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2019 TIGeR CONFERENCE

Pathways towards equilibrium in geological systems

11–13 September, 2019 Curtin University, Perth ABSTRACTS

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Pathways towards equilibrium in geological systems – mechanisms, length scales and microstructures

The aim of this 3-day conference is to promote progress at the leading edge of this topic through presentations and open-forum discussion.

We will focus on questions related to mechanisms of mineral and rock equilibration from the Earth's surface to the deep crust, including:

- Crystallization and re-equilibration in aqueous solutions and its consequences
- *Re-equilibration in crustal rocks and drivers towards equilibrium: a question of spatial scale?*
- Are metamorphic rocks non-equilibrium self-organised systems?
- What mechanisms are available for the re-equilibration of a mineral assemblage?
- What can we learn from mineral microstructures and rock textures?
- Mineralization patterns and ore deposits as nonequilibrium phenomena
- Open and closed systems

The total number of participants will be limited to about 80-100, to facilitate active participation and open discussion. So register early to avoid disappointment.

THE AGENDA

The aim is to have short presentations (20 +10 minutes for keynote speakers, 10 + 5 minutes for other talks) focusing on specific issues for later discussion. Poster sessions throughout the conference will provide further discussion time. The detailed schedule will be sent out after the registration period.

Speakers include:

Lukas Baumgartner (Lausanne, Switzerland) Andreas Beinlich (Curtin, Australia) Shuuun Cao (Wuhan, China) Damien Daval (Strasbourg, France) David Dolejs (Freiburg, Germany) Katy Evans (Curtin, Australia) Matt Fantle (Penn State, USA) Andrew Frierdich (Monash, Australia) Silvia Frisia (Newcastle, NSW) Julian Gale (Curtin, Australia) Juan Manuel Garcia Ruiz (Granada, Spain) Denis Gebauer (Konstanz, Germany) Thorsten Geisler (Bonn, Germany) Marguerite Godard (Montpellier, France) Martin Hand (Adelaide, Australia) Bruce Hobbs (CSIRO, Ausntralia) Benjamin Malvoisin (Grenoble, France) Klaus Mezger (Bern, Switzerland) Eric Oelkers (UCL, UK) Christine Putnis (Münster, Germany) Encarni Ruiz-Agudo (Granada, Spain) Tracy Rushmer (Macquarie, Australia) Aleksey Sadekov (UWA, Australia) Carl Spandler (James Cook, Australia) Simon Turner (Macquarie, Australia)

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VENUE

The Exhibition Area, Building 500, Curtin University, Bentley Campus, Perth.

ACCOMMODATION

Most of the large chain hotels are in the City and there are public transport options (buses) to Curtin. There are also many Airbnb opportunities nearer to Curtin. Further details will follow for registered participants.

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ABSTRACTS

In the sequence of the Conference Program

Predicting Aqueous Mineral Phase Behaviour Based on Non-Classical Nucleation Theory

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Nucleation is the fundamental step towards equilibration of supersaturated aqueous solutions, and phase separation phenomena are of great geochemical importance. While classical nucleation theory (CNT) is associated with a fair explanatory power, quantitative predictions can deviate from experimental observations by many orders of magnitude. Parametrization of CNT can fix the latter issue; however, this requirement also strongly suggests that the corresponding notions are unlikely to reflect the real molecular picture of the underlying processes.¹

In recent years, we have been introducing an alternative, 'non-classical' framework — the so-called pre-nucleation cluster (PNC) pathway. While the concept remains debated,² its molecular level explanatory power has often been neglected. Here, we explicitly demonstrate that the non-classical PNC notion can be developed into a quantitative framework that accurately predicts the aqueous phase behaviour of calcium carbonate. The binodal and spinodal limits of liquid-liquid phase separation are determined by calcium carbonate pre-nucleation ion association, and its temperature dependence. The non-classical theory also quantitatively rationalizes the surprising observation of the formation of amorphous intermediates containing significant amounts of structural bicarbonate at near neutral pH values. Last, we illustrate that the 'non-classical' notion also bears great potential to shed new light on the problem of dolomite formation. The applicability of CNT in all these contexts is questionable and should probably be dismissed in the future.

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Calcite formation and growth via amorphous calcium carbonate nanoparticles

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Crystallization from solution is a fundamental process for the formation of structurally ordered solid phases such as minerals and biominerals, or novel functional materials and drugs (Chernov, 1984; Meldrum and Cölfen, 2008). According to classical crystallization theory, it starts with the spontaneous clustering of ions/molecules leading to nucleation once a free energy barrier is overcome for a critical cluster size; afterward, such clusters grow by incorporation of ions/molecules resulting in the formation of (faceted) crystals, and minimizing the system free energy (Chernov, 1984; Meldrum and Cölfen, 2008). However, classical nucleation theory is currently challenged by an increasing body of computational and experimental studies that indicate the presence of alternative crystallization processes, including the existence of stable pre-nucleation cluster (Gebauer et al., 2008), liquid and amorphous precursor phases (Wallace et al., 2013) or the occurrence and participation of nanoclusters as building blocks in growth processes (Meldrum and Cölfen, 2008; Gebauer et al., 2008; Nielsen et al., 2014; De Yoreo et al., 2015).

In particular, formation of calcium carbonate via amorphous precursors appears to be a general strategy in biomineralization, which could be mimicked by materials chemists to synthesize novel functional materials (e.g. Vidavsky et al. 2014). However, despite recent extensive research, fundamental knowledge on this topic is still lacking. For example, the formation of amorphous calcium carbonate (ACC) and amorphous-to-crystalline transformation is not fully understood. Also, there is still debate about the exact mechanism of carbonate crystal growth via an amorphous nanoparticle precursor phase. Here we show that ACC nanoparticles form after spinodal liquid-liquid phase separation and transform via dissolution/(re)precipitation into poorly hydrated and anhydrous ACC nanoparticles that aggregate into 1D, 2D and 3D structures. The formation of these structures appears to be achieved by oriented attachment, facilitated by the calcite medium range order of ACC nanoparticles. Under humid air exposure at room temperature, these ACC structures transform into pseudomorphs of single crystalline mesostructured calcite. Such transformation in air occurs via an interface-coupled dissolution/precipitation mechanism process triggered and aided by an adsorbed water layer. This differs significantly from the currently accepted model, which considers that the low T ACC-to-calcite transformation in air and during biomineralization is a solid-state process. Also, we present direct nanoscale evidence showing that, in addition to classical crystal growth via incorporation of ions at growth steps, faceted calcite crystals can grow non-classically by a layer-by-layer process involving the attachment of ACC nanoparticles at the calcite-solution interface followed by their amorphous-tocrystalline transformation and fusion with the underlying calcite substrate. These results may help to better understand how calcite biominerals form after ACC and offer the possibility of biomimetically preparing single crystalline calcite structures after ACC by tuning pH₂O at room temperature.

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Crystallisation of biominerals: What can computation tell us?

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Crystallisation of minerals from aqueous solution is important in a wide range of contexts from industrial processing through naturally occurring formation. Arguably one of the most significant classes of crystallisation from the latter category is biomineralization in which controlled formation of phases, morphology and hierarchical structure occurs for a targeted purpose from mechanical strength to optics and vision. Due to the complexity of such processes and number of potential crystallisation pathways it is currently difficult to elucidate the full mechanistic details in situ. Atomistic simulation provides a means to understand a small part of crystallisation processes occurring in aqueous fluids at a detailed level; the aim of this presentation is to illustrate some of the information that can be obtained and the limits of the approach with current high performance computing [1].

Many of the most abundant biominerals are calcium-containing systems and so here the focus will be on a small number of such examples including calcium carbonate, calcium phosphate and calcium sulfate. Direct simulation of mineral nucleation is beyond the feasible scope of atomistic computation. Hence, this presentation will focus on the two readily accessible extremes of crystallisation from aqueous solution that are amenable to studied by such techniques; namely speciation [2] and crystal growth/dissolution [3]. Specifically, it will be shown how the use of carefully enhanced molecular dynamics simulations can provide detailed thermodynamic information for crystallisation that allows experimental measurements to be understood in terms of the underlying component molecular processes, such as the addition or removal of individual ions from the surface of minerals (Figure 1).



Figure 1: Free energy isosurfaces for binding of a carbonate anion at the acute (right) and obtuse (left) steps of the basal surface of calcite in contact with water. Dashed lines are included to indicate the position of lattice planes, while calcium, carbon and oxygen are coloured in blue, green and red respectively.

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Burial-induced oxygen-isotope re-equilibration of fossil foraminifera: experimental evidence and possible impacts on paleotemperature reconstructions

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Among many outstanding scientific contributions, Harold Urey and his students gave the scientific world the first isotopic tool to study past changes in climate: The carbonate oxygen isotope thermometer, which is based on the temperature-dependent equilibrium O-isotope fractionation between carbonate and water caused by different isotope-dependent vibrational energy levels (Urey, 1948). Oxygen isotope compositions of fossil planktonic and benthic foraminifera tests are now used as proxies for surface- and deep-ocean paleotemperatures, with a continuous benthic record for the last 115 Ma (Friedrich et al., 2012).

Whereas Urey and his colleagues identified the potential problem with preservation of the O-isotope composition through geological time, specifically addressing the mechanism of solid-state diffusion, they made one misinterpretation that, in hindsight, could hardly have been avoided: in the absence of knowledge about biogenic carbonate ultrastructure, they assumed a (in this situation reasonable) characteristic crystal size on the order of 1 mm. Carbonate crystals of this size are essentially immune to O-isotopic resetting by solid-state diffusion under normal sediment burial conditions, i.e., near-ambient pressure and temperature on time scales of relevance to climate reconstructions. Thus, the process of solid-state diffusion as an effective mechanism for isotopic resetting was discarded. However, it is now admitted that Urey's assumption of a typical biogenic carbonate crystal-size of 1 mm was wrong by about 4 orders of magnitude...

In addition, Putnis and colleagues have shown that, in contact with a fluid, pseudomorphic replacement of individual crystals can take place through the process of coupled dissolution and precipitation (Putnis, 2009; Ruiz-Agudo et al., 2014). Recent work has demonstrated that, in permeable systems with well-connected porosity, fast fluid transport is driven by pressure gradients and that, even in less permeable rocks, efficient mass transport can take place through transient pore space created by dissolution and reprecipitation (Plumper et al., 2017). In contrast to solid-state diffusion, these processes have the potential to proceed on very short timescales. Although a large number of studies have addressed the dissolution kinetics of carbonate minerals, the potential impact of coupled dissolution and precipitation on biogenic calcite-based paleo-environmental reconstructions essentially remains a *terra incoginta*.

In this presentation, I will report on the results of our recent study (Bernard et al., 2017), where we showed that visually imperceptible processes can alter oxygen isotope composition during sediment burial. We investigated the re-equilibration process with experiments exposing foraminifera tests to elevated pressure and temperature in artificial, isotopically heavy ($H_2^{18}O$) seawater, followed by electron microscopy and quantitative NanoSIMS imaging. We evidenced that oxygen isotope compositions change heterogeneously at sub-micrometer length scales without observable modification of test ultrastructures. We then examined the most conservative mechanism of isotopic exchange during burial (that is, solid-state diffusion) by means of numerical modeling and showed that oxygen isotope re-equilibration of fossil foraminifera tests cause significant overestimation of ocean paleotemperatures on a time scale of 10^7 years under natural conditions. Our results indicate that Cretaceous and Paleogene deep-

ocean and high-latitude surface-ocean temperatures were significantly lower than generally accepted, thereby having the potential to explain the paradox of the low equator-to-pole surfaceocean thermal gradient inferred for these periods. Finally, I will briefly discuss our going strategy to refine our understanding of oxygen isotope re-equilibration in abiotic and biogenic calcites, which is carried out within the framework of the ERC project UltraPal managed by A. Meibom, which has just started this year.

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Experimental investigation of the short-term exchange of foraminiferal calcite: Implications for the nature of diagenetic imprints on the geochemical proxy record

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Fossilized foraminiferal tests are valuable proxy archives for exploring the past. Using a range of geochemical proxies that are stored within foraminiferal carbonate, geochemists can constrain important climatic and geochemical indicators of Earth's functioning in the past (e.g., sea surface and bottom water temperatures, pH, and seawater chemical evolution; e.g., Elderfield and Ganssen, 2000; Lea et al., 2000; Pearson et al., 2007).

The fidelity of the archive, however, can be impacted by post-formational exchange, which can occur in either the water column or the sedimentary column. The reactions that act to alter primary geochemical compositions are generally termed "diagenetic", and it is in the diagenetic realm that carbonates undergo changes that are "complex and prolonged in comparison with the brief flickers of their exposures in the original deposition environments...." (Bathurst, 1975).

Given that an understanding of the importance of diagenesis has existed for nearly 125 years (Walther, 1893), relatively little is known about the geochemical consequences of diagenesis on calcareous tests. Studies of bulk carbonates in natural systems have provided valuable constraints on the reactive environment in which individual components sit (e.g., for summary pre-2010, see Fantle et al., 2010; also: Fantle, 2015; Chanda and Fantle, 2017; Huber et al., 2017), but it is not clear how much individual tests are impacted. Recent experimental work has suggested exchange on the test/particle scale might be extremely fast or significant enough to impact interpretations of the past (e.g., Bernard et al., 2017; Oelkers et al., 2019). More work, however, is needed.

Laboratory-based mineral–fluid exchange experiments can serve as probes of mineral reactivity, offering insights into the rate and extent to which particles react. The current study (Chanda et al., 2019) presents results of experiments aimed at quantifying the extent and rate of foraminiferal calcite-fluid exchange over a three-month period using a 45 Ca radiotracer. A total of 138 batch reactors were run, each of which contained ~500 to 700 µg of foraminiferal carbonate. Experiments occurred in solutions that were close to chemical equilibrium, as this is one of the common geochemical conditions to which carbonates are exposed in the sedimentary column. The exchange behavior of modern (*O. universa* and *G. ruber*; 250-500 µm, Cariaco Basin sediment traps) and fossil (*O. universa*, *G. sacculifer*, and *G. bulloides*; 250-500 µm, ODP Site 807, Hole A) tests were evaluated relative to an inorganic Iceland spar control.

We found that all tests reacted over the experimental timeframe, taking up more ⁴⁵Ca tracer from solution than could be accounted for by surface sorption alone. Modern tests reacted at the fastest rates $(2.6 \cdot 10^{-4} \text{ to } 2.0 \cdot 10^{-5} \text{ mol/m}^2/\text{d})$, while fossil tests reacted slower still $(7.6 \cdot 10^{-5} \text{ to } 5.3 \cdot 10^{-6} \text{ mol/m}^2/\text{d})$, and inorganic calcite slowest of all $(6.6 \cdot 10^{-6} \text{ to } 5.9 \cdot 10^{-7} \text{ mol/m}^2/\text{d})$. Reaction rates were markedly higher in the early stages of the experiments, and decreased as time progressed. The release of Ca²⁺, Mg²⁺, and Sr²⁺ to solution in parallel tracerfree reactors indicates that test experienced dissolution, though no overt changes in test morphology – as indicated by scanning electron microscopy and μ -CT imaging – were detected (in addition, there were no overgrowths, and no evidence of test fragmentation or euhedral calcite). These observations, in addition to the accumulation of ⁴⁵Ca in the solid phase, support

the hypothesis that calcite-fluid exchange occurred via dissolution-reprecipitation, ostensibly driven by intra-test chemical heterogeneities.

Time-dependent box model simulations of aqueous elemental and solid ⁴⁵Ca chemistry are used to explore our preferred hypothesis that the experimental observations are explained by dissolution of more soluble, and hence more reactive, Mg- and Sr-rich calcite and the precipitation of less soluble, less trace element-rich calcite. Understanding the underlying mechanism is critical, as it allows for an exploration of the potential to overprint the chemistry of foraminiferal tests.

Subsequently, we use our time-dependent models to simulate alteration (or diagenetic) trajectories for Mg/Ca and δ^{18} O, assuming that a mix of dissolution and recrystallization occur. The simulations demonstrate that temperatures derived from Mg/Ca and δ^{18} O are not altered proportionally during the experiments and, by extension, in natural systems. Applying experimentally-constrained rates and mechanisms suggest that absolute proxy-based temperatures may be altered over short time scales by as much as ~0.5°C (δ^{18} O) and ~2-3°C (Mg/Ca), assuming a temperature difference of ~27°C between the surface and alteration regimes. The simulated diagenetic trajectories demonstrate a strong dependence on the dominant mechanism of alteration: the alteration slope between Mg/Ca- and δ^{18} O-derived temperatures fluctuates from positive to negative depending on whether dissolution or recrystallization operates. No matter what the mechanism, our results suggest that there is potential for significant diagenetic biasing of Mg/Ca-based temperatures, which will impact reconstructions of fluid δ^{18} O.

