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Key issues in fluid-rock interaction:
From the nano to the macroscale

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ABSTRACTS

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Invited Speakers

Rare Earth Element Mobility in the Middle to Lower Crust and Subduction Zones

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The rare earth elements (REE) are critical tracers of magmatic processes and source regions, and are essential for high-precision dating of orogenesis via the Sm/Nd and Lu/Hf isotopic systems. Moreover, REE mobility, or lack thereof, exerts critical controls on the REE budget of lithosphere subducted deep into Earth's mantle beyond the arc magma window. REE transport has been convincingly demonstrated in some settings, including ore deposits, contact zones around magmas, hydrothermal alteration, and regions of melt extraction. What is less clear, however, are patterns and magnitudes of mobility due to fluid flow in typical regional metamorphic and subduction environments. This study reviews geochemical data for a wide array of metamorphosed mafic, quartzofeldspathic, pelitic, and carbonate rocks. The most common types of REE behaviours observed, in no particular order, are: (1) little or no REE mobility; (2) LREE gains; (3) HREE gains; (4) mid-REE gains; (5) REE leaching; and (6) local REE redistribution. REE transport is always accompanied by the mobilization of non-REE major and trace elements. However, extensive mobilization of non-REE can occur without significant transport of the REE. Mobility of the REE is strongly tied to metasomatic mineral growth or breakdown. For example, garnet or xenotime growth can enrich rocks in HREE and Y, whereas monazite growth can drive LREE gains. Europium gains or losses relative to other REE are controlled by the precipitation or breakdown of plagioclase or lawsonite. Thorium is mostly immobile; Th transport was observed only in the most extreme fluid-rock interaction environments involving magmas or magmatic-hydrothermal fluids, or large fluxes through high-pressure/ultrahigh-pressure rocks. Uranium and REE can be mobilized without transport of Th. The general pattern that emerges is that REE mobility is most likely in settings where fluid fluxes are high due to channelization into flow conduits including veins, lithologic contacts, and shear zones.

Scapolite, sulfides, seismicity and fluid induced eclogite- and amphibolite facies metamorphism of thickened continental crust.

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The S-scapolite silvialite (ideally $\text{Ca}_4\text{Al}_6\text{O}_{24}\text{SO}_4$, but typically also containing Na and C) is one of the few volatile bearing minerals present in granulite facies terrains world-wide and so also in the Grenvillian (930 ma) granulite facies anorthosites of the Bergen Arcs, W-Norway. During the Caledonian (430 ma) continent collision between Baltica and Laurentia these granulites underwent a partially fluid-induced transformation to eclogite- and amphibolite facies assemblages. Pseudotachylyte veins (frictional melts and ultracommunitated materials formed by seismic events) are present in the granulites along the reaction front, locally following scapolite-enriched layers in the anorthosite where they become enriched in sulfur. Based on the oxidation state of S two types of pseudotachylytes can be distinguished: A flow banded type where a second generation of scapolite together with garnets forms dendrites overgrowing the flow banding and a sulfide-enriched type containing pyrite and pyrrhotite.

The scapolite may play several critical roles in transforming the anhydrous granulites to their hydrous eclogite and amphibolite facies equivalents: Dehydration embrittlement may explain the intermediate deep earthquakes. Such earthquakes may open the rock for fluid flow needed to induce the metamorphism. The composition of the fluid phase and thus the mineral paragenesis may be influenced by volatile components from scapolite breakdown. The sulfide impregnation along the pseudotachylyte may enhance the conductivity of the lower crust.

The dynamics of fluid flow in high fluid flux fault regimes: implications for fluid-rock reaction

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A vein-rich, regional-scale fault network, that is exceptionally well-exposed in Mesozoic limestones in NE Oman, provides an example of a fault-controlled hydrothermal flow system generated by breaching of a deeper level, overpressured fluid reservoir in the continental seismogenic regime. Oxygen isotope studies of fault rocks and associated calcite vein arrays provide unique insights about the distribution of high fluid fluxes in this network. Several key points emerge: (1) the distribution of high fluid flux was very heterogeneous; (2) fluid flow was episodic and influenced by repeated cycles of co-seismic permeability enhancement and interseismic permeability reduction; (3) high fluid fluxes were localised on segments of the major high displacement faults, as well as on arrays of smaller subsidiary faults; (4) changes in fault kinematics produced major changes in hydraulic connectivity between the fault system and the underlying reservoir.

Evaluation of fluid-rock reaction, isotopic exchange and time-integrated fluid fluxes in fracture-controlled flow regimes has classically assumed essentially steady state flow and reaction. However, the field and microstructural observations in Oman and elsewhere indicate a more complex behaviour in high fluid flux seismogenic regimes. Seismological observations from deep fluid injection experiments and some contemporary, high fluid flux faulting regimes provide novel insights about the dynamics of flow, reaction and faulting in overpressured, fluid-active settings that cannot be obtained from the rock record. In particular, it is shown that earthquake swarm behaviour is the characteristic response to fluid injection into faults within low permeability host rocks. The style of injection-driven swarm sequences refines our understanding of fault-valve behaviour and provides new constraints on volumetric flow rates, the durations of flow, and several aspects of fluid dynamics in high fluid flux faulting regimes.

These insights require a re-analysis of our understanding of the dynamics of flow and reaction in seismogenic regimes. They also have implications for our understanding of (1) where and why some styles of hydrothermal ore deposits occur within particular parts of fault networks, (2) the dynamics of ore deposition, and (3) the rates of formation of hydrothermal ore deposits fault-controlled, high fluid flux settings.

Eccentric zoning in pyrite: what does it record?

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Zoning in minerals is usually taken to record changes in the equilibrium mineral composition driven by changing pressure and/or temperature and/or fluid composition conditions, or depletion in elements sequestered by the minerals as it grows. Both these mechanisms require chemical equilibrium between the rim of the growing mineral and the immediate vicinity of that rim. Such growth zoning usually produces concentric zoning, which may or may not exhibit textural sector zoning.

Pyrite grains in metamorphic rocks sometimes exhibit eccentric zoning patterns cannot be explained easily by a simple equilibrium growth model. Such zoning may involve sulphur isotopes and trace elements such as cobalt. Features that can be expected due to processes such as interface-coupled dissolution-precipitation reactions, limited lengthscale chemical equilibrium and non-hydrostatic stress conditions will be discussed and compared to the observations. The implications for pyrite growth, and its use as a record of geological conditions will be discussed.

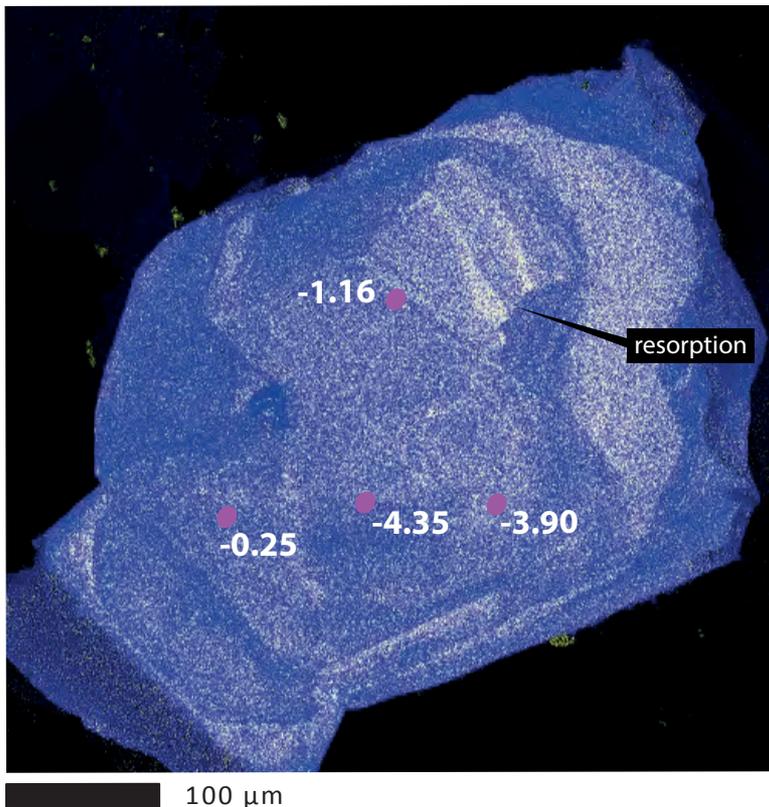


Figure 1: Eccentric zoning revealed out by Co distribution in pyrite in UHP metasediment from Lago di Cignana, Switzerland.

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Exploring the Aqueous Interface with Carbonate Minerals using Computer Simulation

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Crystallisation of carbonate minerals from aqueous solution is an important process in the environment as part of the process of biomineralisation. Technologically, there is also considerable interest in precipitation of carbonates for long-term geo-sequestration. Despite this significance there are many aspects of the formation of carbonate minerals that are only now becoming understood, such as the role of pre-nucleation clusters [1,2], liquid-liquid phase separation [3] and the change in stability of phases as a function of nanoparticle size [4]. In all of these processes the interaction between water and metal carbonates plays a critical role.

In this presentation the value of computer simulation to explore the properties of the interface between carbonate minerals and aqueous solution will be highlighted. Using molecular dynamics simulations based on accurately calibrated force fields [5], it is possible to obtain data on both the structure and dynamics of water as it interacts with mineral surfaces and to compare this against experimental data where available [6]. Here we will especially focus on the solvation of the basal surfaces of calcite, dolomite and magnesite, both for the terraces and also in the vicinity of steps, as well as other surface defects. Thermodynamic data on the interfacial energies with water can also be obtained using simpler continuum solvation models, as will be demonstrated for calcite [7].

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The CarbFix project: solubility and mineral storage of gas mixtures in basalt

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The long-term security of geologic carbon storage is critical to its success and public acceptance. Much of the security risk associated with geologic carbon storage stems from its buoyancy. Gaseous and supercritical CO₂ are less dense than formation waters providing a driving force for it to escape back to the surface. This buoyancy can be eradicated by the dissolution of CO₂ into water prior to, or during its injection into the subsurface. The dissolution makes it possible to inject into fractured rocks and further enhance mineral storage of CO₂, especially if injected into silicate rocks rich in divalent metal cations such as basalts and ultra-mafic rocks.

We have demonstrated the dissolution of CO₂ into water during its injection into basalt leading to its geologic solubility storage in less than 5 minutes. This process was verified via the injection of 175 tonnes of dissolved CO₂ into porous basaltic rocks at 20-50°C located 400-800 m below the surface at the CarbFix-1 field injection site in SW Iceland. Two years later, much of the dissolved constituents in the first monitoring well have returned back to the pre-injection concentrations, the waters are sitting at calcite saturation and calcite precipitation has been verified by solid calcite samples taken within the first monitoring well. Mass balance calculations on co-injected conservative tracers, suggest that more than 80% of the injected CO₂ was mineralised within a year from its injection.

The CarbFix method requires substantial water. Therefore, the estimated cost of storing and transporting a tonne of CO₂ at maximum reservoir exploitation at the CarbFix-1 site via dissolved water injection is about twice that of geologic storage via direct CO₂ injection in typical sedimentary basins. However, the cost of carbon capture and storage is still dominated worldwide by capture and gas separation. This capture cost could be lowered by injecting gas mixtures into rocks rather than pure CO₂ as is now being tested at the CarbFix-2 site in SW-Iceland. There, 70% CO₂ and 30% H₂S gas mixture is dissolved in waste water and condensation water from the Hellisheidi geothermal power plant and injected down into the basaltic rocks at about 700 m depth. In the first phase of the experiments about 8000 tonnes of the gas mixture will be injected per year.

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Role of organic geochemistry in mineral deposits

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Many major mineral accumulations contain substantial quantities of organic matter (OM), which plays a critical role in the formation of many deposits. Until recently many questions have remained unanswered on the association between OM and mineral accumulations globally. These include (i) What is the role of OM in the transport and/or precipitation of metal types? (ii) What are the main source(s) of the OM? and (iii) What geological environments (redox conditions, temperatures) have the OM been exposed to? Some examples of very recently published data on OM associated within the mineral matrices of several Australian mineral deposits will be presented. These include the world class 'Here's Your Chance' lead-zinc-silver deposit showing evidence for sulfur-cycling bacteria that led to changes in the water chemistry essential for the formation of such a deposit. Other deposits include uranium-rich samples from the Mulga rock, WA. Detailed organic geochemical and stable isotopic analyses shows that the OM associated with the uranium in the deposit is derived from highly aliphatic biopolymers present in a variety of extant organisms. These aliphatic biopolymers break down by radiolysis yielding a unique suite of compounds attributed to radiolytic cracking. A series of novel analytical instruments have also been developed and have been published, allowing the measurement of compound-specific sulfur isotopic composition ($\delta^{34}\text{S}$) of key organosulfur compounds in mineral deposits. Methods developed to isolate OM inside various minerals. Further, application and development of hydrolysis to study highly altered OM from gold deposits will be presented.

Equilibrium in stressed solid/liquid and solid/solid systems.

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The influence of stress on mineral reactions and on mineral phase equilibria has been a recurrent question in the geosciences since the work of Sorby and Harker and has re-emerged in various forms (Paterson, 1973; Wheeler, 2014). In 1876 Gibbs examined conditions for equilibrium in solid/fluid systems with large deformations and what we would now call elastic-plastic constitutive behaviour. He arrived at a Clapeyron relation defining equilibrium between a stressed solid (under a fixed strain) and a fluid and showed that departure from hydrostatic equilibrium exists but is small. This conclusion is confirmed by studies by Sekerka and Cahn (2006) and Frolov and Mishin (2010). Such a conclusion contrasts with most discussions in the geological literature. The question is: *why?*

To establish the conditions for chemical equilibrium in a polycrystalline, multi-component, stressed solid one begins by establishing the Gibbs-Duhem relation describing the inter-relations between state variables for each phase (Johnson and Schmalzried, 1992). From these relations one derives the Clapeyron equations and compares them with those for the hydrostatic situation to see if stress has a significant effect on phase equilibrium. This approach is quite general and follows that of Gibbs; it also defines the system phase rule.

