre-existing data shows that apatite within the Castlemaine Group is sourced from a diverse array of lithologies including felsic, intermediate and mafic igneous rocks, and metamorphic rocks. A population of apatite of unknown lithology source was also recognised. Most apatite grains are interpreted to be of igneous and metamorphic origin aged between 580-480 Ma, likely originating from the nearby Adelaide Fold Belt and Delamerian/Ross Orogens. Older apatite populations are associated with Grenvillian (1300-900 Ma), Rodinian rifting (850-650 Ma) and Early Pan-African (650-580 Ma) events. The number of older (1300-580 Ma) apatite grains is significantly smaller than populations observed in previously published zircon data, and is used here to suggest the older apatite and zircon grains have gone through multiple cycles of sedimentation. This comparison between detrital apatite and zircon geochemistry and geochronology provides insight on the sediment source and enables an understanding of whether the sediment was directly deposited or underwent a multi-cycle process involving intermediate sediments.

### The Cryogenian to Ediacaran of Oman - new geochemical, sedimentological and temporal constraints on the Saqlah, Fiq and Hadash Formations

#### Nicholas Wyndham, University of Adelaide

The Neoproterozoic is an increasingly studied period in earth's geological history. Yet, despite lots of previous work on the geology of this Era, our understanding of the earth system at this time is far from complete. The Cryogenian Period, commonly referred to as 'Snowball Earth', lies in the middle of the Neoproterozoic and is known as having two global-scale glaciations interrupted by a significant interglacial period. The subsequent Ediacaran Period saw continuing climate fluctuations and considerable changes in the biosphere, including the first evidence for animals. However, like much of the Precambrian earth, the Cryogenian and Ediacaran remain highly ambiguous. North Oman is host to some of the best-preserved complete sequences of these ages accessible to geologists today. Our study has focussed on upper Cryogenian and lower Ediacaran lithologies of North Oman: the Saqlah, Fiq, and Hadash Formations, interpreted to represent rocks formed in the intra-Cryogenian interglacial, the second 'Marinoan' glaciation, and the immediate aftermath, respectively. We use the preceding interglacial sedimentological observations, geochemical analyses, and emerging geochronological techniques to better understand the frequency and timing of, and environmental conditions accompanying, the Snowball Earth events.

The earliest Ediacaran Hadash Formation 'cap' carbonate is one of many similar carbonates that overlie Cryogenian glacial sedimentary rocks on multiple continents. We present new carbon isotope data from multiple sections to constrain any diachroneity in deposition and attempt to reproduce published palaeomagnetic reversals from the formation to address the rapidity of deposition. In addition to dating these carbonates, we present new LA-ICP-Ms/Ms Rb–Sr dating of authigenic clays within shales of the Fiq Formation and volcanics within the Saqlah Formation. These age data are combined with sedimentological interpretations, water chemistry proxies, and organic carbon isotope data from the Fiq shales to better understand the nature and evolution of the Cryogenian to Ediacaran of Oman.

### Mineral carbonation through mineral replacement reactions of pyroxenes in alkaline fluids

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Mineral carbonation is one of the most commonly observed natural phenomena which captures  $CO_2$  from atmosphere and subaerial aquifer, and permanently locks it as stable carbonate minerals. This process offers a great opportunity to achieve net-zero

emission through human-engineered geological operations by reacting  $CO_2/CO_3^{2-}$  bearing fluids with underground Mg-, Ca- and Fe- rich rocks. Pyroxene group minerals are one of the most important rock-forming mineral types in the Earth's Crust and the major components in mafic/ultramafic rocks. Pyroxenes can carry significant amounts of Mg, Ca, and Fe, making them promising targets for mineral carbonation. Yet, the reaction between pyroxenes and  $CO_2/CO_3^{2-}$  bearing fluids could be slow, and current understanding of the key reaction mechanisms at fluid-mineral interface is extremely limited, which makes it challenging to optimize the conditions for large-scale operations.

Here we performed hydrothermal mineral replacement experiments to investigate the reactions between Ca and Mg-rich pyroxenes (e.g., diopside, augite) with c arbonate-bearing fluids at various chemical and physical conditions. Ca-rich carbonates were formed in experiments reacting diopside in alkaline solutions carrying Na<sub>2</sub>CO<sub>3</sub>, NaHCO<sub>3</sub>, and NH<sub>4</sub>HCO<sub>3</sub> respectively at 200°C and for 28 days. Trace amounts of Ca were found in fluid samples after the experiment, with extremely low or undetectable Mg and Fe. By contrast, Mg was found to be preferentially enriched in secondary silicate minerals, yet rare Mg was found to form carbonates or detected in the solution. NH<sub>4</sub>HCO<sub>3</sub> was found to be more effective in dissolving silicates compared to  $NaHCO_3$  or  $Na_2CO_3$  at comparable conditions. In a more complex mineral system (60% augite + 35% quartz + minor feldspar), solutions carrying NH4HCO3 are also found to be more effective in leaching Ca and Mg into the solutions at alkaline conditions. The presence of chloride (e.g., NaCl) in all sets of experiments did not have a significant influence on the reaction kinetics. These results indicate a promising potential of carbonation of pyroxenes in  $CO_3^{2-}/HCO_3^{-}$ experimental investigation alkaline solutions. Combining with bearing geochemical modelling, this study allows us to design and optimise engineered mineral carbonation processes to achieve the net-zero mission.