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The kinetics of isotope exchange during ambient temperature water-mineral interaction

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Chemical reactions at the mineral-water interface proceed by the two-way transfer of material to and from the mineral surface during dissolution, precipitation and at equilibrium. This latter two-way transfer is commonly referred to as dynamic equilibrium. Due to this two-way mass transfer, the isotopic composition of a mineral will tend to evolve towards a fluid-mineral isotopic equilibrium state even during stoichiometric dissolution and at bulk chemical equilibrium.

Over the past decade we have performed a large number of experiments exploring the rates of isotopic exchange towards mineral-fluid isotopic equilibrium. These rates for many mineral systems are similar to the bulk dissolution/precipitation rates of the minerals themselves, at least at the mineral near surface. For example, we have observed the near instant equilibration of C and Mg isotopic compositions in the water-nesquehonite/dypinite system, the equilibration of the Ca isotopic composition in the calcite-water system over week-long time scales, and the month-long equilibration of the Si isotopic composition in the amorphous silica-water system. In each case the observed isotope exchange occurred when the solids were in bulk chemical equilibrium with its co-existing fluid. This presentation will review these observations and explore some of the possible reaction pathways of this isotope exchange process.

Dynamic equilibrium during calcite-water interactions

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Direct *in situ* experiments using atomic force microscopy (AFM) show that when a calcite (01-14) cleavage surface is in contact with a CaCO₃ solution saturated with respect to calcite, the surface dissolves and grows simultaneously and continuously. Furthermore the growth occurs predominantly through the formation of nanoparticles, probably amorphous. Initial nanoparticles form immediately on contact with the saturated fluid, first seen in areas of increased dissolution, that is, around etch pit edges and large steps. The observations indicate that at potential equilibrium a calcite surface reacts dynamically. This is further evidence that a mineral surface is a complex landscape with varying reactivities dependent on potential reaction sites such as kinks and edges. When in contact with an aqueous fluid, a calcite surface can dissolve and reprecipitate as a result of surface reactivity and solution composition. These interface-coupled reactions are only possible as a result of the formation of a mineral-fluid boundary layer whose composition differs from the bulk fluid composition. This is a possible mechanism for the re-equilibration of trace elements and isotopes near equilibrium.

Effect of dynamic equilibrium on REEs geochemistry of deep-sea carbonates and its implication for REEs budget in the oceans

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Neodymium isotope signatures of planktonic foraminifera shells in deep-sea sediments have been used extensively to reconstruct evolution of deep water masses and their interactions with ocean carbon cycle and global climate. Recently, it has been shown that REE patterns of foraminifera shells can also be used in palaeoceanographic reconstructions. Concentrations of REEs in living planktonic foraminifera is around 2-3 orders of magnitude smaller than in shells extracted from deep-sea sediments, implying a diagenetic origin of REE signatures in the latter. A commonly accepted hypothesis is that for a shells in sediments are coated with a thin layer of high Mg carbonates and/or Fe-Mn oxides leading to significant enrichment in REEs. In this work, we investigate the origin of this 'diagenetic coating' using high resolution Laser Ablation ICPMS and focused ion beam scanning electron microscopy of individual planktonic foraminifera shells. A series of core-top sediments and also multi-core and down-core samples were investigated to understand the evolution of REE concentrations and patterns from watersediment interface to deeper sedimentary layers. We also combine these studies with inorganic precipitation experiment and in-situ atomic force microscopy to characterise the degree of surface alteration of calcium carbonates and corresponding incorporation of REEs. Our results demonstrate that contrary to current models of REE incorporation, foraminifera shells from deep-sea sediments lack the discreet layer with high REE concentration. Instead, REE incorporation is driven by continues near-equilibrium precipitation-dissolution of near surface layers of foraminiferal calcite. This process of pore-water alteration of foraminiferal signatures has significant implications for REE budget in the ocean and also interpretation of REE-based proxies which we will discuss in this work.

Crystallization processes in carbonate archives of climate change

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Investigation by high resolution Transmission Electron Microscopy (HR-TEM) and Synchrotron-Radiation based micro X-ray fluorescence (SR-µXRF) of both terrestrial and marine carbonates imposes uncertainties on the boundary between stages of crystal nucleation and growth and diagenetic processes. In the last 20 years, speleothems (defined as cave secondary mineral deposits) consisting of calcium carbonate have proven to be exceptional archives of past climate and environmental changes that parallel ice cores for their accuracy. However, amongst many published speleothem-based records, there are uncertainties that lead to anecdotal evidence. This may generate skepticism in the quality of data, when these are not grounded on a thorough investigation of the material the data are extracted from. An effective approach to tackle uncertainties is a nanoscale investigation of crystallization processes. HR-TEM investigation of in-situ products of instantaneous (30 min.), overnight, annual crystallization experiments suggest that there are many possible pathways leading to speleothem carbonates formation: from classical ion-mediated to particle-mediated, to formation of metastable phases such as amorphous calcium carbonate and vaterite that subsequently transform into calcite (Demeny et al., Frisia et al., 2018). All these diverse pathways influence the potential of a primary carbonate to undergo post-depositional transformation, with obvious consequences on the preservation of original chemical and physical properties used to extract past climate information. The most critical and appreciated property of speleothems is their capability to be precisely dated with U-series based radiometric techniques, which enables us to investigate Earth's past from modern times all the way to the Paleozoic (Woodhead et al., 2010). However, U mobilization results in age inversions and uncertainties and is dependent on both crystallization and diagenetic pathways (Bajo et al., 2016). Through HR-TEM observations of cave precipitates, we have found that organic compounds, and more specifically humic substances (HS), can influence the capacity of original speleothem precipitates to undergo dissolution and re-precipitation. Our hypothesis implies that colloidal HS may actually be conducive to accuracy of the original datum by protecting the initial products of crystallization products from diagenesis. The presence of organic compounds that influence diagenetic pathways becomes crucial for the understanding of the selective preservation of original speleothem chemical signals. Whilst stable isotope ratios, Sr and Fe concentration appear to be reliable proxies of climate very "early" signal, important tracers such as Si, or Cl or even Mg (in the case of speleothems influenced by sea aerosols) are lost. This points to "soon after crystallization" dissolution and reprecipitation processes that dictate the chemistry of the final crystallization phase (usually calcite). By using speleothems as paradigm for all carbonates formed in natural environments where organic compounds are ubiquitous, the presence of organic molecules (which could well be of inorganic origin, not directly related to living organisms) could explain the formation and persistence of primary carbonates, such as dolomite, which should not "form" at Earth's surface conditions. This paradigm has been used to negate the existence of "primary" dolomite and claim that dolomite is a diagenetic mineral (Machel, 2004). Ancient primary dolomite crystals have been proven to exist and be associated with both clay and continentally-derived HS (Preto et al., 2015), which contradicts the notion of dolomite being "diagenetic". Crucially, HR-TEM observations have shown that in modern, shallow, and mildly evaporative cratonic lakes in the Pannonian Basin primary Mg-bearing calcite and nanoscale dolomite crystals form (Nyirő-Kósa, et al., 2018). This has profound implications for our interpretation of the significance of ancient dolomites, in terms of a role of HS and continentally derived colloidal particles. Ionic clusters may have been anchored to the clay surface, presumably initiating calcium carbonate nucleation. If this is the case, our current interpretation of dolomite in Cryogenian beds as documenting "Tropical" conditions, may just be inaccurate. Dolomite nucleation may have just had necessitated the presence of the right clay and organic molecules and a relatively high Mg/Ca ratio in the parent waters. Our body of data suggests that carbonate crystallization pathways in caves, lakes and marine settings are similar. The existence of multiple crystallization pathways for carbonates have repercussion on the accurate interpretation of climate proxy data from carbonates. As opposed to textbook assumptions, early diagenetic processes and the extent to which diagenesis significantly resets the original chemical and physical signals depends on crystallization pathways. This has implications for the interpretation of Earth's past climate history reconstruction.

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Dissolution-recrystallisation of bone in natural environments and controlled diagenesis experiments

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Preserved remains of vertebrates' bones and teeth are invaluable records of Earth's and humankind's past. Indeed, the carbon, oxygen, and calcium isotopic compositions of a vertebrate's diet and drinking water are recorded in its bones and teeth through its metabolism and the process of biomineralisation. Measuring the isotopic composition of fossil remains of vertebrates thus gives insight into past diets and is widely used to reconstruct historical food webs, habitats, environments and climates. However, these remains suffer modifications during the fossilisation process. While the organic components (e.g. collagen in bones) are rapidly degraded, the mineral phase, a calcium phosphate called bio-apatite, undergoes more subtle transformations. Compared to their biological counterparts, fossil apatites generally exhibit an overall decrease in carbonate content, enrichment in fluorine, incorporation of trace elements and an increase in crystallinity. Therefore, a detailed understanding of these transformations induced by fossilisation is crucial to better assess the preservation of geochemical records in apatites and validate their use as palaeo-environmental proxies.

In this contribution, we investigate the crystal-chemical transformations, and more specifically the environment of carbonate groups and fluoridation mechanisms, in modern bioapatites altered under controlled conditions. Modern bone wafers and powders were soaked in aqueous solutions of neutral to alkaline pH for periods up to 3 weeks at various temperatures (20-70°C), with each experiment duplicated in fluorine-free and in 10^{-2} M NaF solutions. Their transformation was monitored through chemical (F, Ca, P) and isotopic (δ^{13} C, δ^{18} O_c, δ^{18} O_p) analysis, and probed using vibrational (Attenuated Total Reflectance - Fourier transform infrared, Raman) and solid-state Nuclear Magnetic Resonance (NMR) spectroscopies. Systematic incorporation of fluoride in the channel sites is observed in all samples altered with a sodium fluoride solution. In contrast, the formation of secondary carbonated fluorapatite, associated with the presence of a clumped (CO₃²⁻, F⁻) defect, detectable with both ATR-FTIR and ¹⁹F NMR spectroscopies, depends on the type of buffer solution used for the alteration experiment. Fluoride ions thus act as a probe revealing dissolution-recrystallisation pathways in bone.

Based on the experimental results¹, and comparison with naturally-fluorinated fossil bones from late Miocene and Plio-Pleistocene deposits of Kenya and South Africa², we discuss the fluoride incorporation mechanisms, including diffusion vs dissolution-recrystallisation processes, and their implications for palaeo-environmental reconstructions based on fossil apatites.

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Crystallographic Control of Apatite Mineral Dissolution

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The dissolution of apatite has biological relevance as it is the mineral comprising bones and teeth, where unwanted dissolution causes problems such as enamel loss and osteoporosis.¹ The classical view of dissolution, where individual ions detach from the surface in a uniform manner, has recently been questioned as a suitable model in many situations.² Rates of dissolution vary depending on both the mineral surface features (e.g. proximity to defects and step edges, substrate structure and composition) and the solution properties (e.g. composition, flow rate, pH and temperature).³ Understanding how each variable affects mineral dissolution has widespread implications for medical science, in the sequestration of metal pollutants, and in preventing the formation of mineral scale.^{1,3,4}

Understanding how the crystallographic structure affects mineral stability can be understood through monitoring dissolution processes, and Atomic Force Microscopy (AFM) allows for in situ nanoscale observation of mineral dissolution at the mineral-fluid interface. In this work, we explore how the dissolution rate of natural (Durango) apatite is defined by the crystallographic orientation of the mineral, specifically the {001} and {100} faces. In addition, molecular dynamics simulations have been applied to determine how each exposed surface interacts with water and how this relates to the orientation-dependent stability.

(a)	(b)
(c)	(d)

Fig. 1: Durango apatite after exposure in 2 M HCl of (a,b) the $\{001\}$ face after (a) 59 minutes and (b) 78 minutes; (bottom) the $\{100\}$ face after (a) 30 minutes and (b) 49 minutes. Inset scale bars correspond to 1 μ m.

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SIMS investigations of recrystallisation of and diffusion in carbonate at low and high temperature

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Carbonates are important components of many sedimentary, metamorphic, and metasomatic rocks. They have been used ubiquitously for determining fluid composition in metamorphic and ore deposit environments, and estimating fluid composition and fluid origin. The trace metal and isotope composition of carbonate shells are a main stay of the paleotemperature scale. Dolomite crystals adjacent to a hydrothermal vein in a roof pendant in the Adamello batholith have epitaxial, up to 100µm thick recrystallization zones surrounding inherited dolomite marble grains. SIMS and NanoSIMS analysis of the recrystallised zones show lower δ^{18} O, δ^{13} C, and slightly higher Fe and Mn concentrations. δ^{18} O, and δ^{13} C isotope profiles were measured with SIMS, in part with spot sizes as small as 3µm. The Fe-Mn- profiles were measured using the RF-Hyperion source on a NanoSIMS with a beam size of ca. 200nm. Mn and Fe trace element profiles define a step function with a sharp boundary. Obtained oxygen profiles are symmetric and wider with respect to the sharper Fe/Mn boundary. All of the profiles are fitted well by simple diffusion profiles. On the same sample, we obtained similar diffusion times for O and C isotope profiles resulting in diffusion distances of 10-20µm. These can be converted to diffusion times of 1-5My, using available oxygen and carbon self-diffusion coefficients assuming a formation temperature of about 550°C. In contrast, diffusion distances of 170-300nm were obtained for the Fe/Mn diffusion distances. Translating these distances into times at 550°C results in unrealistic small times of ca. 1 year! Given the scale of the obtained diffusion profiles we investigated the effect of the 200nm beam size on the profiles fitting a measured Al profile obtained on a nominally sharp Al-Si metal boundary. The result obtained is slightly smaller, but within the uncertainty of the smallest dolomite profiles measured, suggesting that the profiles might indeed be purely a result of the beam size; indeed Fe/Mn profiles might be sharp on a much smaller scale. The isotope diffusion profiles yield geologically meaningful results, while those of the Fe/Mn not. Assuming that the experimental values of the diffusion coefficients are of the correct order of magnitude, this suggests that additional parameters (not just T, P) need to act to slow down Fe/Mn diffusion by many orders of magnitude. These could be a required deformation of the lattice due to volume change (resulting in pressure gradients, for example), or the presence of solid solution mixing gaps, for example. Further research will show, if self-diffusion coefficients of isotopes can be used more reliably for time estimates than tracer diffusion coefficients.

In parallel, we have started experiments on the recrystallisation and the diffusion of isotopes and trace metals in 1abiogenic and biogenic calcites (foraminifera) at low temperature (<100 °C) in autoclaves. Experiments took place over days–months in ¹⁸O-enriched fluids (up to 1000 ‰_{VSMOW}) at calcite saturation. Two distinct periods of recrystallization are identified: (1) rapid recrystallization during the first days followed by (2) a gradually slowing exchange reaction as the experiment progresses. This documents that recrystallisation, at least in biogenetic calcite, shows a change of mechanism. NanoSIMS and TEM analysis are being used to clarify the mechanism.

Real-time, in situ investigations of solid-fluid reactions by fluid-cell Raman spectroscopy

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Information about the mechanism(s) of fluid-driven phase transformations is usually obtained by ex situ analyses of the reaction products after quenching the experiments. Ex situ experiments, however, deliver mineralogical and textural information only after the sample has been cooled down to room temperature and dried so that it is often difficult to gain information about the dynamics of the alteration process. To overcome such drawbacks, we have applied in situ and real-time hyperspectral Raman spectroscopic imaging to investigate the corrosion of borosilicate glasses and the replacement of celestine by strontianite. Using Raman spectroscopy, structural and chemical information can be obtained such as, e.g., interfacial strain, phase composition of binary solid solutions, concentrations of aqueous oxo-anions and their speciation (often pH sensitive) at the solid-fluid boundary. For the in situ investigations, we designed and built special fluid cells that allow measuring the formation of the reaction product(s) and the solution with the direction of the laser beam parallel to the direction of the reaction front plane with a lateral resolution in the order of 5 to 10 µm. With this setup, the dynamics of the respective process could be studied. For example, we will report in situ fluidcell Raman spectroscopic experiments that provided unprecedented real-time insights into reaction and transport processes during the aqueous corrosion of a borosilicate glass in a carbonate solution at 85.2 ± 0.2 °C (Geisler et al. 2019). The formation of a several micrometrethick water-rich zone between a silica-based surface alteration layer (SAL) and the underlying glass, interpreted as an interface solution, is detected, as well as pH gradients at the glass surface and within the SAL. By replacing the solution with a deuterated solution, it is observed that water transport through the SAL is not rate-limiting. This was possible since the stretching vibrations of D₂O are significantly shifted towards lower wavenumbers, so the D₂O diffusing through the SAL could be quantified. The in situ data supports an interface-coupled dissolutionreprecipitation process for SAL formation during glass corrosion as suggested by Geisler et al. (2015). Since the incorporation of ¹⁸O in solid and aqueous species causes new isotopologue bands, the ¹⁸O concentration in the aqueous and solid phases can also be quantified (Geisler et al. 2012). This allowed us to in situ study the time- and space-dependent re-equilibration of strontianite replacing a celestine crystal in a Na₂CO₃ solution at room temperature by Raman spectroscopy. We observe a change in the reaction kinetics when the solution was (super)saturated with strontianite, i.e., when strontianite starts to precipitate at the surface of the dissolving celestine. This change points to an autocatalytical effect, i.e., the product phase expedites the dissolution of the parent phase. In general, fluid-cell Raman spectroscopic experiments open up new avenues for studying solid-water reactions, with the ability to in situ trace specific sub-processes in real time by using stable isotopes.