However, one must ensure that thermodynamically admissible state functions are introduced and that the resulting expressions are consistent with the second law of thermodynamics (Truesdell, 1966). This has not always been the case in the geosciences where the mean stress, \bar{P} , or the normal stress, σ_N , on a solid/fluid interface, or plastic stored energy have been anointed as state variables and included in the expressions for the chemical potential. The use of these quantities leads to very large changes in the Clapeyron “slope” (Sekerka and Cahn, 2006) but one can also show that it leads to nonsense. The state functions that are thermodynamically admissible include the *first Piola stress* and *deformation gradient tensors* (first used for the problem by Gibbs) along with the *Helmholtz energy*, the *fluid pressure* and the *chemical* or *relative chemical potentials* (Gurtin et al., 2010). \bar{P} and σ_N are not admissible state variables since they do not define the energy of the solid. The total stress, not \bar{P} or σ_N , defines both the Helmholtz energy of the solid and the distortion of the crystal structure of the solid and hence the mismatch that needs to be accommodated as new hydrostatically-stressed crystal is accreted/nucleated on/in the stressed solid.

The conditions for equilibrium involve inter-facial relations. Hence the orientations of grain boundaries and interfacial stress and energy relations during nucleation and growth become fundamental in any general theory of equilibrium under non-hydrostatic stress. These are subjects we know relatively little about in minerals; progress will rest on microstructural studies that develop models concerning these issues

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Ore Formation – the product of anomalous fluid flux organisation

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Mass balance and other considerations indicate that the only plausible mechanism for the formation of a major metal ore deposit is the highly-focused advective flux of some carrier fluid (hydrothermal or magma). Although there is a vast potential range of chemical processes involved in ore formation, the parameter space of physical processes is much more restricted and generic. Therefore, it is suggested that better constraining these physical processes is the most effective way to improve our predictive targeting capability.

Recent advances in geochronology have emphasised that ore-formation occurs rapidly in narrow time intervals, within the broader-scale evolution of their host geological environments, and is associated with anomalous geodynamic conditions at the regional scale. This appears to be independent of deposit type and can only implicate fundamental processes of fluid flux organisation. Related to this, it has also become clear that ore-formation is closely associated with settings where the geodynamic environment and/or structural architecture does not favour bulk upward fluid flow but instead rather mostly acts to provide impediments to flow. These observations, taken together, have led to the proposal that ore-formation is an example of a self-organised critical system in the sense of Bak et al (1987).

Refining our understanding of the physical processes of ore-fluid organisation should be a strong focus of future economic geology research because it has many important pragmatic implications. These include improving the resolution of regional targeting by more effectively targeting the key geological intervals that represent ore-forming geodynamic anomalies, helping to elucidate camp rather than deposit-scale controls and better targeting of ore-shoots at depth within known mineralised systems.

Disequilibrium Metamorphism

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In the presence of fluids, metamorphic reactions are fast compared to tectonically induced changes in pressure and temperature. Hence, during fluid-producing metamorphism, rocks evolve through near-equilibrium states. However, much of the Earth's lower and middle crust, and a significant fraction of the upper mantle do not contain free fluids. These parts of the lithosphere exist in a metastable state and are mechanically strong. When subject to changing temperature and pressure conditions at plate boundaries or elsewhere, these rocks do not react until exposed to externally derived fluids. Metamorphism of such rocks consumes fluids, and takes place far from equilibrium through a complex coupling between fluid migration, chemical reactions, and deformation processes. This *disequilibrium metamorphism* is characterized by fast reaction rates, dissipation of large amounts of energy as heat and work, generation of a range of dissipative structures which often controls transport properties and thus further reaction progress, and a strong coupling to far-field tectonic stress. Fluid consuming metamorphism almost invariably leads to mechanical weakening, and we propose that strain localization in the lower crust is often controlled by the availability of fluids. Thus, fault-controlled migration of meteoric fluids from the brittle crust, to the underlying ductile region may provide a spatial and temporal link between localized strain and seismic activity in the upper crust and shear zone controlled deformation below.

Experimental simulation of porphyry copper deposit formation via SO₂ -triggered sulfide precipitation from metalliferous brine.

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Porphyry copper deposits supply 75% of the world's copper. They are typically associated with intrusions of magma in the crust above subduction zones, indicating a primary role for magmatism in driving mineralization. However, given that evolved arc magmas contain little or no sulfur, it is not clear that a single, copper-rich, magmatic fluid could trigger precipitation of sulfide ore minerals within a zone of hydrothermally altered rock. Blundy et al (2015), drawing on observations of modern subduction zone volcanism proposed an alternative process for porphyry copper formation, in which copper enrichment initially involves metalliferous, magmatic hyper-saline liquids, or brines exsolved from large, magmatic intrusions assembled in the shallow crust over tens to hundreds of thousands of years. In a subsequent step, sulfide ore precipitation is triggered by the interaction of the accumulated brines with sulfur-rich gases, liberated in short-lived bursts from the underlying mafic magmas. Using high-temperature/pressure laboratory experiments to simulate such gas-brine interactions, experiments yielded copper-iron sulfide minerals and hydrogen chloride gas at magmatic temperatures of 700–800°C, with textural and chemical characteristics that resemble those in porphyry copper deposits. Thus, it was concluded that porphyry copper ore forms in a two-stage process of brine enrichment followed by H₂S-SO₂ gas-induced precipitation. Subsequently, Henley et al (2015) showed that a very rapid chemisorption reaction occurs between sulphur dioxide gas, a principal component of magmatic gas mixtures, and calcic feldspar, an abundant mineral in the arc crust. The chemisorption reaction generates the mineral anhydrite and hydrogen sulphide gas, and triggers deposition of metal sulfides. This work suggested that SO₂ alone may trigger deposition of copper sulfide from brine in porphyry settings. However, the Henley et al experiments document anhydrous 1 atm gas reactions rather than more realistic hydrostatic simulations. To test if SO₂ reduction via anhydrite formation can efficiently trigger copper sulphide deposition, we experimentally reacted SO₂ gas with calcite plus Cu-Fe-Na-Cl-brine at elevated pressure and temperature. An un-sealed gold capsule containing sodium sulphite was sealed inside an outer gold capsule containing calcite plus brine. Capsules were then placed in cold-seal vessels and run for two hour at 650° C and 1.5 kbar, and rapidly quenched. During the experiments sodium sulphite decomposes by the following reaction: $\text{Na}_2\text{SO}_3 + 2 \text{H}^+ \rightarrow 2 \text{Na}^+ + \text{H}_2\text{O} + \text{SO}_2$. Run products show chalcopyrite with anhydrite grown at the expense of calcite. Thus, for the first time, chalcopyrite has been experimentally synthesised by reaction between SO₂ gas (the dominant sulphur component of magmatic gas) and brine. This work may highlight the key reaction in porphyry copper deposit formation and has obvious implications for the development of metal-bearing skarns.

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Fluid mass transfer and rapid rates of deposit formation contrasted against gold remobilisation and high grade oreshoot formation.

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Self-organising phenomena, such as earthquake-aftershock sequences, seismic swarms and fluid pressure-driven failure are the physical manifestations of fluid mass transfer in the crust, potentially leading to mineralization. In considering such processes it becomes possible to estimate durations of mineralization in orogenic-type mineral systems, using a combination of field observations, experiments and numerical modelling. Permeability increases and decays during the seismic cycle but it is shown, despite permeability decay, that large volumes of fluid can transfer through the crust over short periods of time following seismic events. The fluid volumes are such that a 5 Moz goldfield could feasibly form in 1-16 earthquake-aftershock sequences, representing durations of just 10-8000 years. Similar rapid durations for goldfield formation have been inferred for Carlin, porphyry and epithermal deposits. Our results have significant implications for fluid chemistry during rapid ascent, including the saturation of metals, ligands and other species and the extent of fluid-rock reaction. However the formation of high grade oreshoots and the phenomenon of gold remobilisation remain difficult to explain.

In the second part of this talk, we describe primary auriferous arsenopyrites and overprinting networks of microfractures, which contain native gold. Using a combination of quantitative electron backscatter diffraction analysis, ion microprobe imaging and synchrotron XFM mapping it is shown that gold can be remobilised from the crystal lattice of sulphides and precipitated in anomalously high concentrations, via infiltration of only small volumes of fluids. The critical factors appear to be (1) low strain crystal-plasticity and microfracturing that allow fluids to access arsenopyrite crystals, (2) a dissolution-reprecipitation reaction that replaces auriferous arsenopyrite with nickeliferous arsenopyrite whilst releasing sulphur, and (3) gold complexation with high concentrations of sulfur at the crystal-fluid interface, enabling remobilisation. Given the low fluid volumes and localised but low-strain microfracture networks, the remobilisation process may relate more to fluid movement during development of microseismic swarms.

The chemical signature of syndeformational fluid-rock interaction: Nano- to microscale

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Field studies show that there is a strong interaction and feedback between physical and chemical processes that occur when rocks deform while interacting with externally derived, infiltrating fluids. The relationships between microstructures and local variations in chemistry can potentially be used to derive the timing relationships between deformation and fluid-rock interaction, the conditions of the interaction and the changing nature of the infiltrating fluid.

Here, we use examples of such interactions including field studies and experiments to discuss the potential of utilizing nano- to micro-scale patterns of chemical and microstructural signatures. Only now, these patterns can be recognized by combining a variety of traditional techniques with the emerging possibilities offered by, for example, NanoSIMS analysis, transmission Kikuchi diffraction analysis and atom-probe tomography.

Rock transformations controls shallow creep in active faults

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Several large continental active faults show evidence of aseismic creep in the first kilometres of depth. Such creep participates to the release of the tectonic load and represents an important component of the energy budget of these faults and their ability to produce large earthquakes. Such creep has been observed using time-lapse satellite imaging (InSAR) and creepmeters installed along the San Andreas Fault (USA), the North Anatolian Fault (Turkey), the Long Valley Fault (Taiwan), the El Pilar fault (Venezuela), and the Haiyuan fault (China), among others. In some fault segments, it accommodates up to 80% of the tectonic loading. This creep is either permanent or follows major earthquake during several months and is then called afterslip or post-seismic creep.

In the field, the same active fault can show locked segments, that produce large earthquakes, and segments with active creep. The question arises then on the control parameters of such rheological behaviour. We performed microstructural observations of rocks coming from the fault zones of the creeping segments of the San Andreas Fault and the North Anatolian fault. At least three micromechanisms of creep exist in the upper crust: pressure solution creep, grain frictional sliding and subcritical crack growth (i.e. stress corrosion). In the samples collected in creeping fault gouges, two of them could be identified unambiguously, i.e. pressure solution creep and frictional sliding. By comparing rocks outside of the fault zone and those inside the active creeping zone, the main differences in microstructures and rock composition could be identified. If the average chemical composition of the rock is not significantly different in the fault zone and in the host rock, the presence of weak minerals in the active creeping zone has been identified in both the San Andreas and the North Anatolian Fault. Such weak minerals, with a friction coefficient lower than 0.2, are organized into an anastomosing microstructure that makes the fault weak, and therefore prone to creep because elastic strain energy cannot be stored in such microstructure. We propose here that the transformation of the host rock, with the formation of weak minerals under the circulation of fluids, and the creation of a typical microstructure, represents a key ingredient to explain aseismic creep in major continental faults. The initial composition of the host rock is the main factor that explains the formation of weak minerals in the gouge and represents a common characteristics of creeping faults.

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The control of mineral weathering by dissolution-precipitation processes at the mineral interface

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Multicomponent silicate and carbonate minerals are major components of many rocks, and consequently their low-temperature weathering is of paramount importance for understanding a wide range of geochemical processes (Weissbart and Rimstidt, 2000). Many of these minerals dissolve incongruently, as reflected in the observed pattern of element release to aqueous solutions during laboratory dissolution experiment. This phenomenon results in the formation of so-called leached layers, which are chemically and structurally altered zones at the fluid-solid interface as much as several thousand angstroms thick and depleted in some elements relative to the bulk mineral composition (Casey et al., 1993; Brantley, 2008; Hellmann et al., 2012). The mechanism of formation of these layers is critical for understanding and evaluating dissolution kinetics of major rock-forming minerals, and is a matter of vigorous debate and controversy. Here we present *in situ*, high spatial resolution data on the evolution of mineral surface topography and interfacial fluid composition during dissolution of a model silicate, wollastonite (CaSiO₃) (Ruiz-Agudo et al. 2012). Our study provides clear, direct experimental evidence that leached layers are formed in a two-step process: stoichiometric dissolution of the pristine mineral surfaces and subsequent precipitation of amorphous silica from a supersaturated layer of fluid in contact with the mineral surface. This occurs despite the fact that the bulk solution is undersaturated with respect to the secondary phase. The thickness of the supersaturated zone depends on fluid flow rate and suggests an origin for the well-known discrepancy, of up to four orders of magnitude, between dissolution rates measured in the field and in the laboratory. We can speculate that the potential importance of our results extends to other multicomponent minerals or glasses in contact with acidic, CO₂-rich solutions. Thus, they may have implications for many Earth surface geochemical processes, including weathering and subsequent soil formation, evolution of climate, and the composition of the atmosphere and oceans, as well as important environmental and technological issues such as the deterioration of concrete and building stone, possible mobilization of nuclear wastes, and CO₂ sequestration. Demonstration that these layers form as a consequence of an interface-coupled dissolution-precipitation process is critical for the correct implementation of such a process in the formulation of codes aimed at quantifying reaction rates.