# Constraining trace/minor element behaviour in large, chemical and structurally complex atomic systems – a role for machine learning potential methods?

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Current *ab-initio* methods based on the density functional theory (DFT) have proven accurate for predicting the crystal structures of minerals and dynamic properties of liquids. DFT-based approaches are however limited to applications that yield suitable solutions on relatively small simulation cells (hundreds rather than thousands of atoms) in crystal structures or short simulation times for liquids. Recent developments with 'on-the-fly' machine learning potential (MLP) methods trained from the *ab initio* data have shown that these difficulties can be overcome without loss of accuracy.

Large volumes of experimental and empirical data show how potentially valuable trace and minor elements are incorporated within or released from mineral crystal structures or glasses cooled from melts. The incorporation of foreign atoms within mineral lattices is achieved via changes to larger structures involving ordering of vacancies or superstructure formation. Melts also change their structure during cooling and can host exsolution of other liquids or crystallization of discrete minerals within glasses. What are less well constrained are the solubility limits for trace and minor elements within superstructures and the growth parameters of crystals during melt cooling. MLP-assisted *abinitio* molecular dynamics methods open new possibilities to address these long-standing topics: behavior of trace/minor elements in large atomic systems (superstructures, melts). We showcase 3 applications that could be resolved using MLP methods.

Prompted by the ground-breaking discovery of pentavalent uranium in hematite ( $\alpha$ -Fe2O3) and its stability over geologic time, we model the crystal structural changes induced by atom vacancies and their long-range ordering relative to solubility limits. Outcomes will provide solutions to the long-term storage of nuclear waste and design of new materials.

Likewise, the solubility of precious (Au, Ag) and critical metals (Co, Bi, Te etc.) in copperiron-sulphides is an uncharted topic that if addressed and tested against ores from world-class deposits can predict the critical mineral potential of sulphides.

The phosphate mineral monazite is a major source of rare earths essential for adaptation of green low-carbon technologies. We aim to model structural changes from Si-Fe-oxide melts to glass and monazite crystals, obtaining the growth parameters required for metallurgical design and understanding of analogous rock-forming processes.

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### New constraints on the origin and post-depositional history of Neoproterozoic Breamar ironstones from South Australia: Insights from micro-scale mineral mapping and in-situ Lu-Hf dating of apatite, Rb-Sr dating of biotite and U-Pb dating of hematite

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The Braemar Iron Formation is located in the Yunta-Olary region in South Australia (SA), 400km north-east of Adelaide, and is one of the largest undeveloped Neoproterozoic iron formations in the world. The Braemar iron formation (BrIF) was deposited during the Sturtian glaciation (dated between ~717 Ma to 660 Ma) almost coeval with the less weathered Holowiliena ironstone located in the Flinders Ranges, which are composed of only hematite, while the Braemar Iron Formation is dominated by magnetite. A model for the depositional environment of the BrIF suggests that iron was deposited in the glaciomarine environment under an ice shelf.

Here we present results from new laser-based Lu-Hf, Rb-Sr and U-Pb dating applied to apatite, biotite and hematite phases, identified in the Braemar Iron Formation, which were analysed via in-situ LA-ICP-MS/MS (Alexander et al., 2021; Redaa et al., 2023). Briefly, our Lu-Hf dating of apatite yield the age  $655 \pm 62$  Ma, pointing the depositional age of Braemar Iron Formation in the Sturtian Glaciation. Our U-Pb dating of hematite yielded the age  $501 \pm 34$  Ma, pointing to later / post-depositional recrystallisation during the Cambrian, in line with the timing of the peak of Delamerian Orogeny or deformation. The in-situ Rb–Sr biotite dating yielded systematically younger ages, ranging from  $\sim 451 \pm 7$ Ma to 483 Ma  $\pm$  8 Ma, likely linked to post-Delamerian cooling and associated resetting of the Rb-Sr isotope system in studied biotite. Future work done as part of this project will employ redox-sensitive metal isotope tracers such as Fe and Cr isotopes and REE to further test possible depositional models and scenarios for the Braemar Iron Formation. A comparison from the relatively more 'pristine' Holowiliena ironstones will also be undertaken to assess the effect of secondary processes on geochronological data, redoxsensitive metal isotopes and local Fe enrichments in the above and rather unique Sturtian ironstone deposits in South Australia.