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Iron Oxide Recrystallization Mechanisms Captured by Atom Probe Analysis of Isotopic Tracers

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Iron oxides are dispersed throughout Earth's surficial environment and their propensity to recrystallize in aqueous solutions determines whether these minerals are a source or sink for critical trace elements in geological systems. Under reducing conditions, Fe(III) oxides commonly co-exist with aqueous Fe(II) (Fe(II)_{aq}), which accelerates recrystallization by coupled electron transfer and atom exchange. The cryptic nature (i.e., no phase or compositional change) of such Fe(II)-catalyzed recrystallization and the nano-particulate character of iron oxides makes it challenging to quantify the extent of the mineral phase that exchanges its structural Fe(III) atoms with Fe(II)_{ad}. Recrystallization models with isotopic tracers are often used but these may yield disparate results depending on their assumptions of whether, and to what extent, the recrystallized portion of the mineral continues to interact with the solution. Atom probe tomography (APT) is capable of resolving the 3-dimensional isotopic composition of a mineral at the sub nm scale and thus is a critical tool for probing the recrystallization mechanism(s) of nanoparticulate minerals. Here, we react goethite nanoparticles with ⁵⁷Feenriched Fe(II)_{aq} for 30 days at pH 7.5 and describe a method to prepare and analyze these samples by APT. The 3-dimensional distribution of the tracer isotope from APT reconstructions is used to determine the extent and mechanism of recrystallization.

The encapsulation of nano-particulate goethite grains in ZnO by atomic layer deposition vielded a robust matrix for specimen fabrication and APT analysis. APT reconstructions reveal that the recrystallization of goethite is exceptionally complex. In some cases, APT reconstructions show that the ⁵⁷Fe tracer is dispersed throughout the particle with the fraction of ⁵⁷Fe values close to the value expected for a completely mixed system. Therefore, the majority of the solid appears to have undergone recrystallization via exchange with Fe(II)_{aq}. The tracer isotope penetrated >10 nm into the goethite in most cases. Although the isotopic distribution of the tracer isotope is heterogeneous at the nano-scale, the variation in the isotopic composition was small. Proximity histogram analyses revealed that the isotopic composition of goethite is consistent with the isotopic values measured by ICPMS after the sequential dissolution of bulk goethite powders. Hence, bulk dissolution of goethite in strong acids reasonably approximates a layer-by-layer removal of surficial Fe atoms and may be a useful estimate of the distribution of tracer isotopes or trace elements in these phases. Our results demonstrate the utility of encapsulation for the APT analysis of nano-particulate goethite, and may be extended to study recrystallization processes in other nano-phase minerals. The significant amount of recrystallization observed here suggests that structurally-compatible elements (e.g., Ni²⁺) may incorporate deep into the bulk structure or can be redistributed from iron oxide crystals to their surfaces and then released to solution during Fe(II)-catalyzed recrystallization.

When is an equilibrium thermodynamic approach applicable?

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Metamorphic rocks provide records of the way the outer part of the Earth works, but that record is incomplete and needs to be decoded. Conventionally, interpretation of the metamorphic record uses the assumption of thermodynamic equilibrium at a point or points during the metamorphic evolution. The outcomes have been the values of parameters such as pressure, temperature, and fluid composition, which have led to reconstruction of the thermal and physical structure of the Earth and the processes that affect it. However, the validity of the equilibrium concept has been questioned, and the underlying assumptions must be scrutinised carefully if we are to interpret the fragmentary geological record properly.

Here we investigate these assumptions through an exploration of conceptual models that describe the progression evolution of rocks through a generalised, idealised, regional metamorphic example terrane, from burial to exhumation. The conditions that drive formation of structures, microstructures, mineral compositions, and mineral assemblages, and the potentially different conditions that those features preserve are discussed, along with the implications for application of equilibrium thermodynamics to mineral assemblages. Finally, we discuss the use of dimensionless numbers as a way to quantify the probability that the features of interest can be considered as records of equilibrium or non-equilibrium processes.

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Crystallization and re-equilibration in copper-sulfides – insights from the mineral replacement of chalcopyrite by digenite/covellite

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Primary and secondary copper sulfides such as chalcopyrite (CuFeS₂) and digenite (Cu_{1.8}S)/covellite (CuS) constitute an important group of copper bearing ore minerals. In hydrothermal (180° C - 300° C) copper-rich acidic solutions (CuCl₂ + H₂SO₄), chalcopyrite undergoes mineral replacement to digenite/covellite (Sequeira et al., 2008). The replacement follows a coupled dissolution and reprecipitation mechanism with pseudomorphic replacement of primary chalcopyrite by digenite and a porous layer of covellite in the rim (Fig. 1). We have systematically studied the evolution of aqueous Cu and the mineral during the replacement process using in-situ synchrotron XAS and a ⁶⁵Cu isotopic tracer. In-situ synchrotron XAS experiments revealed the fast reduction of $Cu^{2+}(aq)$ to $Cu^{+}(aq)$ and $Fe^{3+}(aq)$ to Fe^{2+} (aq) in the solution. To understand the reaction mechanism and the extent of fluidmineral exchange during the replacement process, a solution enriched with ⁶⁵Cu was used in a set of hydrothermal experiments and the isotopic composition of mineral grains were analyzed by NanoSIMS. Isotopic mapping revealed elevated ⁶⁵Cu/⁶³Cu ratios in the reprecipitated digenite and covellite phase indicating fluid driven exchange. A set of time series (30 mins – 50 hours) experiments revealed distinct zones of elevated ⁶⁵Cu/⁶³Cu ratio from the reprecipitated rim to the chalcopyrite core in shorter run durations and a homogenous ⁶⁵Cu/⁶³Cu distribution in longer run duration. The redistribution of the ⁶⁵Cu/⁶³Cu ratio with the run duration is suggestive of significant mineral-fluid re-equilibration with time. In lower temperature experiments (180°C - 220°C) distinct zones of elevated ⁶⁵Cu/⁶³Cu in the reprecipitated digenite/covellite phase extending to the chalcopyrite core, both of these observations are suggestive of porosity – both internal to chalcopyrite and generated during the replacement reaction as the key driver of mineral-fluid exchange and aiding diffusion of ⁶⁵Cu across the replacement rim.

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Figure 1. Optical image showing the pseudomorphic replacement of chalcopyrite (yellow core) by digenite and covellite (porous rim), from an experiment at 200 C with 4 hour run duration.

Chalcopyrite core

Digenite/Covellite rim

Figure 2: HSI maps showing the distribution of ${}^{65}Cu/{}^{63}Cu$ ratios across the chalcopyrite core and digenite/covellite rim as function of run duration, the numbers on bottom of the image show the numerical value of the ${}^{65}Cu/{}^{63}Cu$ ratio and its corresponding color on the map.

Effect of Metal Substitutions (Al, Ni) on Fe(II)-Catalysed Recrystallisation of Goethite

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Goethite (FeOOH), an abundant iron oxide mineral in Earth's surface environments, is highly stable and insoluble under oxidising conditions. However, in the presence of aqueous Fe(II), which is soluble under reducing conditions, goethite undergoes extensive and rapid recrystallisation. Such Fe(II)-catalysed recrystallisation occurs via coupled dissolution-reprecipitation reactions between structural Fe(III) and aqueous Fe(II), with no secondary mineral phase transformation. Natural goethite commonly hosts metals within its mineral structure (up to several wt%) but it is unknown how these substitutions affect goethite recrystallisation. Here, we investigate the relationships between Al substitution in goethite, the extent of Fe(II)-catalysed recrystallisation, and Ni release. We synthesised several Alsubstituted goethite samples (0 – 5 mol%, Al co-precipitated with Fe) and one sample with co-substituted Al and Ni (1:1 mol%), all with fixed crystallinity. These were reacted in ⁵⁷Fe enriched aqueous Fe(II) solutions for 60 days at pH 7.5. Before and after reaction, the goethite was sequentially dissolved to reconstruct the distribution of Al, Ni and ⁵⁷Fe in the crystallisation and metal concentration including Ni release.

Results indicate Fe(II)-catalysed recrystallisation of goethite is indeed inhibited by metal substitution, and that Ni has a greater inhibitory effect than Al. After 14 days of reaction, the un-substituted control goethite undergoes \sim 72% recrystallisation, compared to \sim 65% recrystallisation for the 1 mol% Al-goethite sample, and just \sim 30% for 1 mol% Ni-goethite. The higher solubility of Ni may inhibit recrystallisation more than Al because it can be released into solution and then redistributed onto the surface of goethite, limiting interaction with aqueous Fe(II). Understanding the controlling mechanisms of goethite recrystallisation is important for environmental issues such as the mobility of metals hosted within the goethite, as they may act as either essential nutrients or toxic contaminants. Predicting the amount of metal release from Fe(II)-catalysed recrystallisation of goethite has the potential to assist in environmental planning or remediation efforts of a relevant area.

Processes and Mechanisms of Giant Quartz Reef Formation Part 1: Observations

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Giant quartz reef formations are found worldwide, with exposures upwards of tens of metres wide and several kilometres long. While several studies have looked at answering specific elements regarding the formation of these phenomena, there remains the unresolved question regarding the complete set of criteria which defines giant quartz reef formation within a specific framework of space and time.

Large exposures of quartz reef exhumed along the Heyuan fault, South China, provide an excellent example to study the interplay between dissolution/precipitation, mixing of metamorphic and meteoric fluids and tectonics through observations of plastic deformation, fracturing, crystallisation, microstructure, geochemistry and hydrology. A multi-scale approach is used here in order to take into account information from outcrop fracture mapping to understand the apparent contradiction between idiomorphic 5 cm long quartz crystal growth in mode I fractures embedded at large scale inside far from thermos-mechanical equilibrium fault zones with mylonitic and cataclastic microstructures. Additional geomechanical, geochemical and hydrological analyses aid the investigation to provide a multi-disciplinarily insight into the feedbacks of chemo-mechanical processes operating during quartz reef formation.

The contrast between far from equilibrium macro-scale condition and local equilibrium crystallisation is proposed to be resolved by following conditions for the formation of a massive quartz reef: (1) A geodynamically slow macroscale opening displacement to provide the driving force for abundant endothermic fluid release as well as dissolution reactions and delivering mode I accommodation space for idiomorphic quartz crystal growth (each around ~5 cm long) from both sides of the opening displacement direction; (2) An optimum temperature window ~200-350°C providing conditions for dissolution reactions; (3) A phyllonitic cap rock seal in order trap the fluids and maintain fluid overpressures supporting mode I fracture opening with progressive normal faulting. VPSE microscopy also identifies a later cataclastic overprint with neo-crystallisation of quartz in brittlely deformed fracture zones suggestive of an episodic slow-ductile and fast-brittle interplay. The above described model may be understood as the extended brittle-fault valve mechanism, including additionally ductile deformation and dissolution/precipitation processes.

Processes and Mechanisms of Giant Quartz Reef Formation Part 2: Model of the Dynamics

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In our companion presentation in part 1 we have presented an observations to propose a model where the dynamics of giant quartz reef formation is caused by fluid release and precipitation in the metamorphic equivalent of Sibson's brittle 'fault valve' mode. Here we present a theoretical model compatible with the observation of oscillatory multiscale far from equilibrium conditions followed by long periods of macro-scale far from equilibrium conditions supporting a local equilibrium. The model can in particular describe mechanisms of abundant SiO₂ dominated fluid releases reaching episodically above hydrostatic pressures followed by long periods of SiO₂ precipitation, allowing growth of up to 5 cm long idiomorphic quartz crystals in subparallel open channels, which presumably were held open by lithostatic fluid pressures.

In this interpretation, the observations instabilities are seen to stem from the multi-scale and multiphysics of the mineral reactions at the brittle-ductile transition, promoted by a slow extensional geodynamic driver at the Heyuan fault. The new approach allows interpretation of rock physics properties in terms of recently discovered Thermo-Hydro-Mechanical-Chemical (THMC) cross-diffusion waves, which rely on the previously overlooked coupling of THMC processes across scale. In this approach instabilities can be characterized by critical conditions of the product of a THMC self-diffusion- with a THMC cross-diffusion matrix. These conditions give rise to short wavelength cross-diffusional chemical dissolution-precipitation reaction waves bouncing between the phyllonitic cap rock and the mylonitic shear zone below. A resonance phenomenon of constructive interference in a finite width around the future quartz-reef triggers the long-time scale steady-state attractor allowing quartz reef growth over geodynamic time scales. We show that this solitary wave limit forms a standing wave and matching the characteristic periodic pattern of mode I quartz veining around the reef and also explaining the fluid overpressures leading to local hydro-fracturing.

Future work will be to test the new approach in carefully calibrated laboratory ex-situ experiments in X-Ray and Neutron beam transparent flow and deformation cells to study the dynamics of mineral reactions under loading. The subsequent step would be to extend the experiments to develop digital rock physics models to the full range of in-situ properties and assess their changes on the time- and space- scale of fluid flow through a chemically reacting deforming specimen in the lab to the scale and lifetime of making an entire quartz-reef mineral factory.

Reprocessing of Chondrules during Early Solar System Evolution

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Chondrites are the most primitive rock samples from the Solar System available for direct study in the laboratory. Chondrules are an essential component of all primitive meteorites and are among the oldest known solar system materials. They provide unique constraints on the conditions that prevailed in the protoplanetary disk and the processes that led to the formation of solids that accreted to from planetesimals and subsequently planets. Almost all primitive meteorites contain chondrules indicating that the chondrule forming process was prevalent in the protosolar nebula and, by extension, possibly in all protoplanetary disks. Time constraints using the ²⁷Al-²⁶Mg chronometer yield a narrow range of formation ages that started ca. 1.7 Myrs after the beginning of the solar system and lasted for little more than 1 Myrs (Pape et al., 2019). Thus chondrule formation seems to have been close to an instantaneous event. In addition to the melt-formation that is associated with the chondrule forming process, many chondrules, but not all in a given chondrite sample, show effects that indicate partial equilibration under new and different chemical and physical conditions. This partial reprocessing affected some chondrule prior to incorporation into their parent body and was followed by some metamorphic overprint on the parent body. Texturally it is possible to distinguish between high-T reprocessing via partial melting of chondrule and apparent low-T alteration by aqueous (?) fluids, although no trace of this fluid seems to be preserved.

The two figures show representative examples for high- and low-T alteration:

Replacement of glass (dark grey) by fine- Resorption and new crystallization via melt grained porous mesostasis (intermediate grey) (image 500µm)

Since not all chondrules in a given chondrite show signs or alteration or reprocessing and hydrous alteration and partial re-melting must have occur under dramatically different thermal regimes and within a short interval. This implies that chondrule formation occurred by several thermal pulses, followed by rapid cooling and subsequent accretion of the solid material in planetesimals. The observed reactions record different stages in the thermal and chemical evolution of the solar nebula and attest to a highly dynamic and rapidly changing thermal and chemical environment that affected the chondrules.

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Different modes and time-lines of alteration in

carbonaceous chondrites

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Meteorites provide invaluable evidence of formation and alteration processes active on their parent body and the prevailing solar system environment at the time at which they were extracted. Carbonaceous chondrites provide specific information into the role of volatiles in the early solar system and have become increasing important in understanding the evolution of the planets and their atmospheres. This study explores the different types of volatile processes that can occur in the early solar system by examining the microstructures, microtextures and elemental composition of three carbonaceous chondrites; CV NWA 3118 and two CMs – Murchison and Sutter's Mill. All three chondrites have undergone some amount of alteration. These samples were analysed using traditional methods SEM-EBSD, and micro-XRF but also a new method – the FEI Teneo Lovac FEG-SEM with dual Bruker Series 6 detectors, a "NanoMin". From the results, a possible sequence of alteration events can be established and we suggest a time-line of chondrule and chondrite formation plus alteration processes on their respective parent bodies. The observed microstructures and mineral characterisation also provide criteria to assess whether the chondrites preserve primary formation or secondary alteration processes.