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Critical Stress-Overpressure States in Seismically Active Fault Zones and their Significance for Mineralization

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Frictional strength of faults in the upper crust is approximated by a Coulomb criterion, $\tau_f = C_f + \mu_s(\sigma_n - P_f)$, where τ and σ_n are, respectively, components of shear and normal stress acting on the fault, P_f is the pore-fluid pressure, C_f is the fault cohesion and μ_s is the coefficient of friction. Borehole stress measurements have shown that near-surface stress states in the crust are governed by the strength of faults with ‘Byerlee’ friction coefficients ($0.6 < \mu_s < 0.9$), optimally oriented for reshear in the prevailing stress regime under hydrostatic pore-fluid pressure (pore-fluid factor $\lambda_v = P_f/\sigma_v \sim 0.4$) – the ‘hydrostatic-Byerlee’ critical state (Townend & Zoback, 2000). These stress measurements are, however, all from strike-slip or normal fault environments where subvertical fractures facilitate fluid drainage.

The extent to which the earth’s crust is critically stressed to the edge of failure has been revealed by the growing incidence of earthquakes induced by deep injection of liquids into basement rocks (Ellsworth, 2013), emphasizing that fault reshear can be brought about by increasing pore-fluid pressure as well as by rising shear stress during tectonic straining. Moreover, there are indications that many seismically active fault zones are fluid-overpressured above hydrostatic, especially in the lower seismogenic zone ($z > 7$ km) (Sibson, 2014). This is especially the case for reverse fault regimes ($\sigma_v = \sigma_3$) which have the greatest capacity for generating and containing overpressure. Indeed, subduction megathrusts accounting for >90% of global seismic moment appear overpressured to near-lithostatic values ($\lambda_v \rightarrow 1.0$) across their full seismogenic depth ($z < 45$ km).

A small fraction of earthquakes exhibits a high diversity of aftershock focal mechanisms about the mainshock rupture suggesting near-total relief of shear stress along the fault rupture (i.e. $\Delta\tau/\tau_{fail} \rightarrow 1$). As $\Delta\tau < 10$ MPa in most cases, this has the implication that τ_{fail} is of the same order, requiring either exceptionally low fault friction ($\mu_s < 0.1$) or strongly elevated fluid overpressures ($\lambda_v \rightarrow 1.0$) within the fault zone. Examples include the 1952 M7.8 Kern County earthquake (Castillo & Zoback, 1995) and the 1989 M6.9 Loma Prieta earthquake (Beroza & Zoback, 1993), both involving components of steep reverse slip on faults poorly oriented for reactivation. **Critical stress-overpressure** (CSO) states are likely to prevail in rupture nucleation sites within such systems with differential stress and fluid-overpressure acting separately as time-dependent variables, enhancing chaotic behaviour.

Criteria for various modes of brittle failure (extensional and shear failure in intact rock, reshear of existing faults) can be represented on plots of differential stress ($\sigma_1 - \sigma_3$) versus λ_v constructed for a particular depth. Such plots illustrate the precarious inverse balance between levels of differential stress and fluid-overpressure in CSO states, both of which are buffered by rupturing and/or subsidiary brittle failure creating fracture permeability. They also illustrate the sensitivity of failure to $\Delta(\sigma_1 - \sigma_3)$ and ΔP_f for different stress regimes, faulting modes and fault orientation. CSO domains along faults poorly oriented for reactivation are conducive to *extreme fault-valve action* involving discharge of significant volumes of overpressured fluids along and around the mainshock rupture plane postfailure (Sibson, 1992). Alternation between a substantial prefailure differential stress and a postfailure state of near-zero differential stress suggests that exhumed CSO domains should

be characterized by mutual cross-cutting relationships between systematic vein-sets developed in the former and non-systematic veins developed in the latter.

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From Fluids – Realizing, Refurbishing, and Refining Resources

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Fluids do it all! It is not possible to understand how the world's resources are formed, or to engineer the beneficiation and recovery of resources without equations that put fluid at the center of the action. The fact that resource geology routinely refers to “plumbing systems” and “fluid migration” says that at some level we know fluids are central to the story. Nevertheless, we often unify our thoughts around other related topics, for example the structure, layout, alteration and zonation of an ore deposit or oil field. No doubt, a deeper understanding requires integration of knowledge extracted from many different vantage points.

There are two imminent challenges in the coming decade. *First*, it is essential that our thinking on metal and hydrocarbon resources be carried out under a single roof. *Second*, three-dimensional spatial relationships must be replaced by five new dimensions: Lithosphere-Atmosphere-Hydrosphere-Biosphere-Time. The fifth dimension, time, is not just an add-on, but it is the only parameter we have to organize and relate processes in whole earth systems.

In general, the petroleum geology community focuses on seawater anoxia and seeding of the photic zone with nutrients to create blooms or, alternatively, upwelling of less oxygenated bottom water as a source of instability and nutrient flux. Though the outcome is economically important, the causes through time are poorly understood and interrelated. In general, the ore geology community seeks explanations for ore deposition through deep earth, whether intrusion-related or metamorphically-driven. The line dividing intrusion and metamorphism is far too sharp, as ultimately intrusions are part of metamorphic-tectonogenic cycles, and degassing and volcanism have controlled atmosphere through time. Interpretation of ore-forming processes would benefit from more holistic thinking on the processes that really create metalliferous source rocks.

Except for a handful of breakaway thinkers, ore geologists still work from traditional models – metals and sulfur, one fluid or the meeting of separate fluids, temperature and pressure drops – where an ore deposit seemingly appears if the structure or lithostatic load is there to capture the event(s). Similarly, for petroleum geology, the few breakaway thinkers are usually marginalized as “blue sky teams and dreamers”. After all, oil is simply the result of a source rock reaching maturation. That is, basin subsides, geothermal gradient exceeds stability of (some) kerogen, and oil appears and migrates from source rock to waiting reservoir. But unconventional hydrocarbon has challenged this dogma, as has Os isotopic data for oils and fluids associated with oil. We still have a long road ahead, but the era of simple categorization of observations into geographically (geologically) transferable models is behind us.

The chemist's world of organometallic complexes may help draw geologists toward a better understanding of how metals and organic material interact. The experimental world tidies up nature, but geologists know all too well that controlling just a few parameters in an experiment does not begin to imitate the chaos in the natural environment. From two vantage points, ore and petroleum geology, it might just be that we are staring at the same fluid.

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Dramatic effects of stress on metamorphic reactions

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Temperature and pressure are primary controls on mineralogy in the Earth; thermodynamic calculations may predict mineralogy from temperature and pressure and vice versa. Such calculations assume that stress is isotropic despite the fact that differential stresses prevail in the Earth, resulting from large scale tectonics and/or differences between fluid and rock pressures in porous rocks. New calculations show that differential stress can have significant effects on thresholds for metamorphic reactions, depending on the grain-scale reaction pathways. A differential stress may, depending on the reaction pathway, have an effect equivalent to a pressure difference of the order of (assemblage volume)/(reaction volume change) times (differential stress). The multiplying factor is typically 10 or more. For example the onset of a garnet + clinopyroxene breakdown reaction may be offset up or down by the equivalent of 500 MPa in pressure for a 50 MPa differential stress. The effect is equivalent to a temperature difference of the order of (assemblage volume)/(reaction entropy change) times (differential stress). For example the onset of muscovite + quartz breakdown may be offset up or down by the equivalent of 130 C for a 50 MPa differential stress. Much of the Earth is under differential stress, so the new calculations invite a reappraisal of metamorphic mineralogy and microstructure, indicating that new insights into stresses and fluid pressures in the Earth can be won.

If you want to rely on metamorphic mineral assemblages to estimate depths then you won't like this. There are circumstances where that may still be a viable approach – but I challenge the geoscience community to reflect upon what those circumstances are, as well as to become excited about the new insights that may be gained into stresses given an integrated understanding of stress and chemistry. There have been two written comments so far attempting to repudiate this work; neither has achieved that aim. There is much experimental work, mathematical development and observation on natural rocks to be done to move the idea forwards.

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Oral Presentations

Textural and compositional complexities resulting from coupled dissolution-precipitation reactions in ore systems

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Textural observations are key to deciphering the origin and geological history of rocks and their constituting minerals. Over the past decade, experimental studies of ‘coupled dissolution reprecipitation reactions’ (CDR) have revealed a great diversity of textures that arise from the CDR mechanism for ore minerals. **In many examples, reaction mechanism rather than intensive properties such as P-T history control the textures of the products, and far-from-equilibrium or local equilibria at the mineral-fluid interface play a key role in controlling the final textures and mineral assemblages.** These processes can also lead to the scavenging of trace elements from hydrothermal fluids. Because by nature CDR reactions are interface-controlled, many of the products are metastable, which drives further reaction; these subsequent reactions can add to the textural complexity, or on the contrary obscure the original reaction mechanism.

This talk illustrates the diversity of textures that arise from CDR reactions and emphasizes the role of far-from-equilibrium processes in controlling the nature and grades of ores.

Boiled zircons? Vesicular texture in detrital zircons from the Chelmsford Formation, Sudbury impact structure, Canada

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Detrital zircons from the Chelmsford Formation, a post-impact greywacke deposited within the Sudbury impact structure (Ontario, Canada) during the Paleoproterozoic, were surveyed to search for shock microstructures to study the early erosional history of the impact basin. A population of 1,000 zircons was investigated by SEM. No definitive shock microstructures, such as planar microstructures or granular texture [1,2], were identified on exterior or interior surfaces. However, an unusual vesicular texture was observed in 4% of the grains surveyed (~40 grains). Backscattered electron (BSE) images of the exterior surfaces of the grains show that the vesicles are dominantly round, and occur as both open and closed voids that range from ~1 to ~10 μm in diameter. Variations in BSE intensity of vesicles indicate variable compositions. On interior surfaces, the vesicles are dark in CL, and range from 1-10 μm thick. Energy dispersive spectroscopic analysis of vesicles yields spectra consistent with both mineral (zircon, quartz, albite, alkali feldspar) and melt (zircon + aluminosilicate melt) compositions.

The roundness of vesicles is suggestive of volatile release during high temperature boiling. Similar boiling textures have been reported in shocked zircons from K-Pg ejecta [3], and the location of the Chelmsford Fm. within the Sudbury basin is consistent with an impact origin. However, some observations suggest the laboratory separation method, electric pulse disaggregation (EPD), may have formed the vesicles. EPD uses high voltage discharges through a water bath to disaggregate a rock. The dominant minerals that appear to have melted during vesicle formation are anhydrous (Zrn, Qtz, feldspars); an externally sourced volatile phase is thus needed. Both the EPD water bath, and surface water during the Sudbury impact are possible sources. However, the Chelmsford Fm. zircons are detrital, occurring in a post-impact siliciclastic rock; it is difficult to envision the preservation of glass vesicles on grain surfaces during erosion of shocked bedrock, fluvial transport and deposition, lithification, and subsequent greenschist facies metamorphism. The origin of vesicular texture in the Chelmsford Fm. detrital zircon suite thus remains speculative. Ongoing studies are focused on distinguishing the two possible formation mechanisms (impact vs. EPD) described above.

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Why bridge micron- to nanoscale observations in ore minerals?

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Crystal-structural modifications and compositional heterogeneity in ore minerals, if understood at different scales of observation, are paramount for understanding ore-forming processes down to the site where fluid-rock interaction or mineral transformation takes place. Recent examples from our group include: pore-attached Au-Te-nanoparticles in As-free pyrite, which provide nanoscale evidence for devolatilisation (Ciobanu et al., 2012); long-range superstructuring in hematite assisting incorporation of U, Pb and W (Ciobanu et al., 2013); twining that promotes Ge incorporation in Fe-rich sphalerite (Cook et al., 2015); and oscillatory zoning in uraninite precluding Pb-loss during U-decay (Macmillan et al., in review).

Application of different techniques is necessary to fully understand mineral crystal-chemistry, each with its own inherent advantages and disadvantages, and each with limited ranges of observational scale. FIB-SEM platforms open up new avenues for *in-situ* sampling of small volumes of material characterized by other techniques, including SEM, EPMA and LA-ICPMS. Slices lifted from the surface of a sample, can be imaged and prepared for TEM study. This permits bridging of micro- to nanoscale observations on a site of petrogenetic interest.

New generations of TEM instrumentation with aberration-corrected probe atomic resolution can map mineral reaction fronts down to the lattice scale. We show an example using a FIB-TEM foil prepared from a lamella of a rare Bi-sulphosalt. This phase ($\sim\text{Cu}_{2.5}\text{Ag}_{0.5}\text{Pb}_5\text{Bi}_{5.5}\text{S}_{15}$) does not correspond to a named, previously-described mineral species and is part of a complex sulphide-sulphosalt assemblage where native gold is found in abundance across an area with gradational compositional transition between Cu-poor and Cu-rich sulphosalts. Cu-enrichment in the sulphide ore here is a genetic indicator for Au-deposition, as determined from LA-ICP-MS data. STEM imaging on a FEI Titan Themis instrument shows several distinct modules in the crystal structure that are comparable with those interpreted for the neyite-cupronyite series (Makovicky et al., 2001; Ilinca et al., 2012). The structure is however subtly different, and represents an additional member of this series with a smaller unit cell. STEM imaging and EDS mapping shows strong heterogeneity in terms of the composition of one of the main modules, i.e. (111)_{PbS}, which is enriched in Cu but with irregular distribution throughout the crystal lattice. Therefore, considering the fact that the Cu is a proxy for Au enrichment, this is an example of how atomic-scale resolution, both for imaging and compositional mapping, can point to pathways for metal re-distribution within minerals with modular structures. Such pathways are commonly associated with porosity and open-fractures, none of which are present here. The implication is that minerals can trap metals within their crystal structure as a result of superimposed chemical gradients associated with late mineralising fluids. Lattice-scale metal entrapment assists formation of high-grade ore, such as the Cu-Au ore discussed here.