NWA 3118 provides insight into predominantly primary formation features, such as chondrule formation processes whether it be amalgamation or agglomeration and the associated interaction between the newly formed chondrules and matrix. From the NanoMin analysis, matrix grains generally do not have a pervasive petrofabric alignment; however, inbetween the chondrules there is a very weak alignment present, which is further amplified with the 'agglomerations' (Fig. 1). These 'agglomerations' have a flow-like appearance and coalesce in-between the chondrules. The chondrules do not display any shock metamorphism features. It is interpreted from this work and results from Bland et al., (2014) that during chondrite formation, the chondrules acted as 'heat sinks', while the matrix absorbed any formation related stress. The matrix remained relatively unaffected; however, the 'agglomerations' coalesced around chondrules, demonstrating they were still ductile and probably cooling during this process (Akos et al., 2014). In comparison, the microstructures seen in Murchison indicate alteration on its parent body and multiple additions to the chondrite, such as independent ameboid olivine aggregates (AOA) morphologies compared to

the overall chondrite preferred orientation and evidence of fluid activity. Sutter's Mill underwent the same early processes as Murchison; however, its highly unusual lithology is attributed to potential asteroidal mixing. Sutter's Mill is also more homogenous than Murchison which indicates Sutter's Mill underwent further re-crystallisation from potential thermal metamorphism at higher temperatures. Zolensky et al., (2014) suggested that the current observed mineralogy of Sutter's Mill can be attributed to thermal metamorphism that transformed phyllosilicates to fine-grained olivine, tochilinite to troilite, during which carbonates were destroyed. In this study, NanoMin analysis did not detect any carbonates and thus supports this interpretation. These overall results document the range of fluid-mineral interaction that occur both during chondrite formation and while on the chondrite parent body itself. They suggest extensive fluid – temperature – compositional variations are occurring on these bodies before samples arrive to Earth.



Figure 1: Annotated analysis from NanoMin Region of Interest 2. A - BSE analysis of the smaller scale map locations. B - Site 2 - BSE analysis of Chondrule 3 and the coarse-grained matrix. C) Site 3 - Small scale analysis with false coloured meteorite recipe applied on the BSE map in Chondrule 4. D) Site 4 - Small scale analysis of matrix between Chondrules 3 & 4. Green - enstatite zoning. Yellow - outline of coarse grained rim. Blue - outline of agglomerations. MX - matrix, EN - enstatite, FA - fayalite, FO - forsterite, PY - pyrite, MS - mesostasis

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Studies of water on Earth and in the asteroid belt

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It is increasingly accepted that the fast diffusion of water in glass renders measurements of melt inclusions suspect except in very small tephra. Therefore there is much interest in the use of water measurements in nominally anhydrous minerals such as clinopyroxene and application of a partition coefficient as an alternative means to estimate magmatic water contents. Having experimentally determined appropriate partition coefficients we have calibrated water measurements on the SHRIMP SI against both FTIR and Cameca 6f measurements on independently analysed minerals. Adetailed study of clinopyroxenes from the Azores islands demonstrates the potential of this mineral to provide accurate estimates of magmatic water contents and shows that the Azores islands reflect mantle wet-spots within an overall damp area of the upper mantle. Analyses of clinopyroxene from sub-arc mantle xenoliths shows that the arc lithosphere retains significant amounts of water in addition to an arc trace element signature. Clinopyroxene from continental flood basalts suggest that these lavas have similar water contents to arc lavas and could be derived from ancient sub-arc lithospheric domains.

It has often been postulated that Earth's water was at least in part, derived from carbonaceous chondrite meteorites, many of which contain abundant evidence for aqueous alteration. However, the age of this alteration is not well constrained and one recent model suggests that their parent bodies are frozen mud balls. A suite of carbonaceous chondrites has been analysed for U-series isotopes revealing extensive disequilibria that could be explained by fluid movement within the last 1 Myr or less. This could have been triggered by the impacts that broke these meteorites off their parent bodies.

Rare earth elements in olivine: A litmus test for diffusion studies?

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The concentrations and distribution of trace elements in rock-forming minerals is increasingly being used to decipher the petrological and temporal evolution of Earth and planetary materials. Appropriate application of such geochemical data requires knowledge of the rate and mechanisms of element transport through minerals, which largely derive from experimental testing of element diffusion in minerals under controlled conditions of pressure, temperature and chemical potential. Experimentally-determined diffusivities are available for many elements in many common and accessory minerals, but - at least in some cases - there is significant discrepancy between the experimental results and constraints from natural rocks (e.g., U-Pb in titanite; Spencer et al. 2013). There are also very large discrepancies between some experimental studies, such as our previous work on REE diffusion in olivine (Spander et al. 2007; Spandler and O'Neill 2010) and that of Cherniak (2010).

Here we attempt to resolve the differences between the published studies of REE diffusion in olivine, which in turn provides insight into the suitability of experimental determined diffusivity data for natural rocks. We present results from a series of one-atmosphere experiments to; 1) define solubility limits for REE in forsteritic olivine, and; 2) better understand the rates and mechanisms of REE diffusion and incorporation in olivine.

REE solubility experiments

A series of experiments were conducted between 1300 and 1520 °C with forsterite in varying compositional systems (MAS +La, CMS +La, CMAS +REE). Experiments in the MAS and CMS systems were conducted over a range of La contents from 1% to 47% to check for La solubility limits in forsterite. Overall, REE incorporation into olivine is consistent with expected element partitioning behaviour with varying ionic radius. Saturation in a REE phases in the experiments allow us to calculate maximum solubility limits of La in forsterite to be around 12 ppm and 2 ppm at 1400 °C and 1300 °C, respectively. Likewise, maximum Nd and Y contents of forsterite at 1300 °C are ca. 40 ppm and ~1100 ppm, respectively. For La and Nd, values are close to, or well below the limits of detection of Rutherford Backscattered Spectroscopy (RBS), which is the analytical technique used by Cherniak (2010) to measure REE diffusion profiles in olivine.

REE diffusion experiments

Diffusion experiments were carried out on both synthetic Mg₂SiO₄ (forsterite) and natural San Carlos olivines (\sim (Mg_{0.9}Fe_{0.1})₂SiO₄), with a variety of REE diffusant sources. The diffusant sources were chosen to replicate the experiments of Cherniak (2010) using REE aluminates, but also to investigate whether using alternative sources made any difference to diffusion rates. The sources were synthetic powders comprising single REE compositions LaAlO₃, NdAlO₃, Gd₃Al₅O₁₂, YAlO₃ and Y₃Al₅O₁₂, plus a solid solution based on (La,Pr)AlO₃ doped with Eu, Tb, Ho, Tm and Lu. For comparison, we also studied a REE silicate source based on (La,Pr)₂Si₂O₇ and doped with the same elements.

All experiments were run at 1300 °C, and diffusion profiles measured by scanning LA-ICP-MS, as well as EPMA (for Y). All measured profiles conform well to that expected of the diffusion equation. Values of log D_{REE} fall between -14 and -15.6, which is consistent with our previous results (Spandler et al. 2007; Spandler and O'Neill 2010) but is 4-5 orders of magnitude faster than the results of Cherniak (2010). Precision on our log D values is better than 0.1, except for La and Pr (SD <0.24), due to the low concentration of these elements in

olivine, and, hence, decreased analytical precision of profile measurements. REE diffusion in San Carlos olivine is also faster (by log D of ~ 0.2) than in the synthetic forsterite.

The most important outcomes of our new experimental results are:

- 1. We achieve similar REE diffusivities in olivine regardless of whether we use an olivinemelt couple (e.g., Spandler et al 2007; Spandler and O'Neill 2010), or a synthetic REEdoped powder source (this study). This means that the vastly differing measured REE diffusivities of our studies and that of Cherniak (2010) are not due to the experimental design of diffusant sources, as was previously claimed (Burgess and Cooper 2013).
- 2. Low solubility of REE in olivine precludes use of RBS to measure a wide suite of REE in olivine under condition of relevance to natural rock systems. We suggest that the nm-length profiles measured by Cherniak (2010) may relate to surface defects or other features that are of limited relevance to element transport through minerals in nature.
- 3. Our findings for REE diffusion in olivine raise concerns about the applicability to nature of other element diffusivity studies where chemical activities are not controlled, and/or nm-scale profiles were measured by RBS (e.g., REE in feldspar, fluorite, pyroxene, calcite, zircon, xenotime, garnet; Pb in rutile, zircon, titanite, pyroxene, xenotime, etc).

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A Nonlinear Theory of Structures in Layered Intrusions

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Lavering is common in many intrusions, for example Stillwater, Skaergärd and the Bushveld. The explanations for layering are many and diverse but most depend on hypotheses centred around (episodic) crystal settling to form a crystal mush at the base of an intrusion and/or multiple intrusive events. The precise form and distribution of layering developed by such mechanisms are not explained by these hypotheses. We explore a nonlinear process for layering formation in which strong coupling exists between magma flow, mineral reactions and diffusion processes during cooling of the Bushveld complex. The process we explore is shear banding which is well documented in polymer melts and a range of other fluid/solid mixtures. Shear banding takes two forms, namely, gradient banding where layering develops parallel to the shearing plane during simple shearing, and vorticity banding where layering develops normal to the shearing plane and parallel to the shearing direction. Superimposed on this classification in some systems is a concentration dependence on strain rate. The Bushveld layering appears to be a form of gradient banding with concentration dependence. Shear banding of the type discussed here is a phase transition whereby an initially homogeneous suspension spontaneously separates into layers once a critical shear strain is reached. The phase transition is driven by a compositionally dependent viscosity. Microstructures, geometry and organisation of layering and associated structures in the Bushveld are consistent with the layering originating as shear band instabilities in a shearing crystal mush. This includes the multifractal geometry, splitting and coalescence of layers, "pot-holes" and viscous fingering. Any further progress relies on establishing the detailed geometry, and hence the dynamics, of the layers.

The influence of metamorphic reactions on localisation of deformation.

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The conditions for localisation of deformation in a viscoplastic material always involve some form of softening of the material as it deforms. The softening is defined by a softening modulus,

 $h = \left(\frac{\partial \sigma}{\partial \varepsilon}\right)_{\tau, \dot{\sigma}}$, which measures the way in which the stress, σ , changes with increasing strain, ε ,

at constant temperature, T, and strain rate, $\dot{\varepsilon}$. However softening, although necessary for localisation is not a sufficient condition. In order to localise, the softening must exceed the

intrinsic strain rate hardening, measured by the strain rate sensitivity, $m = \left(\frac{\partial(\log \sigma)}{\partial(\log \dot{\epsilon})}\right)_{T} > 1$,

which is a feature of all power law materials with stress exponent, N > 1. The critical condition for localisation is $\lambda = \frac{m(\sigma - h)}{\sigma} \ge 0$ where λ is a measure of the growth rate of the shear band;

at this critical condition the amplification of any incipient shear zone becomes positive and the shear zone grows in amplitude. Below this condition any incipient shear zone decreases in amplitude. In this paper we explore various modes of softening and strain rate hardening but concentrate on two examples: (1) softening induced by recrystallisation of alkali-feldspars + quartz + mica during deformation and (2) softening during recrystallisation and serpentinisation of olivine. We show that a change in the standard deviation of a grain size distribution influences m and hence influences the conditions for localisation.

In order to proceed, we invoke a thermodynamically based logarithmic mixing law that describes the bulk constitutive behaviour of mixtures of deformation mechanisms and of mineralogies with a range in grain sizes. This enables the stress strain curve for the bulk material to be followed during recrystallisation and/or mineral reactions and hence for the evolution of σ , h and m to be tracked along with identification of the critical conditions for localisation.

We discuss the conditions for localisation in a granitic lower crust and for the initiation of subduction zones in the oceanic lithosphere. In particular, one can define a critical (cool) lithospheric geothermal gradient for deforming/reacting lithosphere that enables a throughgoing shear zone to develop as mineral reactions proceed.

Physical and chemical dynamics of hydrothermal systems: non-linear interplay of transport, dispersal and reactivity

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Fluids are frequent and essential agents in phase transformations, mineral reactions and mass transfer. In many geological settings the fluid-rock interaction occurs in response to physical or chemical gradients, and approaches full spectrum of reaction mechanisms from continuous local equilibrium to metastable disequilibrium. Local equilibrium approaches, embodied in transport theory or reactive flow models, assume equilibrium of all components in a homogeneous, textureless chemical system. By contrast, chronometric investigations of mineral-fluid reactions (Camacho et al. 2005; John et al. 2012; Taetz et al. 2018) show that these processes may be extremely rapid and episodic, or controlled by local chemical environment or mechanical anisotropy (Centrella et al. 2015, 2018). On these temporal and spatial scales, mechanically or chemically induced gradients, solute advection or dispersal may effectively compete and selectively control fluid-mediated mass transfer and reactions in rock environment. We use mass-conservation approach to system of interest and evaluate contributions from advection of chemical species by fluid, reaction with host environment, and lateral dispersion and diffusion (cf. Ague 1998). These phenomena operate on characteristic length and time scales, known by experiments, and can in turn provide insight into dynamics such as flow, diffusion and rates or continuous vs. episodic evolution of mineral-fluid reactions.

Mineral replacement or precipitation reactions are recorded by hydrothermal alteration or veining, respectively. The extent of reaction, hence the intensity of alteration, are mainly related to magnitude of disequilibrium at the reaction site. The magnitude of disequilibrium between the hydrothermal fluid and the host environment is determined by: (*i*) overall temperature and pressure gradient along the fluid flow path, (*ii*) unreactive infiltration from a distinct environment where the fluid was sourced (temperature, pressure, distinct lithology) thus inducing disequilibrium, and (*iii*) variations inside the system of interest, which induce transport by dispersion and/or diffusion. Hydrothermal systems dominated by each of these three mechanisms have been described previously, but virtually no attempts were presented to illustrate on what scales these mechanisms may interfere and how they bias our estimates of fluid fluxes and reaction mechanisms.

Consider control volume of interest subject to the mass conservation (e.g., Steefel and Maher 2009): $a(x) = a^2(x)$

$$\frac{\partial(\phi c_i)}{\partial t} = -v \frac{\partial(\phi c_i)}{\partial x} + D \frac{\partial^2(\phi c_i)}{\partial x^2} + \phi R_i$$

where c_i is solute concentration (mol m⁻³), R_i is the reaction rate (mol m⁻³ s⁻¹), v is the flow rate (m s⁻¹), D is the combined diffusion-dispersion coefficient (m² s⁻¹), ϕ is porosity. Assuming equilibrium or steady state, that is, a time-invariant concentration of solute in the fluid, the right-hand side of equation becomes equal to zero. Since precipitation or replacement reactions represent a net result over duration of the hydrothermal event, the time-integrated mass-balance constraint becomes:

$$0 = -L\frac{\partial(\phi c_i)}{\partial x} + A\frac{\partial^2(\phi c_i)}{\partial x^2} + \phi c_i$$

where L is the length scale of alteration and A represents the characteristic area of diffusion and dispersion. Two limiting approaches are conventionally used to interpret the observed mass changes in the alteration domain: (*i*) the solute mainly originates outside the alteration site and has been introduced by advection (dispersive transport is negligible), or (*ii*) the material is of

local origin and has been redistributed internally (advection by the fluid is negligible). As a consequence, the first approximation provides the maximum estimate of the time-integrated fluid flux, whereas the second approach requires no fluid flux to explain the observed alteration or vein-selvage sequence.

In the systems dominated by chemical dispersion, longitudinal mass transport is responsible for redistribution of solute along the flow path and, consequently, leads to the formation of diffuse geochemical fronts and alteration zones (Ague 1998). Transerve transport may provide additional significant source or sink for chemical constituents, hence, diminishing chemical reactivity and preventing estimation of fluid flux. In the limiting case, the precipitation products originate from immediate surroundings and were formed in a stagnant pore fluid (no fluid flux). This mechanism is characteristic for Alpine-style mineralization and numerous vein assemblages in metamorphic terrains, where their formation by dissolution-precipitation is most likely assisted by transient gradients in stress field.

Advection-dominated hydrothermal systems are characterized by limited extent of dispersive transport with respect to the size of the system. This restriction can independently arise from (i) short duration of the hydrothermal event, or (ii) porosity anisotropy, specifically very small porosity in transverse direction. In this case, the mass conservation constraint can be used to convert the alteration intensity into the time-integrated fluid flux provided that the change in concentration over distance is known. In the advection-dominated systems, chemical reaction can be induced by two unrelated mechanisms: (i) temperature and/or pressure gradient, which affects solute-mineral equilibria along the flow path, or (ii) solute-mineral disequilibrium when a fluid enters the system. The first approach applies to slow fluid flow rates (e.g., dispersed metamorphic fluid flow) and settings with negligible variation in the host lithology, whereas the second one is characteristic for fast, possibly variable fluid flow rate, and promoted by changes in host rock lithologies.

Our analysis shows that interpretation of hydrothermal reaction dynamics requires coupling between environmental factors (e.g., time scale of hydrothermal event or fluid flow rate), observables (e.g., spatial scale of alteration), and intrinsic properties of the system (e.g., reaction rates or chemical diffusivity). Constructing a general factor-oriented classification scheme of hydrothermal processes should facilitate identification of the principal driving forces that define spatial and temporal scales of mass transport *vs.* reactivity.

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Timescale of mid-crustal fluid-mediated rock re-equilibration

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In the presence of reactive fluid, anhydrous igneous and high grade metamorphic rocks inevitably alter to secondary assemblages in response to the locally changed system composition – and if chemical equilibrium is attained also to the prevailing pressure and temperature conditions. Such fluid–rock interactions are important because they link mass and energy transfer with large-scale tectonic deformation, drive the formation of mineral deposits, carbon sequestration, and rheological changes of the lithosphere, and may even be linked with the emergence of life ¹⁻⁷. While spatial evidence indicates that fluid–rock interactions operate on length scales ranging from the grain boundary to tectonic plates, the timescales of regional fluid–rock interactions remain essentially unconstrained, despite being critically important for quantifying the duration of fundamental geodynamic processes.

Addressing this issue, here we investigate a locally equilibrated fossil hydrothermal system to define the boundary conditions for a numerical model that integrates mass conservation, local equilibrium thermodynamics, and advective-diffusive-reactive transport to constrain the timescale of fluid–rock interaction. Our modelling approach in combination with the field observations unequivocally indicates fast reaction front propagation through low-permeable serpentinite on the order of ~10 cm year⁻¹, equivalent to the fastest tectonic plate motion and mid-ocean ridge spreading rates. This reaction front propagation rate implies a transient, reaction-induced permeability increase by ~4 orders of magnitude, consistent with previous theoretical predictions ^{8, 9}. Consequently, in the presence of reactive fluids, large-scale fluid-mediated rock transformations in continental collision and subduction zones occur on timescales of tens of years, implying that natural carbon sequestration, ore deposit formation, and transient and long-term petrophysical changes of the crust proceed, from a geological perspective, instantaneously.

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Fate of fluid pathways during reaction in closed system

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The presence of fluid is required for replacement reactions to occur during metamorphism. The fate of fluid pathways strongly depends on solid volume change during reaction. Solid volume change indeed affects the porosity and can generate fractures by modifying the stress state in the rock. It can theoretically vary by up to several tens of percent during reaction in closed system. Determining how fluid is transported thus requires to estimate solid volume change and its impact on the evolution of fluid pathways. Here, I present results acquired on two natural samples in which reactions inducing large changes in volume occur: (1) serpentinisation with a positive change in volume and (2) eclogitisation with a negative change in volume. Sample (1) displays very limited changes in composition perpendicular to a serpentinisation front. The zoning in Al, Ti, V and Cr of the primary olivine is even preserved in the reaction products. We use clinopyroxene/magnetite inclusions initially parallel in olivine to estimate solid volume change during reaction. The deformation of the inclusions provides estimates of solid volume changes of approximately 60 %, that is close to the theoretical value of 50 % for reaction in closed system. Nanotomography reveals that the structure of serpentine and mineralogical processes at the nanometer scale allow to maintain fluid pathways while solid volume is increasing. We use numerical modelling to determine the consequences of preserving a nanoscale porosity for the overall rate of serpentinisation. Sample (2) records the incipient stage of eclogitisation. Amphibole composition and water content in garnet both indicate reaction in closed system. A decrease in pressure is recorded in parallel to fluid consumption. Numerical modelling suggests that a fluid pressure decrease by several tenths of gigapascals should occur during eclogitisation. Such a process could lead to brittle deformation and further fluid transport into the rock.

Probing Metal Transport in the Deep Earth Using Molecular Simulations

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Metals are transported within the deep Earth at high pressure and temperature by fluids possessing a complex chemical makeup. The hydration and complexation of metals in hydrothermal fluids are key processes controlling the mobility of elements in the Earth's crust, leading to the formation of ore deposits from which the World's supply of Fe, Mn, Ag, Au, Pd, Cu, Zn, Co, Pb, U, Mo is mined. Reliable knowledge of metal behavior in the deep Earth fluids is essential for understanding the enrichment, transport and precipitation of metals and the formation of ore deposits. In the past 20 years, a large amount of *in-situ* spectroscopic data, complemented by increasingly accurate *ab-initio* molecular dynamics simulations and geochemical modelling, have dramatically improved our understanding of the chemical processes of metal transport in the upper crust.

Ab-initio molecular dynamics (MD) simulations, whereby inter-atomic interactions are described by quantum mechanics, provide a means to determine the nature and stabilities of metal complexes under conditions that are beyond experimental practicality. This approach is made possible by the availability of high-performance computing resources and the implementation of density functional theory. We have tested this approach on Cu¹⁻², Au²⁻³, Zn⁴⁻⁶, Pd⁷, Pb⁸ complexing in chloride (Cl-)⁹ and bisulfide (HS-) rich aqueous fluids under extreme T-P conditions, and the behavior of Cu and Au in low-density vapor^{2,10} and CO₂ rich fluids¹¹. Encouraging agreement with experimental results demonstrates that *ab initio* MD simulations are able to provide quantitative energetic properties for metal complexation and hydration under hydrothermal conditions in fluids beyond experimental conditions.

In this presentation, I will summarize our recent studies that combine computational chemistry approaches with synchrotron-based X-ray absorption spectroscopy experiments to understand the thermodynamics of metal and ligands in ore-forming fluids. Coupled with experimental studies, the simulations give molecular-level insights into the chemical processes responsible for the formation of ore deposits.

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Integrating Evidence from Peridotite Mylonites and Earthquake Stress Drops to Understand Slip on Oceanic Transform Faults

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Earthquakes on mid-ocean ridge transform faults (RTFs) exhibit many of the most systematic and predictable behaviours known in seismology. On short time scales (hours to days) earthquakes on RTFs display extremely high levels of foreshock activity. On intermediate time scales (years) RTFs show the clearest evidence of quasi-periodic seismic cycle behaviour in the instrumental record. And on long temporal and spatial scales (decades & 100s of km) the size and frequency distributions of RTF earthquakes can be predicted from scaling relations dependent only on transform fault lengths and slip rates. However, despite the relative predictability of earthquakes on these faults, many facets of slip accommodation on RTFs remain poorly understood, including:

- the controls on the size and location of fully-coupled rupture patches,
- why portions of the deep fault zone (600°C-1100°C) slip seismically, while others are fully ductile, and
- why abundant microseismicity nucleates in the parts of the fault that are barriers to large earthquake propagation.

We explore the roles of fluids and fault zone damage in controlling along-strike variations in mechanical behavior and the occurrence of deep microseismicity on mid-ocean ridge transform faults (RTFs) by investigating (1) earthquake stress-drops determined from a year-long ocean bottom seismic dataset that captured the end of the seismic cycle on Gofar Transform Fault on the East Pacific Rise and (2) peridotite mylonites dredged from Shaka and Prince Edward Transform Faults on the Southwest Indian Ridge.

On Gofar Transform Fault, the largest earthquakes $(6.0 \le M_W \le 6.2)$ have repeatedly ruptured the same portion of the fault, while intervening fault segments host swarms of microearthquakes. These long-term patterns in earthquake occurrence suggest that heterogeneous fault zone properties control earthquake behavior. Using waveforms from ocean bottom seismometers that recorded seismicity before and after an anticipated 2008 M_W 6.0 mainshock, we determined stress drop for 138 earthquakes $(2.3 \le M_W \le 4.0)$ that occurred within and between the rupture areas of large earthquakes. Stress drops were calculated from corner frequencies derived using an empirical Green's function spectral ratio method, and seismic moments were obtained by fitting the omega-square source model to the low frequency amplitude of the displacement spectrum. Our analysis yields stress drops from 0.04 to 3.2 MPa with statistically significant spatial variation, including ~2 times higher average stress drop in the rupture patches (i.e. fault segments where the largest earthquakes occur) compared to fault segments that host swarms of microseismicity. We find an inverse correlation between stress drop and P wave velocity reduction, which we interpret as the effect of fault zone damage on the ability of the fault to store strain energy that leads to our spatial variations in stress drop. Additionally, we observe lower stress drops in the rupture zone following the M_W 6.0 mainshock, consistent with increased damage and decreased fault strength after a large earthquake.

The dredged mylonite samples show variable degrees of deformation, ranging from proto- to ultra-mylonitic textures. The most deformed zones of the mylonites are characterized by an increase in the proportion of fine grained (<10 micron) mylonitic shear bands composed of polymineralic mixtures of olivine, pyroxene, spinel and high temperature amphibole. The

textural characteristics of amphibole indicate that they crystallized during shear band development, while their high chlorine concentrations indicate seawater-peridotite interaction. Some olivine grain boundaries are irregular, displaying triangular or pyramidal etch pits that are filled with nano- to micro-metric amphibole, pyroxene and spinel grains. This suggests that dissolution/precipitation occurred during deformation due to fluid percolation along grain boundaries. Porphyroclasts contain subgrains, high aspect ratios, and internal misorientations crosscut by fractures, indicating that deformation occurred by a dislocation mechanism prior to fracturing. A subset of fractures provide evidence for cycles of brittle and ductile deformation, as they are sealed by high temperature amphibole and offset by the fine-grained shear bands. We suggest that permeability enhancement and fluid pumping during brittle deformation were responsible for grain size reduction and phase mixing, leading to ductile weakening of the peridotite. Empirical thermometers indicate that shear band creep and coarse grain fracturing occurred from 700°C to ~1000°C, above the 600°C velocity weakening to strengthening transition for olivine at geologic strain rates. We suggest that the fracturing of coarse grains was due to high stress accumulation during flow of surrounding weak and hydrated mylonitic shear bands.

From our seismic and geologic results, we propose that along-strike variations in mechanical behavior of RTFs originate from along-strike variations in fault zone damage. Higher degrees of damage lead to greater fluid-infiltration, and therefore enhanced fluid-mantle interaction. We interpret the fully-coupled rupture patches to be composed of dry oceanic lithosphere, whereas the intervening barrier zones are weaker, with abundant fluids and alteration phases. At temperatures greater than ~600°C, the mantle beneath rupture zones is more evolved, with >50% of weaker, hydrated mylonitic shear zones, while less evolved mantle with >50% lenses of coarse-grained peridotites, is found beneath the barrier zones. Thus, brittle and ductile behavior of RTFs both appear to be strongly influenced by the intensity of damage in the crust and the ability for fluids to access the deeper portion of the fault zone.

Equilibrium and disequilibrium crystallisation and melt segregation in kimberlitic melt inclusions from Monastery mine, South Africa

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The 89 Ma Group I Monastery kimberlite contains a suite of primary kimberlitic megacrysts of olivine, ilmenite, pyroxenes, garnet, phlogopite and zircon. Olivine contains <1 to 12 mm sized spherical to ellipsoidal melt inclusions comprising predominantly glass, phlogopite, serpentine, spinel, perovskite, ilmenite, \pm monticellite, \pm calcite and \pm clinopyroxene. Glass is commonly fresh but may show secondary alteration and devitrification in places (Howarth and Büttner, 2019).

Crystals and glass in the melt inclusions were shielded from contamination and alteration that commonly destroy textural and petrogenetic evidence for the evolution of kimberlitic magma. Therefore, the melt inclusions from Monastery mine do not only contain batches of uncontaminated kimberlitic or proto-kimberlitic magma from the source region close to the bottom of the SCLM (Howarth and Büttner, 2019) but also provide evidence for their crystallisation history in the source and during kimberlite ascent and emplacement.

The most abundant glass is mafic to ultramafic, and predominantly contains Mg, Si, Fe, and H₂O, in places with minor Na, Al, and K (Howarth and Büttner, 2019). Ca, Ti, K and Al are primarily contained in the crystalline phases perovskite, spinel, phlogopite and ilmenite. Some melt inclusions show \sim 20-300 µm sized globular domains of glassy material randomly distributed in the mafic/ultramafic glass. We refer to these domains as spherulites. The spherulites contain high proportions of CaO (\sim 12-35 wt%) and TiO₂ (\sim 1.6-11.5 wt%). Most, but not all, contain central Ca-Ti or Fe-Ti oxides crystals (perovskite, spinel, ilmenite), which commonly show skeletal habits. Some spherulites contain monticellite-rich olivine as a central crystal.

Glass/melt pools occupied by the Mg-Fe rich silicate glass show coherent domains with different FeO content forming high-Fe glasses (10-15 wt% FeO) and low-Fe glasses (3-9 wt% FeO). These domains show variably sharp or, over distances of ~10 μ m, diffuse boundaries. Skeletal and euhedral high-Fe serpentine (10-17 wt% FeO) is present only in the high-Fe glass domains.

The melt inclusions in megacrystic olivine from Monastery mine show several stages of melt segregation and crystallisation. At an early stage, potassium and aluminium were extracted from a primary kimberlitic melt during the crystallisation of euhedral phlogopite, which along crystal margins is ferrian, suggesting progressive aluminium depletion of the melt. The segregation of the Ca-Ti component formed spherulitic melt droplets from which subsequently perovskite, high-Ti spinel, ilmenite and, less commonly, monticellite-rich olivine crystallised. In a further stage, the residual Mg-Fe silicate melt segregated in high- and low-Fe melts. Iron-rich serpentine formed most likely as a metastable phase from high-Fe melt.

The skeletal shape of crystals associated with glassy spherulites and with high-Fe glass suggests rapid growth in an environment of strong supersaturation and undercooling, consistent with cooling during the ascent and emplacement of the kimberlite. Other spinel and perovskite crystals show euhedral habits, which may indicate equilibrium magmatic growth. This suggests that the segregation of Ca and Ti from the primary melt already took place in the kimberlite source, allowing the early crystallisation of euhedral crystals probably under equilibrium conditions. Only in few melt inclusions the Ca-Ti melt droplets still existed during kimberlite ascent and were preserved as spherulites after quenching. In melt inclusions where they are absent, the growth of Ca-Ti oxides may have entirely consumed segregated Ca-Ti-rich melt. Similarly, euhedral and skeletal high-Fe serpentine in high-Fe glass supports an early segregation of high-Fe melt that was consumed by progressive serpentine crystallisation.

The melt inclusions remain intact from their primary capture during megacryst growth in the SCLM and through much of their exhumation in the kimberlite magma. At, or close to, their near-surface emplacement level, olivine-hosted melt inclusions form radial expansion fractures and apophyses developing into a vein network through which some high- and low-Fe and residual melt is extracted at a time when melt segregation and crystallisation of the observed mineral assemblage already had taken place. Subsequent quenching of residual melt in melt inclusions and veins forming indicates a sudden drop in temperature at emplacement level, preserving the textures and phase compositions that document the textural and compositional evolution of the melt inclusions from the SCLM to the shallow crust.

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Serpentinization and carbon trapping in peridotite basements: New insights from reactive percolation experiments

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Serpentinization is an ubiquitous process that extensively modifies the geophysical, rheological, mineralogical and geochemical properties of mantle rocks exposed at the Earth's surface, from oceanic spreading centres to ophiolitic settings. It results from the penetration of (sea-)water into cooling/cooled mantle rocks, which triggers a suite of chemical and mineralogical reactions in addition to the hydration of olivine to serpentine, such as the oxidation of Fe(II) and reduction of water to di-hydrogen and/or the formation of carbonates when CO₂ is present in the system. Efficient serpentinization thus implies efficient renewal of fluids at the mineral-fluid interfaces. However, the formation of low density secondary minerals (e.g., serpentines) should clog flow paths and thus quickly hinder fluid pathways in the already low permeability mantle basement. To better understand the physical and chemical mechanisms allowing efficient serpentinization and their impact on reaction paths, we realized a series of reactive percolation experiments using the ICARE Lab flow-through systems (Géosciences Montpellier) over a range of PTX conditions similar to natural hydrothermal environments. The ICARE Lab flow-through systems allow measuring continuously permeability changes during experiments and sampling the outlet fluids passing through the sample. Rock and fluid samples before and after the experiments are characterized using a combination of structural, mineralogical and geochemical approaches (SEM, EBSD, TEM, TG, EPMA, ICPAES, ICPMS, HR utomography...). We review here the results of a series of experiments performed on peridotite analogues (sintered and pressed olivine cores) at different injection rates and for different fluid compositions (cationic content, salinity, pCO₂, pH) (Godard et al, 2013; Peuble et al, 2015a, b, 2018, 2019; Escario et al, 2018). We discuss the linkages between hydrodynamic processes and reaction rates, their effects on serpentinization efficiency and their possible feedbacks on carbonate formation reactions, with a focus on the role of solute transport, structural changes of the rock (development of microporosity, localization of precipitation and dissolution) and local flow properties (diffusive vs advective flow) on reaction pathways.