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Charnockites, chickens and eggs

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Charnockite is orthopyroxene-bearing granite. It is typically produced by solidification of hot, dry, felsic magma, but there is considerable confusion over “incipient” charnockites (Rajesh & Santosh 2014), which are coarse-grained patches of orthopyroxene-bearing felsic rock within a finer-grained biotite- and/or hornblende-bearing gneissic host. Such patches are identified by the distinctive dark brown or green colour of their quartz and feldspar compared to the pale quartz and feldspar of the host rock. These dark patches always contain variably retrogressed orthopyroxene and markedly reduced biotite and/or hornblende contents compared to the host that is orthopyroxene-absent. These differences in mineral mode imply that orthopyroxene in charnockite patches grew at the expense of biotite and/or hornblende via some form of dehydration. This is often ascribed to influx of low- $a_{\text{H}_2\text{O}}$ fluid based on (1) the shape and distribution of the dark patches around orthopyroxene grains; and (2) an apparent increase in CO_2 fluid inclusions in dark patches compared to the host. This led to suggestions that such fluids are responsible more generally for dehydration of the lower crust, conflicting with conventional petrological wisdom that anhydrous lower crust forms by melt extraction in the absence of volatile fluid.

There are several overlooked features of incipient charnockite that complicate this story. Firstly, it has long been known that the dark colouration around orthopyroxene is due to fine-grained chlorite and other iron-rich hydrous minerals. This low-temperature alteration must post-date orthopyroxene and the shape and distribution of the dark patches will therefore reflect passage of late hydrothermal fluids rather than any fluid present during orthopyroxene growth. Secondly, the host gneissic rock is migmatite that contains garnet-bearing leucosome with similar grain sizes and shapes to the charnockite patches. There is also some indication that garnet leucosome has the same increased abundance of CO_2 fluid inclusions seen in charnockite, weakening the link between low- $a_{\text{H}_2\text{O}}$ fluid and orthopyroxene growth. These observations are more consistent with orthopyroxene forming in leucosome as a peritectic product of dehydration melting in bulk compositions with lower Al or Fe^{2+} than those that stabilised garnet. In this model the low- $a_{\text{H}_2\text{O}}$ inclusions are residual fluids left after extraction of H_2O -rich melt from both garnet- and orthopyroxene-bearing leucosome.

This model fails, however, to explain the spatial link between orthopyroxene growth and hydrothermal retrogression. Why is evidence for hydrothermal alteration always present around orthopyroxene but never seen away from orthopyroxene? Perhaps the hydrothermal fluid passed through all rock types, but only caused visible alteration if it intersected orthopyroxene causing retrogression and release of FeO and other components into adjacent rock. If so, the dark patches that dominate incipient charnockite are linked to orthopyroxene breakdown rather than orthopyroxene growth, and incipient charnockites will remain a spectacular example of mineral reaction driven by external fluid flux but this reaction is low-temperature hydration around pre-existing orthopyroxene rather than high-temperature dehydration that stabilises orthopyroxene. This model has no need for substantial flux of externally derived low- $a_{\text{H}_2\text{O}}$ fluid, and instead requires influx of retrograde hydrothermal fluids that could be provided by granite plutons crystallising at depth.

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Magma emplacement in 3D

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Magma generation and emplacement is an important material and geochemical transfer process that shapes much of Earth continental crust. Molten material formed in deeper crustal levels or below the lithosphere contributes to the growth of the continental crust, forming magma eruptions in near-surface regions or large growing magma bodies at subcrustal levels. Understanding the physical processes involved in magma generation and its emplacement requires knowledge about the geochemical and physical properties of melt, magma (melt plus crystals) and host lithologies. Despite the fast growing volume of geological, geophysical and experimental data on magma rheology, chemistry, structure and emplacement, numerical simulations on the dynamics of magma ascent and emplacement are comparably rare. Because numerical studies devoted to magmatism have mainly focused on the internal dynamics of magma chambers (e.g.: Bergantz 2000, Dufek and Bachmann 2010), little is known about the visco-brittle/plastic interplay between magma and crust. In one of the few studies on magma rise and emplacement, Gerya and Burg (2007) have demonstrated the importance of host rock rheology upon emplacement in a two-dimensional setting. However, emplacement dynamics are intrinsically three dimensional phenomena and two dimensional studies lack to resolve the different shapes of magma. This study focuses on the large-scale ascent of magma from a sublithospheric source region along a magmatic channel to give first order estimates on intrusion geometries and related feedbacks between intruding magma and host lithologies. Here we focus on characterising magmatic intrusions shapes in different environments: variable rheology, existence of pre-existing shear zone, simultaneous extension during emplacement. The models show that all of the tested variables: rheology, pre-existing architecture, extension, have a impact on intrusion development and shape.

The numerical model is based on the I3VIS code and resolves magma ascent and emplacement on a lithospheric to upper mantle crosssection in three dimensions. Magma ascent in these models develops spontaneously and is controlled by magma rheology and density. Partially molten material has a much lower viscosity than the surrounding dry mantle or the continental crust and can move along the magmatic channel as a crystal/melt mixture.

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The “exsolution” or fluid catalysed unmixing behaviour under hydrothermal conditions

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Exsolution is generally considered as a solid state driven diffusion process at ‘high’ temperature, while the coupled dissolution-reprecipitation replacement (CDR) is fluid-driven mineral replacement reaction mechanism under mild conditions. In some systems, such as Au-Ag-Te and Cu-Fe-S, where ionic mobility is relatively high at relatively low temperatures (<250 °C), the interaction and competition between exsolution and CDR reactions can be expected. One of such example is the transformation from sylvanite [(Au,Ag)Te₂] to Au-Ag alloy (Figure 1)(Zhao et al 2013). In this process, sylvanite was initially replaced by an Au-Ag alloy following a CDR mechanism (Figure 2), depending on the dissolution rate of sylvanite and the solubility of tellurium in the system. Once the concentration of Te in the solution reach a critical state, instead of the continued precipitation Au-Ag alloy, a metastable Ag-rich-Te-depleted calaverite [(Au_{0.78}Ag_{0.22})Te_{1.74}] started to precipitation at the reaction interface. This Ag-rich-Te-depleted calaverite decomposes via ‘exsolution’ or fluid catalysed unmixing to stoichiometric calaverite (Au_{0.93}Ag_{0.07})Te₂ and phase *X* (Ag_{3+x}Au_{1-x}Te₂ with 0.1 < x < 0.55) (Cabri 1965), which in turn breaks down to a mixture of petzite (Ag₃AuTe₂) and hessite (Ag₂Te) below 120 °C via exsolution (Cabri 1965). As the reaction continues, the calaverite and phase *X* are all transformed to Au-Ag alloy via CDR.

A second example of this fluid catalysed unmixing or “exsolution” is in the hydrothermal synthesis of the bornite-digenite solid state solution (*bdss*). Here the solid solution unmixes to a mixtures of *bornite* and *digenite* under hydrothermal conditions and with the appreance of an exsolution texture. *Bdss* over the interval Bn₁₀₀ to Bn₆₀Dg₄₀ were synthesized by replacing chalcopyrite under hydrothermal conditions via CDR mechanism (Zhao et al. 2014). The “fluid catalysed unmixing” kinetics is very rapid and the lamella of Bn₉₀Dg₁₀ sample is readily observed under the SEM after only 1 hr annealing at 150 °C (Figure 3a). This occurred only when the sample was annealed in the synthesis solution by directly lowering the temperature of the autoclaves to annealing temperature. It can be contrasted with the behaviour of the system in dry runs, by sealing the CDR synthesized *bdss* in silica glass tubes and annealing the cells at the same temperature (exsolution pattern shown in Figure 3b), while

the breakdown of bornite under hydrothermal conditions is significantly rapid and the coarsening is effectively within the first 2 hours. This suggests that the fluid within the open porous microstructure plays an important role in driving the ‘exsolution’ or unmixing process, and it seems likely that the breakdown of the solid solution under these conditions is driven by dissolution-reprecipitation reactions rather than solid state diffusion. Hence we propose to call the process “fluid catalysed unmixing” rather than exsolution.

In conclusion, the unmixing process of a hydrothermal synthesized metastable mineral has been observed to be catalysed by CDR mechanism under hydrothermal conditions, which is significant more rapid (1000 times) than those traditional solid state driven exsolution patterns. The textures are however very similar to both mechanisms and mimic those observed in nature.

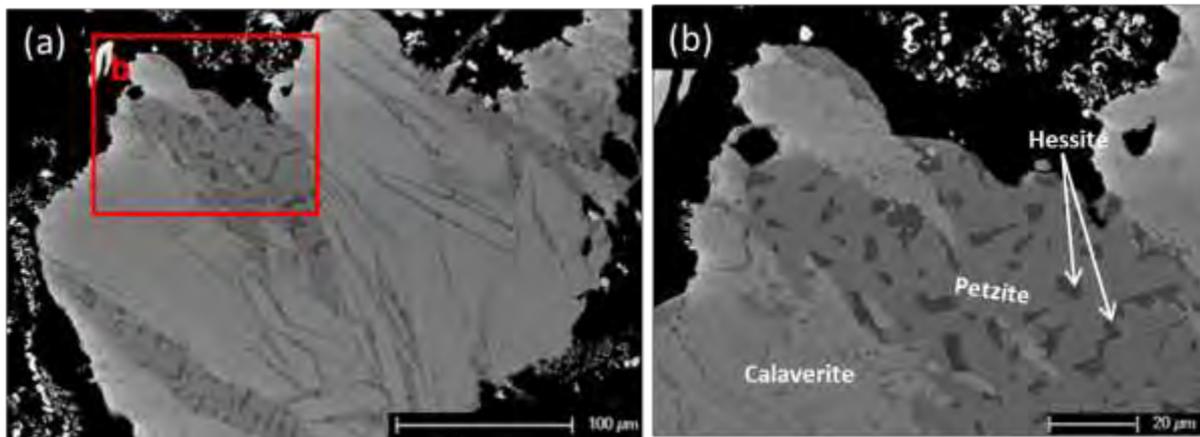


Figure 1 Backscattered electron and electron microprobe elemental images of cross section of a partially reacted grain illustrating the range of products and textures. (a) Overview of a grain. (b) Vein of petzite-hessite in calaverite [area shown in a].

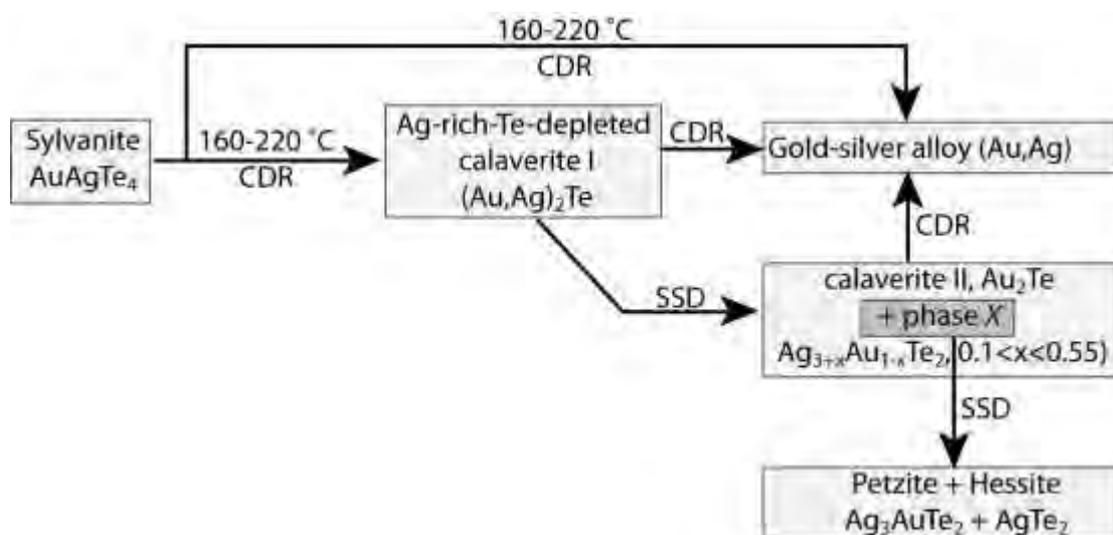


Figure 2 Overview of the proposed reaction paths of the hydrothermal reaction of sylvanite.

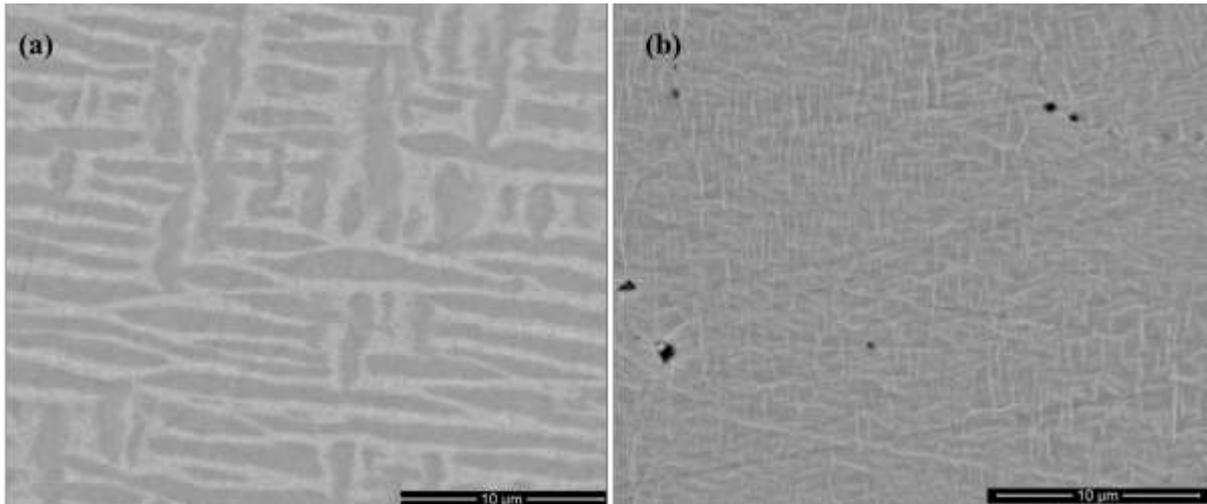


Figure 3 (a) Exsolution pattern of the annealed $Bn_{90}Dg_{10}$ sample obtained after 1-day annealing at 150 °C under hydrothermal conditions showing characteristic “basket weave” microstructure defined by exsolved *bornite* and *digenite*, and (b) exsolution pattern of hydrothermal synthesized *bdss* under dry conditions, showing very fine line of *digenite* in the matrix after 5-day annealing at 150 °C.