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Graphitic material in fault zones: Implications for fault strength and carbon

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The study discusses the presence, formation and destruction of graphitic material in fault rocks of exhumed fault zones. Numerous natural faults contain graphitic material. The presence of graphitic material has a strong effect on fault rock properties, e.g., on deformation, foliation development and fault strength. Because of the low strength, the presence of lubricating graphitic material along fault zones has important implications for understanding tectonic movements in various crustal levels. Fault zones are permeable for ascending and descending fluids and represent, therefore, effective pathways of fluids between deep lithospheric levels and Earth's surface, and this plumbing system is part of the carbon exchange system of the global carbon cycle between deep lithosphere and atmosphere. Processes of formation, structure and microfabrics of the graphitic material and the implications for the global carbon cycle in natural fault zones are still poorly understood. This study gives an overview on the range of the origin of graphitic material along fault zones (e.g. organic vs. carbonatic vs. fluid origin) and its physical formation and destruction mechanisms. The presence of graphitic carbon permits: (1) to recognize faults with graphitic lubricants during faulting and allow assess, therefore, crustal strength over various temporal and spatial scales, (2) how carbon-bearing material is moving through the fault zone hence recording the complex structural history, (3) how carbon represents a monitor of fluid transport through fault zones, and (4) how graphitic material allow to pinpoint peak temperature conditions of the faulting process. The data implies also carbon transfer between depth and surface, which contributes to the global carbon cycle, but to a hitherto unknown extent. The presence of graphitic carbon in fault rocks has also implications on fault mechanics, engineering geology, nuclear waste repositories and assessment of seismic hazard.

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Using rare earth elements in zircon to investigate the thermal history of a UHT terrane

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In order to investigate the extent to which volume diffusion can modify rare earth element abundance signatures of accessory minerals during high-temperature metamorphism, we conducted numerical models of diffusion of REE in zircon under different temperature-time conditions. The modelling shows that under short-lived UHT conditions (e.g. ~1100°C for 1-5 Myr) diffusion is sufficiently rapid for REE in igneous zircon to fully equilibrate with the new metamorphic mineral assemblage. In contrast, at temperatures below 900°C (recrystallised) zircon will largely retain its original REE composition, with little modification even when the thermal event is long lived (≥100 Myr). Hence the diffusion rates of REE in zircon are highly sensitive to the maximum temperature experienced during UHT metamorphism. In situations where volume diffusion is the dominant process, i.e. fluid-absent, this sensitivity can be used to help constrain a temperature-time (T-t) path for a high-grade metamorphic terrane independent of whole-rock phase equilibria modelling. Applying the modelling to wellcharacterised natural samples from the regional aureole surrounding the Rogaland Igneous Complex (RIC) in SW Norway, the observed variations in REE in zircon across the sample suite indicate that during contact metamorphism the samples >10 kms from the RIC experienced conditions below ~950°C with samples at the RIC contact experiencing ~1100°C for between 1–5 Myr. These temperatures at the contact are higher than current P-T estimates, as the activity models used cannot currently account for osumilite which is present within some of the previously studied sample parageneses and could stabilise the assemblages to higher temperatures. These P-T estimates likely represent a minimum for the conditions experienced during contact metamorphism and highlights the need for updated pelite models including osumilite for modelling pelitic UHT assemblages. The inferred T-t histories for the samples at different distances from the RIC contact are best explained if the Complex was emplaced rapidly in a series of pulses over 1 to 5 Myr.

Protolith heterogeneity, melt loss and the development of microstructures in granulites

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Phase equilibrium models are commonly employed to constrain the pressuretemperature (P-T) evolution of granulite facies rocks, from which their geodynamic setting may be inferred. However, defining a suitable equilibrium volume in such rocks is non-trivial due to heterogeneities in protolith composition and open system behaviour, including melt loss or gain and deformation. Consequently, equilibrium volumes and the mineral assemblages they contain may vary both temporally and spatially. Additionally, despite the extreme temperatures they attained, granulites commonly contain microstructures indicative of local equilibrium, developed at or close to the metamorphic peak. This study assesses the processes that control and preserve the development of a range of microstructures in granulites with different protolith compositions. An approach combining phase equilibrium forward modelling and chemical potential diagrams is used to simulate the suprasolidus evolution of an average metapelite and an Mg-rich metapelite. Assuming equilibrium within different compositional domains, evolving granulite facies assemblages vary significantly along a modelled high T/P (125 °C/kbar) clockwise P-T path. Most retrograde microstructures in metapelitic rocks can be reproduced by considering chemical potential (u) gradients in μ_{MgO} , μ_{FeO} and μ_{CaO} between pre-existing phases, assuming the presence of melt on grain boundaries, that Al₂O₃ is perfectly immobile and that K₂O and Na₂O are perfectly mobile. Additionally, documented microstructures in granulites imply SiO₂-undersaturation locally; requiring that μ_{SiO2} is not superimposed on these microstructures by matrix quartz. Preserving such chemical potential gradients requires that solid phases are chemically and physically isolated from melt. Efficient melt loss along a high T/P P - T path to > 900 °C leads to an order of magnitude increase in melt viscosity. This may isolate solid phases in granulites from melt, allowing element mobility to be controlled by solid state diffusion.

Mg isotopes trace the carbonation of ultramafic mine waste

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Weathering of ultramafic mine tailings at the Woodsreef Asbestos Mine, New South Wales, Australia, sequesters CO₂ in hydromagnesite $[Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O]$, pyroaurite $[Mg_6Fe_2(CO_3)(OH)_{16} \cdot 4H_2O]$ and coalingite $[Mg_{10}Fe_2(CO_3)(OH)_{24} \cdot 2H_2O]^{1,2}$. Meteoric water infiltration drives CO₂ mineralisation in above-ground, sub-aerially stored tailings and potential Mg sources are thus limited to the bedrock minerals present in the tailings. Bulk tailings ($\delta^{26}Mg = -0.29 \pm 0.03 \%_0$) and stream/run-off water ($\delta^{26}Mg = -0.36 \pm 0.04 \%_0$) are isotopically lighter than the serpentinised harzburgite bedrock ($\delta^{26}Mg = -0.10 \pm 0.06 \%_0$) at Woodsreef. Hydromagnesite crusts forming on the surface of the tailings ($\delta^{26}Mg = -1.48 \pm 0.02 \%_0$) are enriched in ²⁴Mg but significantly less than bedrock magnesite ($\delta^{26}Mg = -3.26 \pm 0.10 \%_0$)³. Dripwater ($\delta^{26}Mg = -1.79 \pm 0.02 \%_0$) and coexisiting hydromagnesite ($\delta^{26}Mg = -2.01 \pm 0.09 \%_0$) from a tunnel within the tailings are more enriched in ²⁴Mg than surficial fluid and hydromagnesite, respectively.

Both the enrichment of ²⁶Mg in secondary silicates during ultramafic-rock weathering³ or carbonation^{4,5,6} and in aqueous carbonate and bicarbonate complexes in alkaline fluids⁷ favour enrichment of ²⁴Mg in hydromagnesite. Mg-isotope signatures of hydromagnesite can thus be reconciled with serpentine, forsterite and brucite $(\delta^{26}Mg = -1.11 \pm 0.12 \text{ }\%)^8$ dissolution, consistent with the isotopic composition of the stream/run-off water reflecting that of bulk tailings. Furthermore, bedrock carbonate recycling, which would not lead to net CO₂ storage in the tailings, can be excluded based on the stronger enrichment of ²⁴Mg in magnesite relative to hydromagnesite. Isotopically distinct fluids and hydromagnesite formed in the tunnel and on the surface of the tailings further suggest that Mg isotopes may record different fluid pathways and/or carbonate formation conditions. Low pCO_2 and high ¹⁴C content indicate that, the dissolution of hydromagnesite or magnesite does not control the composition of dripwater in the tunnel⁹. However, the enrichment of ²⁴Mg in dripwater and associated hydromagnesite relative to surficial fluid and hydromagnesite is consistent with access to more reactive brucite along the flow path of dripwater percolating through the tailings, compared to fluid wicking, leading to surficial formation of hydromagnesite. Our study thus demonstrates that Mg isotope signatures trace the fate of Mg to gain hitherto unavailable insights into the carbonation of ultramafic rocks.

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Stress orientation-dependent reactions during metamorphism

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Grain-scale pressure variations have been recognized as important driver for the formation of distinct mineral assemblages during high and ultra-high pressure metamorphism. However, the effects of differential stress acting during hydration of granulite remain underexplored. Here we present textural evidence for the orientation-dependence of two distinct amphibolite-facies plagioclase grain boundary replacement assemblages that formed in response to differential stress during the early stage of lower crustal hydration. The two assemblages, A1 (zoisite, kyanite, and quartz) and A2 (plagioclase and K-feldspar), are indicative of contemporaneous formation at local equilibrium conditions at ~700 °C and 11 kbar and 9 kbar, respectively. Mineral replacement was accompanied by minor redistribution of chemical components by the alteration fluid in response to the heterogeneous stress field and local equilibria. Thus, our observations provide new insight into the driving forces for pressure solution and indicate that differential stress and fluid-induced mass transfer may define the evolution of metamorphic assemblages.

Chloro-hydroxy-zircon nanoprecipitates fingerprint fertility and mineralization potential of granitic magmas

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Zircon micron- to nanoscale structures and trace element signatures offer an exciting opportunity to delve into the genesis of large magmatic-hydrothermal ore systems (Courtney-Davies et al., 2019a). Based on zircon within different Proterozoic granites in the Olympic Cu-Au province (Gawler Craton, South Australia), either hosting, proximal to, or distal from iron-oxide-Cu-(U)-Au (IOCG) style mineralization, we characterize and interpret features that have application as potential discriminants in exploration for IOCG deposits. This subject is of interest to igneous petrologists and mineral deposit specialists alike, since the evidence contradicts long-held consensus regarding the processes and timescales of zircon alteration in magmatic-hydrothermal environments (Geisler et al., 2007 and references therein).

Magmatic zircon was studied from two distinct granite suites: ~1.85 Ga Donington Suite and ~1.6 Ga Hiltaba Suite. Although both suites host mineralisation, only the Hiltaba Suite granites are genetically associated with IOCG mineralization. The Hiltaba Suite-affiliated Roxby Downs Granite (1593.87+0.21; Cherry et al., 2018), host to the Olympic Dam deposit, is an outstanding case of a fertile granite, whereas the Donington Suite provides examples of pristine (Cape Donington, Eyre Peninsula) to hydrothermally-altered zircon (Wirrda Well prospect), the latter impacted by the same ~1.6 Ga hydrothermal event.

Zircon grains were studied by complementary micron- and nanoscale techniques: High Angle Annular Dark Field Scanning Transmission Electron Microscopy (HAADF STEM) imaging and STEM energy-dispersive (EDS) X-ray spectrometry mapping and spot analysis, supported by STEM simulations and complemented by electron microprobe analysis (EPMA). The aims were to characterise and interpret; (1) crystal zoning with respect to 'non-formulae' elements such as Fe, Ca and Cl; (2) the nature of a characteristic inclusion mottling in zoned bands; (3) lattice defects; and (4) the relationship between metamictization and alteration. Zircon grains were selected after imaging in BSE mode. Foils for TEM study were extracted in-situ, thinned to <100 nm by ion beam (Ga+) milling, and attached to Cu grids on a FIB-SEM platform. Of seven foils, five were cut across oscillatory zoning observed on grain surfaces in zircon to target their development at depth, also allowing correlation between micron- and nanoscale characteristics. HAADF STEM imaging and EDS spot analysis and mapping, was performed using an ultra-high resolution, probe-corrected, FEI Titan Themis S/TEM operated at 200 kV.

Crystal oscillatory zoning is expressed in all zircons, but with respect to different elements. In unaltered zircon, variation is, as expected, expressed with respect to common magmatic trace elements (REE and actinides), whereas altered zircon features crystal oscillatory zoning with non-formula elements, particularly Fe, Ca and Cl. Such patterns are depicted on both EPMA and STEM-EDS maps. In zircon proximal to mineralisation dense inclusion mottling becomes typical within bands enriched in non-formula elements. At higher resolution, the mottled areas (dark nanodomains in HAADF STEM images), concentrate Cl in particles ranging in size from nanoparticles (<100 nm) to fine particles (up to hundreds of nm). The largest particles, with well-defined geometrical shapes are crosscut by veinlets with lattice-scale defects proving they are inclusions rather than pores; the latter can nonetheless be present within the inclusions. Based on EPMA data and nanoscale characterisation we define these as chloro–hydroxy–zircon nano-precipitates formed by substitution mechanisms involving replacement of O by Cl and/or OH⁻. Remobilised U and Pb was not found to be concentrated within such precipitates.

High-resolution imaging on four main zone axes in zircon shows lattice-scale disorder expressed as screw dislocations and lattice stretching but no amorphous domains, despite a

'metamict' appearance at the micron-scale. The most complex defects were imaged in Fe-rich bands from Roxby Downs Granite zircon on $[1\overline{1}1]$ zone axis. In this case, changes in the atomic arrangement along (011) can be interpreted as displacements with anti-phase modulation along fault planes. In contrast, defects within the particles described above are interpreted as the result of local fluid–mineral interaction leading to an increase in OH/halogen content.

Overall, chloro-hydroxy-zircon nanoprecipitates in the Fe-Ca-rich zones become volumetrically more significant in close proximity to the Olympic Dam deposit. An association between Fe and Cl would be expected in early IOCG fluids exsolved after granite crystallization. We thus conclude that Cl is inherent to hydrothermal fluids derived from the Hiltaba Suite granites, which also affected and altered the older Donington Suite granites at Wirrda Well. The absence of non-formula elements in fresh Donington Suite zircon from the Eyre Peninsula rules out a magmatic origin for such elements.

Zircon metasomatism can be attributed to an initial low-fluid, mineral-buffered diffusionreaction process, followed by formation of chloro–hydroxy–zircon nanoprecipitates when fluids become highly focused. Preservation of pre-existing crystal orientation in zircon nanoprecipitates and host zircon is characteristic of reactions via a sharp interface, typical of replacement via coupling of dissolution with reprecipitation rates (CDRR). Transient porosity developed during the progression of CDRR provides sites for deposition of such nanoprecipitates (Putnis 2002).

From high-precision dating of hematite, iron metasomatism is known to have occurred at Olympic Dam shortly after granite crystallization (~2 to 4 Ma later; Courtney-Davies et al., 2019b). The α -dose required to relate zircon alteration to metamictization is calculated at ~100 Ma after crystallization, a period that cannot be reconciled with the timing of Fe-metasomatism in the region (Courtney-Davies et al., 2019a).

These results show that early metasomatic alteration can be recorded in magmatic zircon and that these patterns can be preserved over geological time, even when superimposed by the effects of metamictization. Marked differences in the geochemistry and nanoscale features of zircon across the sample suite imply that nanoscale studies of magmatic zircon, if coupled with careful characterization of textures and compositions at the micron-scale, represent a pathfinder tool that could be used to locate mineralisation. In turn, the presence of chloro-hydroxy-zircon nanoprecipitates would represent a diagnostic tool to assess the 'fertility' of granitic magmas.

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'Invisible' Au in pyrite from Olympic Dam deposit, South Australia: bridging textures with statistical analyses

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'Invisible' Au in pyrite refers to gold present within the sulphide lattice or as discrete nanoparticle inclusions, making it undetectable by conventional optical and scanning electron microscopy (SEM) (Cook and Chryssoulis 1990). Incorporation of Au into pyrite is often mediated by incorporation of As (Reich et al. 2005). Nevertheless, pore-attached Au-Ag-telluride nanoparticles have been documented within As-free pyrite (Ciobanu et al. 2012) thus representing an alternative mechanism for incorporation of Au into pyrite.

Olympic Dam, is an an archetypal iron-oxide copper gold (IOCG) deposit that contains >100 minerals and displays complex, finely intergrown sulphide assemblages (Ehrig et al. 2012). Of these, pyrite makes up ~0.5 wt% of the orebody. There currently exists a significant knowledge gap with respect to the potential presence of 'invisible' Au within pyrite from such IOCG ores, at Olympic Dam and elsewhere. Identification of the physical and chemical state of Au allows new constraints to be placed on ore genesis and also carries implications for mineral processing.

In a first attempt to address this issue, we combine multivariate statistical analyses of LA-ICP-MS trace element datasets for pyrite from Olympic Dam (OD) with micron-scale characterization. Trace element datasets are often presented with a relatively low-level statistical treatment such as two-three component projections accompanied by summary statistics. However, given the ever-increasing size and complexity of LA-ICP-MS datasets, a data-driven, reproducible and quantitative approach is required for processing (Winderbaum et al. 2012). Sixty-seven pyrite grains with measurable Au content were studied from a single polished block representative of a pyrite-chalcopyrite orezone at OD. Pyrite features oscillatory zoning with respect to As(-Co,-Ni) in individual grains (Fig. 1a) and sub-micron-scale inclusions of Bi- and Au-tellurides, among others (Fig. 1b). Gold-tellurides are also found in As-poor pyrite with no visible compositional zoning (Fig. 1c-d). The LA-ICP-MS dataset shows measurable concentrations of Ag, As, Au, Bi, Cd, Co, Cu, Mn, Mo, Ni, Pb, Se, Sn, Sb, Te, Ti, Tl, Th, ²³⁸U, W, and Zn (192 spot analyses). Such elements are likely to be present as lattice-bound as well as inclusion within pyrite. Arsenic concentrations attain up to 3 wt%; mean and median values are 0.64 and 0.72 wt%, respectively.

Principal component analysis (PCA) coupled with construction of hierarchical dendrogram were used to depict geochemical associations among trace elements. Two distinct sub-groups are found: (i) Au-bearing (>10 ppm Au); and (ii) Au-poor pyrite (Fig. 1e-g). These sub-groups are clearly distinguished by different geochemical associations (Fig. 1f-g). In group (i), Au correlates strongly with As and Ag, and to a lesser extent, also with Bi, Sb, Cu, Sn and Pb. This confirms that compositionally zoned pyrite is a host for 'invisible' Au. Group (ii) features the element associations Ni-Co, Te-Se, elements that are easily incorporated in the pyrite structure, and other elements likely to occur as discrete mineral inclusions (Ti, Mn, W, Zn, U and Th). Although Bi-telluride inclusions are observed within As-bearing pyrite (Fig. 1b), PCA results show that Te and As are placed within different clusters. Microscopic observations suggest the presence of Te as telluride inclusions and As-poor pyrite. A possible scenario is that Au is essentially lattice-bond in As-bearing pyrite but present as inclusions of Au-bearing tellurides in As-poor pyrite. This hints at different mechanisms and/or conditions of Au incorporation, consistent with the complex evolution of the ores at Olympic Dam including reworking of primary zoning patterns. Further work includes nanoscale characterization of pyrite which will allow improved discrimination of NPs populations and their formation from lattice-bound elements or by other mechanisms. Statistical analysis could be an important, novel tool to recognise populations of NPs in pyrite relative to well-defined generations and formation mechanisms e.g., exsolutions from solid solution in grains with crystal zoning, or fluid-assisted brecciation leading to pore-attached NPs.



Figure 1. (a-d) Back-scattered electron images of pyrite showing relevant textures as marked. Note presence of sub-micron-sized tellurides. (e) PC scores showing geochemical distinctions among Au-bearing (>10 ppm Au) and Au-poor (<10 ppm Au) pyrite; (f) PC loadings showing geochemical groups associated with distinct pyrite types. Grey colours represent elements with >20% values falling below minimum limits of detection. (g) Hierarchical cluster dendrogram of analysed elements.

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Oscillatory growth patterns in hematite defined by Si-Fenanoprecipitates: ore enrichment processes in BIFs

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'Silician magnetite' refers to magnetite containing up to several wt.% SiO₂ and is wellknown from oscillatory-zoned crystals in a variety of ore types. Nanoscale studies using Zcontrast techniques imaging such as High Angle Annular Dark Field Scanning Transmission Electron Microscopy (HAADF STEM) have shown that the Si-bearing zonation patterns are due to the presence of Si-Fe-nanoprecipitates (NPs) in two different ore types (Xu et al. 2014; Ciobanu et al. 2019). The NPs form crystallographically-oriented strips of n x d_{111} (n=even number) in host magnetite and are considered as γ -Fe_{1.5}SiO₄, one of the maghemite-type structures with vacancy ordering, resulting in $P4_332$ symmetry, a subgroup of Fd3m group known for the spinels (Xu et al. 2014). Rounded to sub-euhedral NPs with no detectable structural changes were also found and interpreted as a variant of the same phase but with disordered vacancies (Ciobanu et al. 2019). Hematite, α -Fe₂O₃, is a polymorph of maghemite but with rhombohedral structure. Oscillatory zoned silician hematite (1.8 wt.% SiO₂) was reported from Neoarchean BIF ores at Iron Knight, Middleback Ranges, South Australia (Keyser et al. 2018). The samples display textures indicative of hematite forming from ironhydroxides, thus implying re-burial of the deposit after supergene enrichment.

Considering that 'silician hematite' is a new discovery, we undertook a nanoscale study to understand: (i) the nature of the Si-bearing zoning in the zoned hematite; and (ii) how this can be used to constrain the model put forward for ore enrichment. The samples were prepared using focused ion beam SEM by cutting across zoning in hematite (Fig. 1A). HAADF STEM imaging and STEM energy-dispersive (EDS) X-ray mapping and spot analysis were performed using a high-resolution, probe-corrected, FEI Titan Themis S/TEM at 200 kV (all instruments are housed at Adelaide Microscopy).

STEM-EDS maps show that the Si-enriched, Fe-depleted, fine-scale bands in hematite display a mottled texture with respect to Si-Fe nanoparticles with rounded to hexagonal morphology (Fig. 1B, C). Chaotic agglomeration of the NPs is observed in areas were the bands are interrupted by microfractures along which discrete SiO₂ inclusions are present and Al is also established as present by mapping, in addition to Si. High-resolution imaging of exposed NPs with hexagonal morphology shows these have atom arrangements different to host hematite viewed on [12-1] zone axis (Fig. 1D). The structure corresponds to [1-10] cubic maghemite (Fig. 1E) as shown for Si-Fe-NPs in magnetite (Ciobanu et al. 2019). Fast Fourier Transform (FFT) patterns obtained show that the NPs are epitaxially related to host hematite. They display satellite reflections indicative of vacancy ordering towards a γ -Fe_{1.5}SiO₄ maghemite phase (Fig. 1F, G).

A model for formation of silician hematite from iron-hydroxides can be outlined. The oscillatory zoned texture is inherited from the iron-hydroxides (Fe³⁺O(OH)), which are finegrained and typically disply concentric banding. Impurities, such as Si and Al, are often part of such aggregates in iron-hydroxides. Upon burial, dewatering and recrystallization of these compounds into hematite leads to formation of Si-Fe-NPs along the bands rich in impurities. During NP coarsening, vacancy ordering in a γ -Fe_{1.5}SiO₄ maghemite type structure occurs within the rhombohedral lattice of hematite. The presence of fractures with other impurities, such as Al, or discrete SiO₂ inclusions, is further evidence for the heterogeneity of the initial material compatible with the assumption of a iron-hydroxide protore. Phase transition between goethite and hematite via dehydration was shown in TEM experiments (Watari et al. 1983).



Figure 1. (A) BSE image showing oscillatory-zoned silician hematite. (B, C) STEM-EDS maps of Si and Fe showing banding and the mottled texture formed by Si-Fe NPs. High-resolution images showing a Si-Fe-NP with maghemite (Mgm) structure in hematite (Hm) (D) and detail of Mgm (E). (F, G) FFT from D and E, respectively showing orientation of Hm and Mgm as marked. Satellite reflections arrowed.

Although further work is needed in order to confirm the above interpretations, preliminary findings support a burial/dehydration model for formation of silician hematite, recognized as a 'microplaty type' in BIF ores at Iron Knight (Keyser et al. 2018). This follows a regional extensional event and contemporaneous emplacement of Gairdner dyke swarms at ~800 Ma. The supergene enriched ores underwent a second burial cycle to form an upgraded hematite ore at ~680 Ma (LA-ICP-MS U-Pb dating of hematite; Keyser et al. in review). 'Silician hematite' may thus represent a potential signature for reburial processes leading to enrichment of BIF ores. These findings carry potentially important implications for ore formation due to the common presence of microplaty hematite ores in BIF-hosted iron ore deposits elsewhere.

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Natural and synthetic aluminium-phosphate-sulphates under acid leach conditions: Pathways to radionuclide reduction in copper processing circuits

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Iron-oxide copper gold (IOCG) deposits such as Olympic Dam represent the primary resource for copper production in South Australia. Uranium and the daughter products of ²³⁸U decay, ²²²⁶Ra^{, 210}Po and ²¹⁰Pb, are present in copper concentrates produced from IOCG ores. Ongoing efforts to identify novel solutions to remove or reduce concentrations of these radionuclides (RN) are benefitting from empirical mineralogical research on ores and concentrates and experimental studies targeting the geochemical behaviour of RN at conditions similar to those in the processing plant.

Aluminum-phosphate-sulfate (APS) minerals within the alunite supergroup have the general formula MAl₃(PO₄)_{2-x}(SO₄)_x(OH,H₂O)₆, and are known to form a broad solid solution series, housing a range of mono-, di- or trivalent cations within their M-sites. Within the Olympic Dam metallurgical circuit, APS minerals of the alunite supergroup were shown to sorb products of ²³⁸U decay, notably ²²⁶Ra and ²¹⁰Pb (Rollog et al. 2019; Owen et al. in review) both over geological time within the deposit and during ore processing. Many APS phases remain stable over a wide range of pH and *Eh* and temperatures up to 450 °C (Kolitsch and Pring 2001; Schwab et al. 2005). As such synthetic APS phases present as viable candidates not only for the removal of radionuclides from metallurgical streams, but also for their safe storage and isolation from surrounding environments.

The genesis of natural APS mineral phases within the Olympic Dam deposit are shown to be paragenetically late, forming via replacement of earlier REE-bearing phosphates (fluorapatite, monazite and xenotime), and local dissolution and replacement of sulphides, with the development of two distinct compositional groups: Ca-Sr-dominant, sulfate-enriched APS minerals that that lie within the woodhouseite and svanbergite compositional fields; and a REE- and phosphate-dominant group trending towards florencite in composition, similar to that reported by Schmandt et al. (2019). Of the two groups, Pb, both commonly sourced and radiogenic in origin, is shown to favor the Ca-Sr-dominated APS phases. Enrichment of these phases by Pb (including ²¹⁰Pb) is suggested to increase throughout the acid leach stages of processing, as evidenced by electron probe microanalysis and NanoSIMS isotope mapping. The data suggests that Pb-incorporation occurs with the replacement of Ca by Pb within the APS crystal structure, an interpretation in agreement with thermodynamic modelling given by Schwab et al. (2005). The same authors show that the thermodynamic stability of Ca-, Sr-, and Pb-bearing APS phases increases in the order Pb>Sr>Ca.

Ca- and Sr-bearing APS phases were synthesised by modifying existing recipes (Schwab et al. 2004) to generate mixed crystals. Ca/Sr ratios were varied according to the below reaction in order to test the role of compositional variability of mixed APS phases on the sorption of Pb via dilute PbNO₃ solution.

Phases which are Sr-, and (Ca,Sr)-bearing were produced. Accessory augelite, Al₂(PO₄)(OH)₃, was also formed within all samples, albeit in minor to moderate concentrations. APS crystals

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showed compositional zoning with Al-, and S-rich cores with <1 apfu at the M-site, to stoichiometric APS at the rims with roughly equal concentrations of P and S.

Pb-sorption experiments were run by placing the synthesized APS phases in reaction vessels containing solutions of $Pb(NO_3)_2$ and diluted HNO₃ for a period of 5 days. The concentration of Pb ($[Pb_{aq}]_0$) in the reaction fluid was set at 10, 100 and 1000 ppm and a pH range of 1.5, 3.5 and 5.5 was tested.

Solution-ICP-MS, EPMA, LA-ICP-MS and EXAFS analysis confirm the sorption of Pb by the synthetic APS phases, with Pb sorbtion favoured at pH 3.5 and above. EPMA spot analyses indicate the preferential sorption of Pb by phases which trend towards higher S/P ratios, as well as those that deviate from ideal stoichiometry (i.e. Al>3 apfu and $\sum M^{2+}<1$). Targeted LA-ICP-MS analyses comparing the ratios of M-site cations indicate minimal change of Sr concentration with increasing Pb incorporation within both Sr-, and (Ca,Sr)bearing APS phases, while Ca concentration within (Ca,Sr)-bearing phases subsides with increasing Pb incorporation, indicating direct replacement of Ca by Pb within the crystal structure of APS phases. Sr-bearing phases more commonly displayed non-stoichiometric values of $\sum M^{2+}$, indicating that Pb incorporation into such phases may arise via occupancy of sites that were previously vacant, or otherwise held by H⁺ or excess Al within the structure.

An EXAFS study on the resulting Pb-sorbed solids was conducted, revealing the nature of Pb sorption by the synthesized APS material. The data showed that the dynamic incorporation of Pb by APS phases occurred overwhelmingly at pH 3.5. Some experiments run at pH 5.5 also favored the formation of Pb-bearing APS whereas other conditions favored dissolution and replacement of augelite to form a pyromorphite-like structure. Fairly featureless patterns in R-space were frequently observed in experiments run at high [Pb_{aq}]₀ (100-1000 ppm) with slightly shifted peaks indicating the prevalence of surface-sorbed Pb. Here, however, solution-ICP-MS data regularly showed undulating sorption trends, particularly in (Ca,Sr)-bearing material, indicating that equilibration between solution and solid may have not yet been

achieved. Thus, synthetic APS phases may provide a novel approach to reducing radionuclides, particularly ²¹⁰Pb, from metallurgical streams.

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Shear heating during exhumation: An example from the Nordfjord-Sogn Detachment, Hyllestad, Norway

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The Nordfjord-Sogn detachment zone in South-Western Norway is a large scale (>100km in length) brittle-ductile extensional structure of Caledonian age, which juxtaposes two distinct lithologies in the Sognefjorden area, the allochthonous Hyllestad Complex (hanging wall) against the (para)autochthonous Western Gneiss Complex (footwall). Based on phase equilibrium modelling, the aluminous garnet-kyanite-staurolite-muscovite-paragoniteilmenite-rutile-quartz schists of the Hyllestad Complex are interpreted to record peak P-Tconditions of 12–14 kbar and 620–650°C, equating to depths of 40–50 km. Peak temperatures for the Hyllestad Complex are some 50 to 100°C hotter than previously calculated based on conventional, and reflect a geothermal gradient that is significantly warmer than recorded by the bulk of analysed samples from the boundary of the Western Gneiss Complex and Nordfjord-Sogn detachment zone. Microshear bands, defined by fine-grained biotite and sillimanite, interpreted to be formed through top west movement of the Nordfjord-Sogn detachment zone and marginal replacement of kyanite porphyroblasts by sillimanite suggests that the rocks were exhumed along the detachment to depths of less than 20 km at high temperatures. Shear heating during exhumation is proposed to account for this thermal perturbation, in which the heat supplied was sufficient to maintain (near)isothermal conditions. U-Pb LASS geochronology of monazite grains aligned within an extensional fabric defined by quartz-muscovite-paragonite constrain the age of exhumation of the aluminous schists along the Nordfjord-Sogn detachment zone to c. 400–403 Ma. These ages provide constraints on the termination of the Scandian Orogeny within the wider Caledonian Orogeny, with termination of the high-pressure event occurring no later than c. 403 Ma to account for the advent of extension: required to create the Nordfjord-Sogn detachment zone. By c. 379 Ma the Hyllestad Complex would have been exhumed to at least 20 km to account for cooling through rutile closure temperatures at 575-600°C with greenschist to amphibolite facies overprinting by this time. The Nordfjord-Sogn detachment zone thus has allowed for rapid exhumation through a very large (20-30 km) section of crust, allowing the preservation of high temperatures at shallow depths.

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Nanoscale investigation of deep, metamorphic fluid

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Exposed portions of lower continental crust and underlying upper mantle rocks represent valuable windows into the deformation and rheological behaviour occurring at depth. Deformation related microstructures are widely used to reconstruct the history of metamorphic rocks, yet their implications for elemental redistribution remains substantially unexplored. At a fundamental level, these processes take place at the atomic scale, but investigations at such high-resolution have been previously limited by technological limitations. The aim of this study is to assess the coupling between microstructures that form during fluid-catalysed metamorphism and deformation at lower continental crust conditions and the redistribution of major and trace elements. In this work, preliminary microstructural characterisation results of deformed olivine from a spinel-lherzolites of the Bergen Arcs (Norway) will be presented. The studied rocks outcrop as ultramafic lenses hosted within partially eclogitised granulites. Together with their granulitic host, they are believed to have shared a fluid-induced eclogite facies metamorphism and deformation during the Caledonian orogenesis at ca. 430 Ma. In the ultramafic lenses the surrounding granulitic foliation is defined by a well-developed compositional layering of olivine-pyroxene and garnet-rich bands, locally crosscut by high strain mylonite structures related to the Caledonian overprint. Electron backscattered diffraction (EBSD) data across the transition from the host olivine to the internal part of the shear zone indicate three different domains of increasing strain: i) high dislocation density zones within the host olivine; ii) recovered areas comprising 10µm subgrains; iii) dynamic recrystallized domains containing dislocation-free olivine neoblasts and high-angle boundaries. In detail, EBSD data has been used to characterize different interface types within and between these different domains. Site-specific, focussed-ion-beam targeting of these interfaces allows nanoscale compositional variations to be characterized by atom probe tomography. These data will provide a greater understanding of element mobility associated with subduction-related intracrystalline deformation, solid-state diffusion, dissolution-precipitation and dynamic recrystallisation in the presence of fluids.