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Application of Automated Mineralogy Techniques to Understanding Fluid-Rock Interactions in Peridotite Xenoliths from Subduction Zones

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In March 2015, the John de Laeter Centre commissioned a Tescan Integrated Mineral Analysis (TIMA) instrument at Curtin University for the purpose of providing a new capability of rapidly determining the chemistry and mineralogy of complex rock samples and fabricated materials. The Curtin TIMA configuration consists of a Schottky field emission gun with 4 Peltier cooled, Si drift detectors enabling ultrafast X-ray data acquisition relative to standard SEM configurations. The integration of EDS-based mineral classification software into the instrument design provides the ability to quantify mineral abundance, grain size and textural parameters at micron scale resolution. This technology is commonly used to optimise mineral beneficiation at producing mine sites, however its application in petrology studies is relatively untested. This presentation will investigate the application of automated petrology on a suite of fluid-metasomatised mantle peridotite xenoliths erupted in a post-collisional arc volcanic environment in Papua New Guinea (Gregoire et al., 2001; McInnes et al., 2001; McInnes et al., 1999).

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Fracture Sealing in Geothermal Reservoirs: Insights from Combined EBSD and Chemical Mapping

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Development of natural and enhanced geothermal resources hosted in crystalline, volcanic and plutonic reservoir rocks, or in indurated, metamorphic basement reservoirs has increased over recent years (Bertani, 2012). In these reservoir rocks, permeability is dominated by faults and fractures, with small contributions made by primary permeability (Brace, 1980). As such the study of how these structures are generated, their properties (e.g. orientation, spatial distribution, aperture, orientation with respect to the stress field), and how they become filled with precipitated minerals is vital to understanding geothermal system evolution, and is key to their successful development. In particular, fracture sealing is known to decrease the overall permeability or create permeability barriers within a geothermal reservoir, limiting its effectiveness as a resource (Batzle and Simmons, 1976).

We use electron backscatter diffraction combined with cathodoluminescence and energy dispersive X-ray methods on quartz and calcite sealed fractures in high temperature geothermal fields in New Zealand to investigate potential controls on the sealing process. Results indicate that while chemical zonation patterns in fracture sealing minerals may be complex, the accompanying physical mineral growth processes and observed microstructure can either be simple or tell a more convoluted story.

Investigated calcite crystals in sealed fractures in a greywacke basement geothermal reservoir had either complex microstructure, including sub-grains and twinning, or had no crystal deformation beyond some low angle, continuous, crystal lattice distortion (McNamara et al., in prep). These observations combined with chemical zonation patterns suggest variable sealing mechanisms from asymmetrical syntaxial sealing to post-kinematic, crystal growth into free space. Additionally, the use of EBSD on fracture calcite holds the potential to inform us on supersaturation levels fluids depositing calcite in these fractures, and the deformation history of the developing geothermal reservoir through examination of sub-grain boundary and twinning properties in distinct, cross-cutting, calcite filled fractures.

Sealed Fractures in a diorite hosted geothermal reservoir show that vein quartz crystal nucleation occurs on quartz crystals in the fracture walls. The fracture wall quartz crystals also control the orientation on the fracture sealing quartz as the fracture closes via syntaxial sealing. Varying fracture quartz chemistry has little to no impact on subsequently developed quartz microstructure. The additional higher density of Dauphine twins in vein quartz may provide information on quartz vein deformation and hence deformation of the reservoir rock during geothermal system development, or may potentially serve as a fluid temperature indicator tool.

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Coupled fluid flow, mineral reactions and deformation in hydrothermal mineralising systems.

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Hydrothermal mineralising systems are treated as open flow systems where deformation by fracturing or brecciation is strongly coupled to fluid flow and mineral reactions at a number of spatial scales. This presentation explores the nonlinear behaviour of such a coupled system and shows that its evolution is characterised by a number of phase transitions some of which are critical and characterised by the development of multifractal geometries with long range spatial correlations in the distribution of alteration mineral assemblages and mineralisation. Such correlations are scale dependent so that no correlation may exist at small scales but long range correlations develop at larger scales. This scale dependent behaviour is related to the development of through-going plumbing systems at larger and larger scales which in turn is coupled to the deformation. The correlations are quantified using wavelet analysis from which we can extract multifractal spectra and Hurst exponents, H , as a function of scale. Systems with $H > 0.5$ have long range correlations whereas those with $H < 0.5$ are spatially anti-correlated. Systems with $H = 0.5$ are random with no correlations. Thus the Hurst exponent is a powerful means of characterising both alteration and mineralisation geometries. The mineral assemblages that develop in these systems are non-equilibrium assemblages and the microstructures resemble those that result from critical (continuous or second order) phase transitions rather than those that form from classical nucleation and growth microstructures. This presentation explores the fluid-chemical-deformation relations that lead to criticality, multifractal geometries, long range correlations and overprinting paragenesis relations. It is proposed that “successful” mineralising systems are characterised by long range correlations ($H > 0.5$) whereas “unsuccessful” systems have $H \leq 0.5$.

Carbonate replacement reactions in hydrothermal systems

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Hydrothermal gold mineralisation is often accompanied by carbonate alteration of the original silicate assemblage. Protracted fluid flow leads to increased alteration intensity and replacement of the existing carbonate minerals by new ones. At the Junction gold deposit, Kambalda, WA, greenschist facies metabasites were altered to a calcite + biotite + chlorite assemblage with pyrrhotite replacing oxide phases¹. Gold mineralisation occurs adjacent to quartz veins associated with the breakdown of biotite to chlorite, muscovite and siderite. During this process, microporous calcite is replaced by euhedral siderite and dolomite. In this study we show how nucleation occurred preferentially along twin boundaries, which acted as fluid pathways². Multiple epitaxial nucleation sites within a large single calcite crystal lead to low angle boundary formation that is not related to deformation and recovery because adjacent grains are similarly oriented.

Contrary to many studies the product minerals are not porous. Porosity generated by the volume change that accompanies sideritisation is consolidated with the initial microporosity ahead of the reaction front. The result of this is that the products are effectively growing into 'open space' and produce euhedral crystal shapes. Whilst the dolomite appears to be filling voids created during the sideritisation reaction, we infer that dolomitisation and sideritisation are coeval based on the alignment of nucleation centres along pre-existing calcite twin orientations.

The microstructural implications of volume change during carbonate reactions were investigated experimentally using a flow through reactor and fractured marble³. Dolomitisation was effected by reacting the marble with MgCl at 200°C. During an initial induction phase the solution, undersaturated with Ca and carbonate ions, accesses the marble along grain boundaries. Access is enhanced by minor dissolution of the calcite. Once the reaction front solution, isolated from the bulk of the fluid, reaches dolomite saturation, dolomite is precipitated following epitaxial nucleation on the calcite grains. The volume change means that the grain boundary porosity is enhanced, but there is no evidence of nano- to micro-scale porosity. In extreme cases, the permeability increase means that the reaction front is quickly no longer isolated and the strong positive feedback causes the calcite to be dissolved completely leaving only the first formed dolomite. This situation is analogous to open hydrothermal systems where early-formed phases may be removed completely during protracted fluid flow.

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Channelized fluid escape from subduction zones

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Within our solar system Earth is the only planet that has both plate tectonics and water. These may not be intuitively linked as the amount of water is extremely small compared to the Earth's entire mass. However, water has an enormous impact on Earth's geodynamics and geochemical cycles at all scales. The most prominent examples of this link between water and plate tectonics are found in subduction zones. In these zones seawater-altered oceanic lithosphere is returned to the mantle, thereby heating up during descent and releasing fluids through hydrous mineral dehydration facilitating global mass transfer. These dehydration reactions e.g., liberate fluids that trigger mantle melting fueling explosive volcanism [ENREF_2](#) and are a source of intermediate-depth seismicity. As the global water input into subduction zones per million years is on the order of the oceans' total water volume efficient, large-scale transport systems need to form to drain the descendent oceanic plates and return subduction zone fluids to the exogenous reservoirs. The fluid escape through these transport systems needs to keep pace with the slab descent velocity of cm/year. Otherwise, even in the presence of other natural outgassing mechanisms the oceans would drain within only a few million years.

If fluid escape would be controlled by the low background permeability at the conditions at which dehydration reactions occur (30 – 300 km, 2 – 10 GPa), resultant slow, static pervasive fluid flow would be insufficient to drain the descending plates. Thus, a fluid escape mechanism is required that allows fluid flow to organize itself into high flux transport systems. Although globally documented vein systems in high-pressure metamorphic terrains confirm that high fluid fluxes are achieved through fluid flow channelization the rate-limiting microscale mechanism that controls the bottleneck coupling of initial fluid production from a zero-porosity, water-rich rock into a rock characterized by high permeability channels is largely unknown.

Here, we show that water release from high-pressure (~2.5 GPa) hydrated mantle rocks is controlled by intrinsic chemical heterogeneities that localize dehydration reactions at specific microsites. This results in fluid pressure variations throughout the rock, which force the fluid release to organize itself into a channelized fluid flow network across length scales spanning six-orders of magnitude (μm -m). We formulate a model that defines the coupling between microscopic fluid release and fluid flow channelization. This is crucial in order to formulating future quantitative models that address spatiotemporal processes, such as the link between fluid release at depth and volcanic eruptions, and the amount of mineral-bound water transferred into the deep Earth.

Coupled mass transfer through a fluid phase and volume preservation during the hydration of granulite: An example from the Bergen Arcs, Norway

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The Precambrian granulite facies rocks of Lindås Nappe, Bergen Arcs, Caledonides of W.Norway are partially hydrated at amphibolite and eclogite facies conditions. The Lindås Nappe outcrops over an area of ca 1000 km² where relict granulite facies lenses make up only ca 10%. At Hillandsvatnet, garnetite displays sharp hydration fronts across which the granulite facies assemblage composed of garnet (55%) and clinopyroxene (45%) is replaced by an amphibolite facies mineralogy defined by chlorite, epidote and amphibole. The major element bulk composition does not change significantly across the hydration front, apart from the volatile components (loss on ignition, LOI) that increases from 0.17 wt.% in the granulite to 2.43 wt.% in the amphibolite.

The replacements of garnet and of clinopyroxene are pseudomorphous so that the grain shapes of the garnet and clinopyroxene are preserved even when they are completely replaced. The textural evolution during the replacement of garnet by pargasite, epidote and chlorite and of pyroxene by hornblende and quartz in our rock sample conforms to that expected by a coupled dissolution-precipitation mechanism. SEM and microprobe analysis coupled with the software XMapTools V 1.06.1 were used to quantify the local mass transfer required during the replacement processes. The element losses and gains in replacing the garnet are approximately balanced by the opposite gains and losses associated with the replacement of clinopyroxene. The coupling between dissolution and precipitation on both the grain and whole rock spatial scale preserves the volume of the rock throughout the hydration process.

However, the hydration involves reduction of rock density and mass balance calculations, together with volume preservation require a significant loss of the mass of the rock to the fluid phase. This suggests a mechanism for coupling between the local stress generated by hydration reactions and mass transfer, dependent on the spatial scale over which the system is open.

Coupled dissolution and precipitation at mineral-fluid interfaces

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The basic principle behind reactions occurring at the mineral-fluid interface is that one mineral may be replaced by another more stable mineral by an interface-coupled dissolution-precipitation mechanism. An aqueous fluid will induce some dissolution even in a highly insoluble phase, such as most minerals, producing an interfacial boundary layer of fluid that may be supersaturated with respect to one or more stable phases. One of these phases may then nucleate at the surface of the parent phase initiating an autocatalytic reaction that couples the dissolution and precipitation rates. If an epitaxial crystallographic matching exists between the parent substrate and the product, the nucleation of the new phase transfers crystallographic information from parent to product.

In order to propagate a pseudomorphic replacement front, mass transfer pathways must be maintained between the fluid reservoir and the reaction interface. This requires that the replacement process is a volume deficit reaction, and that the resulting product is porous and hence allows continued infiltration of the fluid phase to the interface within the parent phase.

Examples will be discussed where this scenario exists in nature to show that this is a ubiquitous mechanism occurring in the crust of the Earth during such processes as metamorphism, metasomatism and weathering.

Fluid-controlled rheological responses during intraplate orogeny

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The intraplate Alice Springs Orogen, central Australia, is characterised by fluid-rock systems that systematically vary in their depth, structural style, fluid sources and magnitude of rehydration and reworking. Discrete metre-scale cataclastic faults in the northwest Reynolds–Anmatjira Ranges progress into ten- to hundred metre-scale metasomatised shear zones at the southeastern margin of this terrane, associated with low $\delta^{18}\text{O}$ and δD values indicative of a meteoric fluid source. Continuing along strike to the southeast, these structures are succeeded by kilometre-scale schist belts transecting Palaeoproterozoic granulites in the Strangways Metamorphic Complex, followed by a $\sim 7500\text{ km}^2$ zone of pervasive Palaeozoic amphibolite facies retrogression and voluminous partial melting in the Harts Range and Entia Gneiss Complex further east. Strongly deformed outcrops of the basal sedimentary unit of the Amadeus Basin (Heavitree Quartzite) are preserved in these areas, and isotopically heavy compositions suggest that shear zones of the Strangways Metamorphic Complex contain fluids sourced from its prograde dewatering.

Intriguingly, despite being part of a laterally-continuous, anastomosing shear belt that forms the dominant structural network of the Alice Springs Orogen, the fluid-rock systems described above appear to be diachronous. Their ages span 120 Myr of fluid-rock interaction and partial-melting, and contain multiple prograde thermal cycles that attest to a prolonged and episodic history of fluid-driven metamorphism. This represents a remarkable natural laboratory to investigate the contribution of metasomatic processes to intraplate orogenesis through space and time.

We explore the possibility that the fluid-rock interaction history of this intraplate orogenic event had a profound impact on its structural/metamorphic expression, and by inference the rheological response of the lithosphere. In particular, we suggest that lithospheric weakening was modulated by regional changes in basin architecture, such that the distribution of sediment thickness prior to the Alice Springs Orogeny had a direct impact on the subsequent degree of rehydration and reworking in its underlying basement. The widespread dewatering of deeply buried sediments becomes increasingly important at the highest metamorphic grades of the eastern Arunta Region, where repeated anatexis occurred in otherwise infertile granulite facies crust. Far from being a purely local phenomena, therefore, deep crustal metasomatism had a profound impact on the large-scale dynamics of basement reactivation, acting in concert with other factors such as regionally elevated heat production to prime the lithosphere for reworking.

A shocking transformation: probing Precambrian reidite using state-of-the-art micro- to sub-nanometer 3D imaging

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The ~1.18 Gyr Stac Fada Member of the Stoer Group, NW Scotland represents a Mesoproterozoic impactite. Zircon from the unit has been characterized by state-of-the-art micro- to sub-nanometer imaging. In two zircon grains (1% of grains analysed) cathodoluminescence reveals variably developed < 2 μm wide lamellae within the host zircon. Electron backscatter diffraction (EBSD) data from these lamellae establish that they are the rare, ZrSiO_4 polymorph reidite. This is the only extant example of reidite in the Precambrian rock record and provides unambiguous evidence of shock pressures in excess of ~30 GPa. EBSD data also confirm the previously reported crystallographic relationship $\{100\}_{\text{Z}}//\{112\}_{\text{R}}$ and $[001]_{\text{Z}}//\langle 110 \rangle_{\text{R}}$ between the host zircon and reidite. However, focused ion beam milling and transmission Kikuchi diffraction (TKD) analysis of a thin foil, taken perpendicular to the EBSD-mapped sample surface, reveals that the interface of the zircon and reidite lamellae are oblique to these crystallographic planes. This observation is not consistent with reidite formation by the purported $\{100\}[001]$ martensitic transformation of zircon.

In detail, the reidite lamellae are locally deformed and EBSD mapping at 50 nm step size shows the sites of deformation to comprise baddeleyite (ZrO_2) and an amorphous phase, interpreted to be silica. This observation marks the first natural example of reidite decomposition to ZrO_2 . In addition, the host zircon and reidite lamellae both contain low-angle boundaries, which are interpreted to represent recovery and the migration of shock-induced dislocations into lower energy configurations in the latter stages of the impact event. TKD analysis of one of these low-angle boundaries, captured within a FIB-milled atom probe needle, reveals a lattice disorientation of 2° across a zone of ~20 nm width. Atom probe analysis reveals elevated concentrations of Y, Be and Al within the low-angle boundary, which we interpret to reflect trace element migration within the cores of mobile dislocations during recovery. The prospect of a dynamic dislocation-migration process being responsible for trace element modification within shocked zircon has potential implications for the dating of impact events by high-spatial resolution U-Pb geochronology.

On the formation, growth, and shapes of solution pipes

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Cylindrical, vertical structures called solution pipes are a characteristic feature of epikarst, encountered in different parts of the world, both in relatively cold areas such as England and Poland (where their formation is linked to glacial processes) [1] and in coastal areas in tropical or subtropical climate (Bermuda, Australia, South Africa, Caribbean, Mediterranean) [2,3]. They are invariably associated with weakly cemented, porous limestones and relatively high groundwater fluxes. Many of them develop under the colluvial sandy cover and contain the fill of clayey silt. Although it is widely accepted that they are solutional in origin, the exact mechanism by which the flow becomes focused is still under debate. The hypotheses include the concentration of acidified water around stems and roots of plants, or the presence of pre-existing fractures or steeply dipping bedding planes, which would determine the points of entry for the focused groundwater flows. However, there are field sites where neither of these mechanisms was apparently at play and yet the pipes are formed in large quantities [1]. In this communication we show that the systems of solution pipes can develop spontaneously in nearly uniform matrix due to the reactive-infiltration instability: a homogeneous porous matrix is unstable with respect to small variations in local permeability; regions of high permeability dissolve faster because of enhanced transport of reactants, which leads to increased rippling of the front. This leads to the formation of a system of solution pipes which then advance into the matrix. We study this process numerically, by a combination of 2d- and 3d-simulations, solving the coupled flow and transport equations at the Darcy scale. The relative simplicity of this system (pipes developing in a uniform porous matrix, without any pre-existing structure) makes it very attractive from the modelling standpoint. We quantify the factors which control the pipe diameters and the distances between the pipes as well as their growth rates. The most interesting result is the existence of two different regimes of the piped growth, depending on the flow rate. At high flow rates, well-separated, cylindrical shafts are formed, of a nearly uniform diameter all along their lengths. They advance quickly into the matrix, with velocities several times larger than that of a unperturbed, planar dissolution front. Conversely, for small flow rates, the pipes are funnel-shaped with parabolic tips and their advancement velocity is of the same order as that of a planar front. The transition between the two forms is abrupt, with no intermediate forms observed. The simulation results are compared with field evidence from limestone quarries in Smerdyna, Poland, where several hundred of solution pipes have been exposed. Interestingly, both forms (shaft-like and tunnel-like) are found in the field, sometimes in close proximity to each other.

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Geophysical signature of fluid-rock interactions

Core-flooding experiments of CO₂-rich fluids in carbonate rocks

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Fluid flow in the Earth's subsurface is accompanied by various fluid-rock interactions, leading to changes in the rock frame and fluid composition and subsequently affecting the physical rock properties such as strength, electrical conductivity, permeability and seismic wave propagation. Studying the coupling between fluid flow, fluid-rock interactions, rock deformation and geophysical observables can greatly improve the understanding of fundamental problems such as diagenesis of sedimentary basins, hydrothermal circulations, earthquake generation etc. as well as that of many geo-engineering applications such as extraction of natural resources of oil, gas or steam, nuclear waste disposal or geological carbon storage. Progress on these areas requires a multidisciplinary approach.

As a PhD student at IPG Paris, and then as a postdoctoral researcher at Stanford University, I have been involved in core flooding experiments consisting of the injection of CO₂-rich fluids in limestones of simple mineralogy (calcite) but complex microstructure (broad pore size distribution), under conditions of a transport-limited regime ($Pe \gg 1$ and $Da \gg 1$ at the sample scale). These experiments used a combination of geochemical fluid analyses to characterize fluid-rock interactions, imaging techniques to document changes in the rock microstructure (VP-SEM, X-ray tomography) and measurements of physical rock properties (permeability, electrical formation factor and P- and S-wave velocities). Some key results obtained from these experiments [Vialle, 2008; Vialle & Vanorio, 2011; Vialle et al., 2014] are that (1) dissolution of calcite leads to an increase of porosity but this increase can be counter-balanced by compaction of the sample depending on the values of pore and confining pressures, (2) there is a preferential dissolution in the most porous part of the sample (*i.e.* connected macropores and microporous micrite) and eventual reprecipitation in the least porous parts (*i.e.* tight micrite); it was shown [Vialle et al., 2013] that this observation can be quantitatively explained through the use of local Péclet and Damköhler numbers expressed as a function of the rock physical properties (namely permeability and surface areas of the different microstructural facies), (3) electrical formation factor tends to decrease, (4) P- and S-wave velocities of the dry-frame decrease, indicating changes in the elastic properties (softening) of the rock. The methodology developed and the data acquired in these experiments set the bases to probe and constrain the development of new rock physics models: most of the current rock physics models used to invert the seismic data into rock and fluid properties do assume constant rock-frame elastic properties (*i.e.* no fluid-rock interactions). However, seismic data from some CO₂ sequestration sites for example (*e.g.* Frio, Cranfield sites) cannot be explained by classical rock physics interpretation and require introducing a softening in the rock elastic properties due to fluid-rock interactions [*e.g.* Al Hosni et al., submitted].

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Monomeric Amelogenin's C-Terminus Modulates Mineralization Dynamics of Calcium Phosphate

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The organic matrix in forming enamel consists largely of the self-assembled nanospheres of amelogenin monomers that play a critical role in controlling crystal growth of the highly organized apatites. However, little is known about the mechanisms of the monomeric form of the C-terminal tail of the molecule in regulating biomineralization dynamics. We investigated brushite–amelogenin's C-terminus interactions by *in situ* atomic force microscopy (AFM).¹ At very low concentrations (1–10 nM) within a monomeric form of amelogenin, we directly observe a strong interaction of monomeric amelogenin's C-terminus binding to the brushite (010) face, which modulates the critical length and terrace width of moving steps through modification of the brushite–water interfacial energies. This in turn inhibits crystallization by delaying the formation of active steps on the growing crystal face. These findings provide the underlying thermodynamics for understanding biomineral formation, reflecting monomeric protein interactions with precursor phases of developing enamel crystals.

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First direct evidence for hydrous mantle transition zone originated continental flood basalts

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It has previously been postulated that the Earth's hydrous mantle transition zone may play a key role in intra-plate magmatism, but no confirmatory evidence has been reported. Here, we demonstrate that hydrothermally-altered subducted oceanic crust was involved in generating the Late Cenozoic Chifeng continental flood basalts of East Asia. This study combines oxygen isotope with conventional geochemistry to provide the first evidence for an origin in the hydrous mantle transition zone (Ref 1)). These observations lead us to propose an alternative thermochemical model, whereby slab-triggered wet upwelling produces large volumes of melt that may rise from the hydrous mantle transition zone (Fig. 2; Ref 1 and 2). This model explains the lack of pre-magmatic lithospheric extension or a hot-spot track and also the arc-like signatures observed in some large-scale intra-continental magmas. Deep-Earth water cycling, linked to cold subduction, slab stagnation, wet mantle upwelling, and assembly-breakup of supercontinents, can account for the chemical diversity of many continental flood basalts.

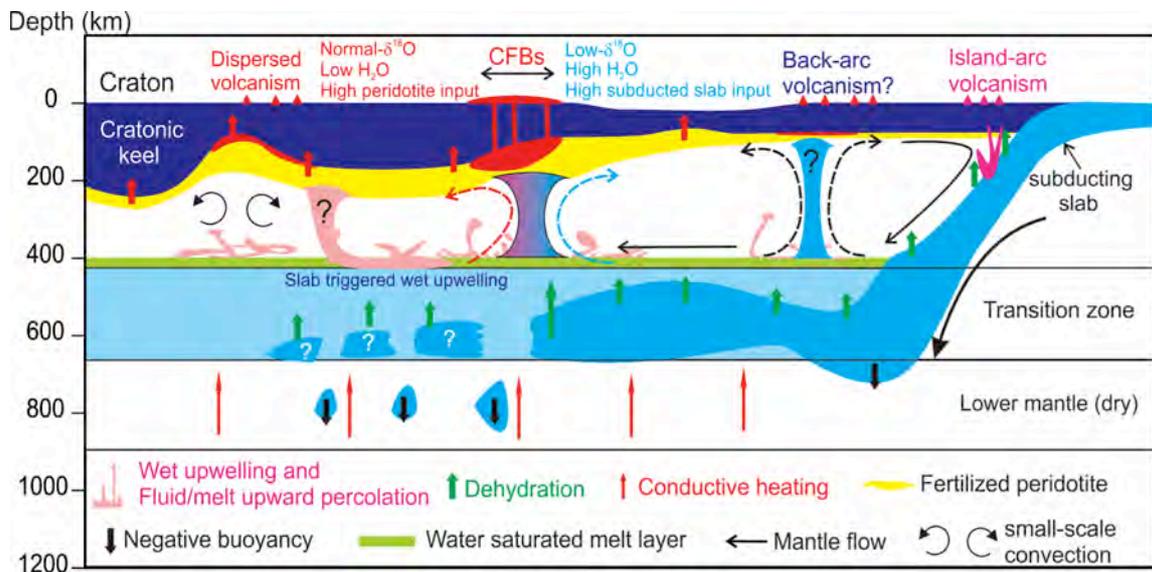


Fig. 1. Effect of slab stagnation and water cycling (wet upwelling, upward percolation, and re-fertilization) on the upper mantle thermochemical state.

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Can we track ore fluid chemistry from the chemical zonation of minerals? An experimental study of arsenic-bearing apatite

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Chemical zoning in mineral grains developed by fluid-rock interactions allows for the assessment of fluid composition and interaction conditions in ancient geological systems. In order to explore the chemical processes of mineral replacement reactions under hydrothermal conditions, and in particular to test the hypothesis that the observed chemical zonation in apatite can track the chemical evolution of hydrothermal ore fluids from which apatite was precipitated, we have conducted a series of hydrothermal mineral replacement experiments to establish a relationship between apatite composition and fluid chemistry.

In the first series of experiments we have reacted calcite crystals with As(V)-bearing phosphate solutions at 250°C. As-bearing apatite were formed in several hours. These results showed that complex zoning patterns and solid solution between apatite and arsenate apatite formed within hours. These zoning patterns were destroyed within days during secondary reactions, reflecting rapid fluid-rock reactions. Ultra-local equilibrium can form complex mineral zoning patterns, even when the overall system is highly fluid buffered (Borg et al., 2014).

In subsequent experiments we reacted calcite crystals with As(III)-bearing phosphate solutions and mixed As(III)/As(IV)-bearing phosphate solutions. As-bearing apatite were also formed in several hours. For As(III) experiments, bulk X-ray Near-Edge Spectroscopy (XANES) measurements showed that the arsenic maintained the oxidation state of 3 in the fully-reacted apatite. The Extended X-ray Fine Spectroscopy (EXAFS) analysis show that these As(III) ions have about three oxygen atoms at the As-O bond length of Arsenate, indicating that they occupy the arsenate sites.

For the mixed As(III) and As(V) experiments, bulk XAS analysis show only As(V) in the fully reacted apatite; in contrast, the micro-XANES mapping of the As oxidation state in partially reacted samples reveals complex distribution of As(V)/As(III) ratios. XANES measurements on natural samples (Ernest Henry IOCG deposits, Australia; As-anomalous amphibolite-facies gneiss from Binntal, Switzerland) revealed only As(V).