The fate of primary fluid inclusions in peritectic garnets from the lower continental crust

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Fluids and melts are important agents of mass and heat-transfer, playing a critical role in the geochemical and physical evolution of the deep Earth's crust. The presence of fluids during high grade metamorphism and crustal anatexis is testified by the occurrence of fluid inclusions in granulitic rocks. In particular, the widespread occurrence of primary CO₂-bearing fluid inclusions strongly indicates the common presence of low-H₂O fluids in the lower continental crust. However, their behaviour, provenance and role during high grade metamorphism still remain matter of active debate.

In this work, we present a detailed investigation of primary multiphase fluid inclusions trapped in peritectic garnets from three world-renowned high- to ultra-high temperature metamorphic terranes [the Ivrea Zone (NW Italy), the Gruf Complex (Central Alps) and the Athabasca granulite terrane (Canada)]. Petrography, combined with micro-Raman spectroscopy and FIB-SEM serial sectioning, revealed the presence of aggregates of solid phases together with the fluid. The fluid phase is mostly CO_2 -rich, with some occurrences of CH_4 and N_2 . No detectable H_2O has been found. The solid phases comprise Fe-Mg-Ca carbonates, quartz, pyrophyllite, corundum, kaolinite, muscovite and graphite.

In all terranes the multiphase primary fluid inclusions coexist with nanogranitoid inclusions. Such inclusions occur in zonal arrangement in the core of peritectic garnets, suggesting the presence of an immiscible COH fluid phase during anatexis of these rocks. Considering the mineral chemistry of the solids found in the multiphase inclusions, the original COH fluid composition must have been modified as a result of post-entrapment interaction with the host garnet during cooling of these rocks. Phase equilibria modelling also revealed that these solid assemblages are metastable. This study shows that in the retrograde path, primary COH fluid inclusions - including the high-density CO₂ inclusions in granulites - are likely to interact with their host resulting in drastic variations of their original composition and the precipitation of a multiphase mineral assemblage.

Evidence for resubduction of lawsonite-eclogite during return flow, Southern New England Orogen, Australia

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Translating burial and exhumation histories from the petrological and geochronological evolution of high-pressure mineral assemblages in subduction channels is key to understanding subduction channel processes. Convective return flow, either serpentinite or sediment hosted, has been suggested as a potential mechanism to retrieve deeply buried rocks and exhume them to the surface. Numerical modelling predicts that during this convective flow, fragments of oceanic crust can be cycled within a serpentinite-filled subduction channel, experiencing multiple burial cycles. Geochronological and petrological evidence for such cycling during subduction is preserved in a lawsonite-eclogite from serpentinite mélange in the Southern New England Orogen, in eastern Australia. Lu-Hf garnet and lawsonite, U-Pb zircon, U-Pb titanite and Ar-Ar and Rb-Sr phengite geochronology, supported by phase equilibria modelling and garnet zonation, suggests two cycles of burial that accompanied more than 1000 km of trench migration. Lu-Hf garnet and lawsonite and U-Pb zircon ages constrain the first burial event to ca. 500-490 Ma. This initial subduction of the eclogite formed Lu- and Mn-rich garnet cores, porphyroblastic lawsonite and micro zircons at P-T conditions of at least 2.3 GPa and 550 °C. Partial exhumation to ca. 1.9 GPa and 500 degrees is recorded by approximately 11 vol% garnet dissolution. Reburial of the eclogite resulted in renewed growth of new garnet, and prograde-zoned phengite and recrystallization of titanite at P-T conditions of 2.7 kbar and 590 °C. U-Pb titanite, phengite Rb-Sr and Ar-Ar ages record the recrystallization of these minerals during this second event at ca. 460 Ma. This was then followed by a second exhumation event, where chlorite and glaucophane partially replaced garnet and omphacite respectively, and garnet rims were again reabsorbed, at approximately 2.0 GPa and 500 °C. These conditions fall along a cold approximate geotherm of 7 °C/km, supported by the presence of pristine lawsonite. Partial exhumation and reburial occurred over ca. 30 Ma over an approximate pressure and temperature fluctuation of 1.2 GPa and 140 °C, providing some estimation on the rates of subduction channel material cycling.

Non-equilibrium and equilibrium sulphide crystallization in modern seafloor hydrothermal sulphide chimneys

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Active seafloor hydrothermal sulphide chimneys and associated seafloor massive sulphide deposits are modern analogues of ancient volcanogenic massive sulphide (VMS) deposits which provide important resources for base metals, like Cu and Zn, and precious metals, like Au and Ag (Hannington et al., 1986; Herzig and Hannington, 1995; Franklin et al., 2005). Those chimneys are formed when hot hydrothermal fluids quickly mix with cold seawater, and the mixing processes usually result in non-equilibrated conditions under which minerals are crystalized (Haymon, 1983). The microstructures of sulphides in hydrothermal chimneys, which provide significant insights into venting fluids-seawater mixing processes, has yet been studied.

This study characterises the microstructures of sulphides in hydrothermal chimneys from Manus back-arc basin, using synchrotron microbeam XRF coupled with EBSD, to reveal different generations of sulphides crystalized from non-equilibrated to equilibrated conditions during different degrees of mixing between venting fluids and seawater. Sphalerite is one of the common sulphides in chimneys, and exhibit various morphologies, such as, euhedral, colloform and clusters of spheres. In particular, the sphalerite clusters are formed via the coalescence of multiple smaller sphalerite globules (Figure 1). Each globule includes an inner zone with fine-grained particles (<1 μ m) and an outer zone with elongated blade-shaped crystals (length up to 40 μ m), in some cases showing branching dendritic habit (Figure 2). The individual globules are interpreted as forming under conditions of supersaturation within high-temperature gradients (Murowchick and Barnes, 1987), for example, during the mixing between high-temperature (e.g., 300°C) hydrothermal fluids and ambient cold seawater. Chalcopyrite is also observed to vary from dendritic structure to euhedral crystals at 100s of μ m scale (Figure 3).

Those observations reflect primary microstructures that reveal the mixing processes between hydrothermal fluids and seawater on the seafloor and that have not suffered any diagenesis and hydrothermal alteration. They bear important implications for identifying fossil chimneys in ancient ore deposits. Moreover, this study emphasizes the benefits of using cuttingedge techniques, such as EBSD and SXRF, in order to characterize sulfides in various hydrothermal chimneys to unravel crystal growth and fluid mixing history and gain further insight into chimney growth processes.



Figure 1 Petrographic observations of sphalerite clusters with serrated edges observed with SEM-BSE and SE imaging. (A) BSE image of the sphalerite clusters (gray contrast) with inclusions of chalcopyrite (dark contrast). The clusters have formed from the coalescence of multiple globules. (B) BSE image showing the serrations on the edge of the globule as indicated by yellow arrows. (C) SE images of the

columnar structures in the cavities, showing the growth of columns consistent with the fluid flow direction. (D) Magnification of SE image showing that the columns consist of multiple small globules.



Figure 2 Pattern quality map of part of a sphalerite globule; lighter gray areas represent the interiors of homogeneous single crystals, the grain boundaries of which are constrained by dark lines. (B) Magnification of the dendritic structure shown in (A). (C) Magnification of fine-grained particles of zone 1, shown in (A). (D) Z direction inverse pole figure (IPF_Z) map of (A). In the box, the branches are dominated by the red color, indicating that these crystals have the similar crystallographic orientation.





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Tungsten-bearing nanoparticles in hematite: insights into open system behaviour of mineral geochronometers

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Formation of metal-bearing nanoparticles (NPs) in minerals can fingerprint replacement processes at the atomic scale, at which element exchange occurs. Advanced transmission electron microscopy, particularly Z-contrast imaging using high-angle annular dark field scanning transmission electron microscopy (HAADF STEM), on a sample extracted *in-situ* from locations of petrogenetic interest is a powerful approach for understanding trace element incorporation in and their release from a host mineral (Ciobanu et al. 2016). Copper-As NPs were documented from oscillatory-zoned U-W-Sn-Mo-bearing hematite that also shows atypical Cu-As-zoning and weave-twinning patterns (Verdugo-Ihl et al. 2017, 2019). These NPs occur either along (i) trails of inclusions interpreted as inclusions opened during sample preparation, or (ii) within Si-Al-K-bearing planes that also host sericite. Formation of the two types of NPs was interpreted as due to interaction between hematite and hydrolytic fluids whereby fluid supersaturation and phase separation during depressurisation account for different regimes of fluid-rate infiltration along pre-existing twin planes. Uranium-Pb systematics in the same type of hematite have been addressed by various microbeam techniques and high-precision U-Pb ID TIMS on material microsampled from U-rich domains (Courtney-Davies et al. 2019), which showed both closed and open system behaviour for U-Pb isotopes.

Here we address the issue of nanoscale manifestation of open system behaviour in hematite from samples that display compositional zoning affected by preferential removal of some elements, in this case W. Selective removal of different elements from the zonation patterns was previously interpreted as replacement reactions coupling dissolution with reprecipitation rates (CDRR; Verdugo-Ihl et al. 2017). The sample was collected from ~170 m below the hematite hosting Cu-As-NPs from a downwards-plunged block in the SE part of the Olympic Dam deposit, South Australia. The TEM foil was obtained by focused ion beam SEM by cutting across microfractures occurring along the boundary between preserved U-W-Sn-Mo zonation (microsampled for ID TIMS U-Pb geochronology) and a W-depleted domain (Verdugo-Ihl et al. 2017). Bright field (BF) and HAADF STEM imaging, as well as STEM energy-dispersive X-ray spectrometry (EDX) mapping and spot analysis, were performed using a high-resolution, probe-corrected FEI Titan Themis S/TEM at 200 kV (all instruments are housed at Adelaide Microscopy). Imaging of the foil shows domains with fractures and splays adjacent to twin planes in hematite which all display W and Pb enrichment on STEM EDX maps (Fig. 1a, b). In addition, W-bearing NPs occur along trails proximal to such structures (Fig. 1c). High-resolution HAADF STEM imaging shows the twin planes have nm-wide crests with defects showing swelling and displacement (Fig. 1d). The hematite on each of the twin planes shows sets of misorientation directions, in addition to superstructuring. In detail, arrangements of the Fe atoms in the dumbbell motif typical of $[12\overline{1}]_{hematite}$ show alternating brighter and darker units indicative of a 2-fold superstructure (Fig. 1e), and also indicated by Fast Fourier Transforms displaying satellite reflections.

The results allow for the following interpretation. Micron-scale fracturing of the oscillatory zoned hematite results in mechanical twinning and these provide nm-wide channels for fluid infiltration resulting in removal of W and Pb from primary zoning. The twin directions are marked by measurable W and Pb inferring these structures are effective traps for them. In contrast, the W-bearing NPs do not concentrate Pb, implying that this element is lost from the

system during fluid channeling. Defects and structural modifications of hematite are evidence for strain-induced effects in the crystal lattice during fluid percolation. As in the case of the Cu-As-NPs, we show that nanoscale studies can fingerprint fluid-mineral interaction. Additionally, the data demonstrates open system behaviour of U-Pb systematics in hematite. This is concordant with ID TIMS data recording high common Pb in the aliquots prepared from this grain (Courtney-Davies et al. 2019).



Figure 1. (a) STEM EDX maps of hematite (Hm) domain with fractures and splays adjacent to a twin plane featuring W- and Pb-enrichment. (b) BF STEM and STEM EDX maps of W- and Pb-enrichment along twin boundary. (c) HAADF STEM image and TEM EDX maps of W-bearing NPs along a trail; note that no Pb is detected within such NPs. (d) HAADF STEM image of Hm with a twin crest (arrowed) enriched in W-Pb, and featuring defects (swelling and displacement). (e) HAADF STEM image of Hm adjacent to the twin plane displaying 2-fold superstructuring (white lines) of the basic dumbbell motif on the $[12\overline{1}]$ zone axis.

Overall, these results attest to the importance of CDRR in the formation of NPs and domains that are relatively enriched in certain trace elements, and how these impact on trace element signatures measured by microbeam techniques (LA-ICP-MS and/or EPMA). If characterized at appropriate scales of observation, such features can provide evidence for open system behaviour in hematite and other minerals. This, in turn, carries implications for the separation of daughter radionuclides from parent isotopes (Rollog et al. 2019) and the modification of isotopic systematics, both impacting on the accuracy and precision of geochronometers (e.g. U-Pb system in hematite; Courtney-Davies et al. 2019).

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Re-equilibration pathways during fluid-mineral interactions in copper-iron sulfides: insights from hydrothermal experiments

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Complex intergrowth textures in copper-iron sulfide minerals are commonly observed in many types of copper ore deposits (e.g., Ciobanu et al., 2017), but the mechanisms of their formation have not been fully unraveled. In the presence of a fluid phase, particularly at low temperatures, fluid-mineral interactions through the interface-coupled dissolution-reprecipitation (ICDR) mechanism contribute significantly to the re-equilibration of ore minerals that are out of equilibrium with the fluid phase (Putnis 2009). In the ICDR mechanism, the parent minerals are progressively replaced by product minerals from the surface or micro-fractures to the interior of the grains. However, in this study, our hydrothermal experiments suggested that the interaction between non-porous stoichiometric bornite (Cu₅FeS₄) grains and hydrothermal fluids at 160-200 °C led to the rapid formation of numerous chalcopyrite lamellae throughout the bornite grains within few hours, together with the formation of digenite lamellae enveloping chalcopyrite; while under dry vacuum condition at the same temperatures, bornite remained stable. This suggests that the exsolution of chalcopyrite and digenite lamellae from bornite is a solid-state diffusion process, and that this solid-state diffusion process is induced and promoted by hydrothermal fluids in contact with the grain surface. Forming chalcopyrite and digenite from the decomposition of bornite requires the removal of about 15% Fe from the bornite structure to the fluid phase by solid-state diffusion of Fe from the interior to the surface of the grains, and this is relatively easy because the crystal structure of bornite, chalcopyrite, and digenite are all based on the same cubic closed packed sulfur framework, with tetrahedra sites filled with cations (Fe and Cu) or vacancies. This means low energy barrier for the diffusion of cations within and across these phases, and indeed rapid cation diffusion has been reported in bornite and digenite (Grguric and Putnis 1999). The proposed fluid-induced solid-state diffusion mechanism is supported by electron backscatter diffraction which confirmed the same crystallographic orientation between bornite, chalcopyrite, and digenite, and by microprobe elemental mapping which showed concentration gradient of Fe from the interior to the surface of the grains. The produced chalcopyrite and digenite were both further altered to covellite and/or chalcocite, depending on fluid composition, through the typical ICDP mechanism, producing complex intergrowth textures similar to what are observed in some nature specimen (Liu et al., 2017). This study highlights that hydrothermal fluids may significantly influence solid-state diffusion processes such as exsolution and that many complex mineral assemblages may have formed through complicated re-equilibration pathways involving the synergy between solid-state diffusion and dissolution-precipitation.

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Sequential sodic and potassic alterations by self-evolved hydrothermal system

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Feldspar is by far the most abundant group of minerals in the earth's crust (>50%). They contain a variety of chemical and structural features that can be indicative of their thermal and fluid-rock reaction history (Parsons et al., 2013). The sequential sodic and potassic alterations of alkali feldspar is common feature of large hydrothermal systems, including the world's most valuable ore deposit, 'porphyry copper' and IOCG (Sillitoe, 2003; Sillitoe, 2010), and it is observed both in single crystals and at deposit scale. However, the mechanism that results in such sequential alteration reactions is still controversial. In this study, a homogeneous sanidine was reacted with concentrated ¹⁸O-enriched or ¹⁶O-enriched NaCl solutions at 600°C and 2 kbar from 1 to 10 days. With increasing of time, reaction products changed from albite to K-feldspar that replaced the initially formed albite. Distinctive Raman frequency shift between the albite/K-feldspar formed in the ¹⁸O-enriched solution compared to that from ¹⁶O-enriched solution, suggesting ¹⁸O from solution was incorporated into the newly re-crystallized Kfeldspar and albite. Though an evident gradient in the Raman shift exists in the interface between albite and sanidine in all experiments, there is no observed gradient between pristine sanidine and the new K-feldspar. Thermodynamic equilibrium modelling of sanidine in NaCl solutions suggests that the cation ratio (K/Na) of the aqueous solution controls the reaction products, with albite initially forming when only minor sanidine had dissolved but with a new K-feldspar phase appearing when enough sanidine had dissolved. The thermodynamic modelling result is consistent with reaction products. We infer that this self-evolved hydrothermal system could be a potential mechanism for both feldspar zonation textures in single crystals or sodic and potassic sequential alteration zones in either porphyry and/or iron oxide copper-gold (IOCG) deposits.

References

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