These results suggest that the incorporation of arsenic in apatite is sensitive to the local fluid composition during crystallisation, and that some of the complexity in As zoning in partially reacted apatite may be due to local fluctuations of As(V)/As(III) ratios in the fluid. The fully reacted grains only record the preferred oxidation state (i.e., As(V)) from mixed-oxidation state solutions. Therefore, the arsenic in apatite may not be able to preserve the original ratios of arsenic oxidation in the fluid, and one should take cautions when interpreting observed chemical zonations in hydrothermal minerals such as apatite.

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Nano-particulates, Silicification and Fluid Pressure Transitions - Fluid Flow versus Mineralization, Kiggavik Region, Nunavut, Canada

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The Thelon basin, central Nunavut, Canada is a major uranium district centred on the Kiggavik area deposits. Basement comprises Neoproterozoic metagreywackes and extrusive volcanics that are overlain by Paleoproterozoic strata characterized by a distinctive basal orthoquartzite and intruded by a 1.83Ga granite. Thrusting, ductile deformation and transposition of Archean and Paleoproterozoic units have created a sub-horizontal regional fabric on which the current Thelon basin architecture is imposed. Crustal-scale dextral transcurrent faults (eg. Thelon, Judge Sissons faults) that define the basin were active from 1.75-1.5 Ga. Periodic reactivation of faults continued throughout mineralization episodes. Mesoscopic structure of the major fault zones demonstrates extensive multiple fluid events, most commonly seen as quartz veining, or more notably, intense silicification and/or hematization of the host rock. Notably, U-mineralization tends to occur associated with intensely altered, brittle cross-structures and not the dominant, silicified zones. To date, two stages of uraninite have been recognized with alteration to coffinite.

Silicification and hematization of the regional fault zones is concomitant with brecciation and microcataclasis of the host units with repeated mechanical cannibalization of fault clasts. In many cases, the end product is a micrometre or smaller grain size aggregate of textureless “cherty” material with nanometer-scale hematite distributed throughout cryptocrystalline silica observed by transmission electron microscopy. The combination of deformation and precipitation textures, in conjunction with the long-term preservation, raises the question of whether gel-like silica-rich fluids are moving through through these dilatant zones. Given the absence of mineralization within the large movement zones, their role seems that of establishing zones of low permeability that restrict hydrothermal fluids associated with mineralizing alteration. Likewise, subhorizontal low permeability zones formed of quartzite layers and/or shallow silicified brecciation zones contribute to three-dimensional structuration of the basement to establish rock volumes within which fluids can be re-circulated over long time periods.

These contrasting faults are strikingly similar to that of Fountain Range fault, Mt. Isa inlier (Seybold et al. 2015). In the latter case, the bulk behaviour has been explained (Ord et al. 2015) in terms of cohesion hardening (silicified) vs. cohesion softening (altered and mineralized). Additionally, the violence of the associated fluid injection and brecciation of the silicified faults suggests repeated breaching of a crustal seal bounding supercritical (lithostatic)-subcritical (hydrostatic) fluid environments by the former (Saishu et al. 2014), while the mineralized zones comprise multiple pass fluid systems in an essentially hydrostatic fluid pressure regime.

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The Origin of Varied Length Scale of Shape Preservation in Mineral Replacement Reactions – Insights from the Replacement of Pentlandite by Violarite

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Mineral replacement reactions, in which the secondary mineral replaces the primary mineral in the presence of an aqueous phase, are widespread in natural hydrothermal processes (Putnis, 2009). The most important feature of mineral replacement reactions is that the secondary mineral preserves the external shape (and sometimes internal fine textural features) of the primary mineral, resulting in pseudomorphism. Many observations on natural specimen showed that the length scale of shape preservation varies from nano to macroscale, and this study tried to understand the reason for this varied length scale of shape preservation. In the replacement of pentlandite, $(\text{Fe,Ni})_9\text{S}_8$, by violarite, $(\text{NiFe})_3\text{S}_4$, under laboratory mild hydrothermal conditions, we found that pentlandite dissolution is rate-limiting under mild acidic to neutral conditions ($1 < \text{pH} < 6$), while violarite precipitation is rate-limiting under strong acidic conditions ($\text{pH} < 1$) (Xia et al., 2009). The difference in rate-limiting steps influences the coupling mechanism and causes the different length scale of pseudomorphism and different morphologies observed at high and low pHs: pentlandite dissolution being rate-limiting results in nanoscale coupling between pentlandite dissolution and subsequent violarite precipitation and thus nanoscale length scale textural feature preservation, resembling remarkably the natural pentlandite/violarite assemblages. In contrast, violarite precipitation being rate-limiting results in microscale pseudomorphism (length scale $10 \mu\text{m}$): the morphology of the pentlandite grains is only roughly preserved and internal details are not preserved. This case study illustrates that primary mineral dissolution needs to be rate-limiting compared to the secondary mineral precipitation in order to achieve nanoscale shape preservation in mineral replacement reactions. Otherwise, pseudomorphism will only occur on micro to macro length scales or in some extreme cases no pseudomorphism will occur.

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Posters

Time-Scales and Physicochemical Consequences of Ultramafic Rock Carbonation

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Ultramafic rock carbonation represents a natural analogue to in situ CO₂ sequestration via mineral carbonation, is often associated with the formation of economically significant lode gold deposits (e.g., Mother Lode, Abitibi, Atlin), and may involve important rock mechanical property changes. Here we discuss observations from a massively carbonated serpentinite complex at Linnajavri, northern Norway^[1]. Several ultramafic fragments of a dismembered ophiolite complex are hydrothermally altered by CO₂-bearing fluids, resulting in coexisting serpentinite, soapstone, and listvenite. Reaction fronts between the soapstone and the serpentinite precursor are sharp down to the thin section scale and can be traced for hundreds of meters. The reaction fronts are defined by the complete replacement of the former antigorite by talc and magnesite. Furthermore, the stability of magnetite within the different alteration assemblages results in distinct magnetic signals which can be used to relate observations from outcrop-scale, geophysical surface mapping to the intensity of CO₂ metasomatism^[2]. The mass-balance calculation suggests that carbonation front progression proceeded isovolumetrically and without significant transport of major, non-volatile elements. In the field, soapstone formation from serpentinite occurs as massive km-sized blocks as well as m-wide reaction selvages around talc veins cross-cutting serpentinite. In the latter, we observe a systematic change in bulk rock Li concentration and $\delta^7\text{Li}$ values in drill core samples from within the soapstone alteration halo and across the soapstone-serpentine interface. Li bulk rock concentrations and isotope ratios seem consistent with an intra-diffusion model^[3] with the diffusion interface (i.e. reaction front) propagating from the central vein towards the serpentinite precursor rock. We discuss how experimentally derived fluid diffusion coefficients of Li^[4] together with measured mineral Li concentrations and bulk rock porosity values can be used to constrain the duration^[5] of the carbonation event. Implications may be important to constrain time-scales of mineral deposit formation, rates of natural CO₂ uptake, and fault zone weakening in areas where ultramafic rocks are present^[6].

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Metamorphic constraints on the fluid assisted transition of granulite to eclogite on Holsnøy in the Bergan Arcs, Norway.

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During orogenesis, it is widely accepted that the conversion of granulite facies rocks to eclogites is controlled largely by changes in pressure and temperature. However, a number of studies have shown that the conversion of granulite to eclogite can also be enhanced by the presence of fluids. Indeed, in the absence of fluid, anhydrous granulite facies rocks appear particularly resistant to reworking under the comparatively refrigerated pressure–temperature (P–T) conditions of eclogite formation.

On the island of Holsnøy, western Norway, white mica- and epidote group-bearing eclogite has extensively replaced granulitic (plagioclase– garnet–clinopyroxene–orthopyroxene-bearing) anorthosite. The anorthositic granulites are Mesoproterozoic (c. 950 Ma) whereas the eclogites are Caledonian-aged (c. 450 Ma) [1]. The conversion is interpreted to have occurred during fluid infiltration along fractures and shear zones during the Caledonian Orogeny [2]. The presence of coexisting phengite and clinozoisite provide mineralogical evidence for fluid infiltration, and locally dramatic enrichments in species such as K₂O provide evidence for open system behaviour.

Numerous studies have investigated the development of the fluid–rock system on the exposures on Holsnøy [3-5] ; however, there are few robust constraints on the P–T conditions at which fluid–rock interaction occurred. The paucity of robust P–T information means that constraint on the conditions and potential source regions of the metasomatic fluid are few. Better constrained P–T information will help constrain the source of fluid which caused rehydration of the dry crustal orogenic root.

This study uses phase equilibria forward modelling to constrain the P–T conditions at which fluids infiltrated the granulites. Preliminary results suggest that the eclogitic assemblages formed at around 14-17 kbar and 675-740 kbar. The fluid source, the fluid driven recrystallisation focused strain into the essentially undeformed granulite protolith providing a kinship between fluid migration and mechanical destabilisation.

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Stress, fluid and metamorphism

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Centimetre-sized grains of Al-rich clinopyroxene within the anorthosites of the Bergen Arcs, W-Norway undergo deformation by micro-shear zones and faults along which fluid is introduced. The hydration is coupled to whitening of the dark primary feldspar reflecting fluid-induced reactions within the feldspar and growth of epidote as very fine inclusions. The Al-rich clinopyroxene (12 wt.% Al₂O₃) equilibrates to the deformation and hydration in two ways:

- replacement of the Al-rich pyroxene by chlorite and
- reaction to garnet (Alm₄₇Prp₂₈Grs₂₄) and a less aluminous pyroxene (3 wt.% Al₂O₃).

The two types of alteration develop in the same grain so that the garnet and the new pyroxene are formed along kink bands while the chlorite is found in dilatational areas. As the lithostatic pressure and the temperature must be constant across the Al-rich pyroxene we are left with two possible explanations. 1. The water is accumulated in the dilatational areas allowing formation of chlorite while the imposed deformation enhances reaction kinetics and forms garnet and a new pyroxene where fluid is deficient. 2. The variation in stress across the grain stabilized the two assemblages, so that the garnet and the new pyroxene formed in the high pressure area and chlorite in the low pressure parts. Possibly the two mechanisms operated together.

This example illustrates the influence of fluid and deformation on metamorphism and it appears that the variation of the local stress within a single grain may determine the location of the new mineral assemblages.

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Trace element zonation of ultramafic sulphides and spinels from Alpine Corsica

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Sulphide and oxide grains within retrogressed ultramafic samples from Alpine Corsica reveal significant trace element zonation. The zonation has the potential to provide a substantial insight into the chemistry of the fluid from which they were precipitated [1]. LA-ICP-MS and EPMA mapping reveal non-concentric zonation in Re, Se, Ni and Co within a single pyrite grain from an ultramafic sample in a shear zone proximal to the boundary between the lawsonite-eclogite and Upper Castagniccia blueschist zones in Alpine Corsica. Non-concentric zonation of Ni and Co has been suggested to record deformation under non-hydrostatic stress, and/or coupled dissolution and precipitation reactions [2]. Semi-concentric zonation of Re and Se towards the rim of a single pyrite grain could reveal the late infiltration of a higher salinity fluid [3], and/or reflect conditions that may have become more oxidising, since reduced Se has limited solubility [4], and/or higher temperatures, under which Se-rich sulphides are more stable [5]. The pyrite grain is texturally related to late exhumation but could provide an insight into the composition of subduction zone fluids released during slab dehydration, where fluids derived from the dehydration of antigorite and brucite could be highly saline [6]. Most spinel grains reveal typical zonation associated with serpentinisation with increasing Fe and decreasing Cr, Mg, Al, Mn, V and Ti towards the rim. However, one spinel grain within a blueschist ultramafic rock distal to contacts with metamafic or metasedimentary rocks reveals concentric zoning of Fe, Cr, Mg, Al, Mn, Si and Ti, where the concentration of Fe is highest in the core, suggesting a secondary origin for this grain. The spinel zonation is suggested to reflect changes in pressure or fluid composition during subduction and exhumation.

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Microporous gold: Comparison of textures from Nature and experiments

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Recent experiments have shown that microporous gold can be obtained via the oxidative dealloying of Au(Ag)-tellurides such as calaverite (AuTe_2), krennerite (Au_3AgTe_8), and sylvanite $[(\text{Au},\text{Ag})_2\text{Te}_4]$ under mild hydrothermal conditions. The same Au textures have been found in natural gold-telluride ores from the Late Miocene epithermal Aginskoe Au-Ag-Te deposit in Kamchatka, Russia. This confirms that natural microporous gold can form via the replacement of telluride minerals. This replacement may take place under hydrothermal conditions, e.g., during the late stage of the ore-depositing event, explaining the wide distribution of “mustard gold” in some deposits. At Aginskoe, the oxidation of Au-tellurides appears to have resulted only in local redistribution of Au and Te, because the associated oxidation of chalcopyrite scavenged the excess Te, inhibiting the crystallization of secondary Te minerals more than a few micrometers in size. Such cryptic mobility may explain the lack of reported secondary Te minerals in many Te-bearing deposits.

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Gold remobilisation from Arsenopyrite through high strain and metamorphism: crystal-plasticity vs fluid-mineral reactions

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Arsenopyrite is the most common arsenic-bearing sulphide and is ubiquitous as a gold-bearing phase in many orogenic gold deposits. In this study we used a novel combination of quantitative electron backscatter diffraction analysis, high-resolution ion microprobe imaging and synchrotron XFM mapping to investigate the crystal plasticity and element mobility behaviour of highly enriched auriferous arsenopyrites through metamorphism (340° - 460° and 2 kbars). Remarkably, the arsenopyrites remained structurally and chemically robust during high strain deformation. It is only during a superimposed lower strain deformation event, at a high angle to the shape preferred orientation of the arsenopyrites, that small amounts of crystal plasticity affected the arsenopyrites. During the low strain event a dissolution-reprecipitation reaction (~15% of grain areas) was facilitated by localised domains of recrystallisation and resulted in loss of trace element content (gold) from the crystal lattice, most likely due to fluid-filled sub-micron porosity along sub- and new grain boundaries. The limited number of slip systems in arsenopyrite and the deformation direction in relation to its acicular crystal shape control the capacity of the mineral to remain stable and retain its gold content during high strain deformation. However, the interaction of small volumes of fluid that had relatively low fS_2 and carried aqueous $NiCl_2$ and the auriferous arsenopyrites initiated the pseudomorphic reaction with the loss of Au and precipitation of Ni-rich arsenopyrite. We suggest the abundance and robust nature of arsenopyrite in giant gold deposits affected by greenschist-amphibolite metamorphism is actually a critical factor in the preservation of those deposits. Notwithstanding this result, the sub- and new grain boundaries allowed fluid access in the arsenopyrite and the remobilisation of gold.

Decarbonation of subducting slabs: insight from petrological-thermomechanical modeling

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Subduction of heterogeneous lithologies carry a mixture of volatile components ($H_2O \pm CO_2$) into the mantle, which are mobilized during breakdown of hydrous and carbonate phases at shallow forearc depths and by silicate and carbonatite melting [1] at depths beneath arcs. Petrologic, thermodynamic, and geodynamic studies investigate volatile cycling at convergent boundaries to better understand arc volcanism sources, metasomatism in the wedge-arc, and subduction zone evolution. The investigations demonstrate the great importance of water in subduction zone processes, however the role of CO_2 transfer into the arc and wedge remains poorly understood. Petrologic and thermodynamic investigations show that little decarbonation occurs along present day subduction zone geotherms and carbon remains within carbonate beyond the subarc.

Sediment diapirism is hypothesized as a mechanism for CO_2 transfer into the wedge and acts a driver for slab decarbonation. Therefore, we employ high-resolution 2D petrological-thermomechanical modeling to elucidate the role subduction dynamics has with respect to slab decarbonation and sediment diapirism. Our original thermodynamic database [2] is modified to account for H_2O - CO_2 binary fluids present within the following subducting lithologies: GLOSS average sediments (H_2O : 7.29 wt% & CO_2 : 3.01 wt%), carbonated altered basalts (H_2O : 2.63 wt% & CO_2 : 2.90 wt%), and carbonated peridotites (H_2O : 1.98 wt% & CO_2 : 1.50 wt%). We parameterize our model by varying the following two components: slab age (20, 40, 60, 80 Ma) calculated by a half-space cooling model [3] and convergence velocity (1, 2, 3, 4, 5, 6 $cm\ year^{-1}$) between a subducting oceanic plate and a continental plate.

59 numerical models were run and show excellent agreement with the unmodified I2VIS code. Three geodynamic regimes show decarbonation. 1) Sedimentary diapirism acts as an efficient physical mechanism for CO_2 removal from the slab as it advects into the hotter mantle wedge. Fluid is produced on the inner side of the rising diapir. 2) If subduction rates are slow and accompanied by a young oceanic plate, frictional coupling between the subducting oceanic plate and the overriding continental plate occurs. Altered mafic crust is mechanically incorporated into a section of the continental lower crust where it undergoes decarbonation within a subduction mélange. 3) Lastly, during episodes of extension and slab rollback, interaction between hot asthenosphere and sediments at shallow depths result in a small window (~ 12.5 Ma) of high integrated CO_2 fluxes ($205\ kg\ m^{-3}\ Ma^{-1}$).

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The preservation of framboidal pyrite in blueschist

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Framboidal pyrite is widely believed to form in low temperature near surface environments. Consequently, its preservation in lawsonite blueschist grade sediments is unexpected. Samples of calcschist taken from the *Schistes Lustrés* of Alpine Corsica have been observed to contain framboidal pyrites ranging in size from 5 μ m to 30 μ m within rocks of garnet grade and below. Framboidal pyrite is thought to recrystallise on normal geothermal gradients in the lower greenschist facies and while some minor recrystallisation has occurred the overall structure of individual frambooids is still visible, particularly when included within lawsonite. The low geothermal gradient associated with subduction or perhaps the lack of available fluids may account for this unusual preservation.

120 Myr of episodic mid-crustal metamorphism and fluid-rock interaction during the Alice Springs Orogeny: the Strangways Range, central Australia

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Garnet Sm-Nd isochrons and monazite U-Pb geochronology from the Strangways Range, central Australia, indicate that metamorphism and fluid-rock interaction associated with kilometre-scale mid-crustal shear zones occurred over a period of *ca* 120 Myr during the Palaeozoic intracratonic Alice Springs Orogeny (ASO). The shear zone samples span a region of approximately 5000 km² across the entire length and breadth of the Strangways Range. The shear zones transect *ca* 1700 Ma granulite facies metasediments and felsic gneisses, and are characterised as hydrous schist belts containing garnet-staurolite-biotite-muscovite-quartz ± kyanite ± sillimanite assemblages. The ages obtained in this study indicate that fluid-assisted metamorphism occurred within the shear zones at *ca* 445 Ma, *ca* 380 Ma, *ca* 360 Ma and *ca* 330 Ma, suggesting a protracted and episodic history of fluid-rock interaction during the ASO.

Garnet major element X-ray maps suggest multiple thermal events across this time period. Zonation patterns typical of a retrograde thermal history are associated with *ca* 445 Ma metamorphism in the eastern Strangways Range. In the western and southern regions, zonation patterns indicate prograde thermal histories at *ca* 380 Ma and *ca* 330 Ma, respectively. Mineral textures from the shear zones also suggest varying thermal histories; *ca* 380 Ma shear zones show late kyanite porphyroblasts while *ca* 330 Ma shear zones show late staurolite porphyroblasts.

Kinematic indicators across the Strangways Range are often ambiguous. However, in the eastern region, ultramylonitic shear zones with reverse-sense kinematics are truncated by ultramylonites with normal-sense kinematics. Monazite U-Pb geochronology from the normal-sense ultramylonites predominantly record *ca* 380 Ma metamorphism but also preserve single *ca* 445 Ma ages from some grains. In combination with the observed kinematics, this suggests that *ca* 445 Ma contractional faults were extensionally reactivated at *ca* 380 Ma.

The results obtained in this study suggest that structurally-controlled metamorphism and fluid-rock interaction was associated with multiple prograde thermal episodes and spanned almost the entire duration of the *ca* 450-300 Ma Alice Springs Orogeny. The spatial scale and regional dominance of hydrous schist belts transecting anhydrous basement, along with their protracted activity over *ca* 120 Myr, suggests a substantial and enduring source of fluids during the ASO. Conceivably, the spatial and temporal evolution of the ASO shear zones may be linked to the availability of fluids in the mid-crust. The data presented in this study provides a foundation for further research to the sources of fluids and the role of fluid-rock interaction in intraplate reactivation.

Geologic applications for high-resolution secondary ion mass spectrometry (SIMS) to study fluid-rock interaction

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Sulfur acts as the main complexing ligand in mineral deposits, and measuring its isotope ratios in sulfide minerals is important for the understanding of fluid-rock-mineral interaction in these environments. In-situ analysis/imaging at the micro- to nano-scale using high-resolution secondary ion mass spectrometry (IMS1280 and NanoSIMS) makes sulfur isotope studies even more powerful because within-grain/between-phases sulfur isotope variations can be investigated. However, due to mineral- and/or chemistry-specific instrumental mass fractionation (IMF) during SIMS analyses, it is essential to analyse samples together with well-characterised and isotopically uniform reference materials. To date, universal sulfide reference materials for sulfur isotope analysis do not exist, despite the increasing interest of in-situ sulfur isotope studies in mineral systems.

The Ion Probe Facility at UWA has been developing sulfide standard materials for the past three years, and we have accumulated long-term data sets for our in-house pyrite (Sonora-3), pyrrhotite (Alexo 3-4), and pentlandite (VMSO) standards since 2012, using the CAMECA IMS1280 large-geometry ion probe. Each of these reference materials has also undergone a thorough evaluation of their chemical uniformity. They show high precision over the three-year period. For example, the external precision for >1000 analyses of Sonora-3 is less than 0.1 ‰ (1 σ) for both $\delta^{33}\text{S}$ and $\delta^{34}\text{S}$. We are also developing standard materials for the analysis of chalcopyrite and arsenopyrite, intending that these materials be adopted globally as S isotope standards (LaFlamme et al., in prep).

In conjunction with the in-situ isotopic measurements, high spatial resolution mapping of very low concentration trace elements in sulfide minerals is routinely available using NanoSIMS. In particular, trace concentrations of Au can be mapped with sub-micron resolution to reveal varying fluid compositions and complex depositional histories within individual sulfide grains.

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The long-term strength of the lithosphere as determined by gravity and topography

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The long-term strength of the lithosphere is quantified by its flexural rigidity, a measure of a plate's resistance to bending under applied loads. The flexural rigidity is commonly represented by a geometric analogue, the effective elastic thickness (T_e), though in general this thickness does not correspond to a particular depth within the crust or lithospheric mantle. Rather, it provides the thickness the lithosphere would have were it to be represented by an elastic plate. The oceanic lithosphere, and younger continental regions, almost meets this idealistic condition, but the older continental lithosphere, of highly variable composition, temperature, and thus rheology, does not always do so.

Nevertheless, many estimates of T_e exist in the oceans and continents (and other planets), primarily made using gravity anomaly and topography data. While some of these estimates have been made using forward modelling (in the space domain), most have been obtained via frequency-domain methods, whereby the spectra of gravity and topography are correlated and compared against theoretical predictions (e.g. Kirby, 2014).

The authors have pioneered a wavelet transform method to estimate T_e , which allows for the production of maps of its spatial variation. This poster will outline the method and some of its results, but will also briefly introduce another spectral estimation method, the so-called multitaper method which is based upon the Fourier transform.

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Feldspar replacement reactions in IOCG systems: The Olympic Cu-Au Province

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The presence of feldspar replacement reactions has long been recognised as a diagnostic property of iron-oxide copper-gold (IOCG) systems (e.g., Groves *et al.*, 2010); however the exact role they play in the genesis of such deposits remains poorly constrained. Detailed studies of deuteric coarsening (e.g., Parsons and Lee, 2009) and albitisation (e.g., Putnis, 2002; Plümer and Putnis, 2009) have highlighted the ability of such reactions to alter the physical and chemical properties of the host rocks during fluid-rock interaction at the micro- and nanoscale. This invokes the idea that feldspar replacement reactions might be more important than once thought, and may even be a prerequisite stage for the deposition of IOCG mineralisation.

The Olympic Cu-Au province, situated in the eastern Gawler Craton, South Australia, provides a unique opportunity to constrain the role feldspars play in IOCG genesis. Recent studies have combined microanalytical techniques with macroscopic observations to outline changes in textures and geochemistry of feldspars from fresh to altered host rocks in different settings within the province (e.g., Kontonikas-Charos *et al.*, 2014; in review; Ismail *et al.*, 2014). Such studies have highlighted the applicability of feldspars as geochemical tracers of the magmatic-to-hydrothermal evolution of a system, and for understanding the effects abundant *in-situ* feldspar replacement reactions have on the host rocks (e.g., increase in porosity and remobilisation of trace elements).

Further work is still required to provide constraints that can explain and help interpret observations from IOCG systems at province, ore deposit, hand-specimen, and micro- and nanoscales. Transmission electron microscopy on foils prepared *in-situ* by FIB-SEM is particularly invaluable and can assist in determining the behaviour of trace elements in feldspars during fluid-rock interaction (e.g., the presence of Fe as Fe-oxide nanoparticles or incorporated in the crystal lattice of hydrothermal K-feldspar), as well as identifying high- and low-temperature structural modifications and degrees of ordering in feldspars (e.g., high and low albite). The overarching goal is to trace fluid-rock interaction using feldspars as a proxy for complex metasomatism involving Fe-REE-U during sequential alteration stages in an IOCG system.

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Contrasting record of fluid history in garnet: examples from Alpine Corsica and the Bergen Arcs

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Garnet is a common mineral of metamorphic rocks owing to its stability in a wide range of PT conditions and rock composition. It typically shows complex chemical zoning that reflects the evolution of its environment in term of pressure, temperature, rock and fluid chemical compositions. *In-situ* oxygen isotope analyses performed in zoned garnet can be used to identify the origin of the fluid equilibrated with garnet and reconstruct the fluid history of metamorphic rocks.

Large radius SIMS instruments allow oxygen isotope analyses with a precision down to 0.2 per mil (2s) and a spatial resolution of 15-20 μm , which is necessary to resolve garnet internal zoning. However, the complexity of garnet chemistry is an obstacle to accurate oxygen isotope measurements by SIMS, which can be overcome by using a set of garnet standards with variable compositions. The method developed here proposes a multi-component approach to correct oxygen isotope measurements in garnet with composition comprised between almandine, grossular, pyrope and andradite end-members. This method allows a better flexibility of the correction and the results confirms that almandine and pyrope components do not significantly affect oxygen isotope measurements ($<1\text{‰}$). Long-term monitoring of the analytical bias produced by each component on oxygen isotope measurements shows that it is relatively stable through time.

We use two case studies of oxygen isotope in garnet from Alpine Corsica (09028) and Bergen arcs (EJ1205b) to illustrate the contrasting ability of this mineral to record fluid flow in metamorphic rocks. Both samples are HT metamorphic rocks partly transformed into HP rocks. Field and petrological (crystallisation of lawsonite in 09028) evidences attest that this transformation was accompanied by fluid flow (e.g. Austrheim, 2014).

Garnet-bearing blueschist 09028 is composed of lawsonite, glaucophane, white mica garnet and titanite. In this sample, HT garnet crystals were dislocated and each garnet cluster shows a strong chemical zoning associated to a dramatic decrease in $\delta^{18}\text{O}$ from their HT core ($11.1 \pm 0.5\text{‰}$, 2σ) to the HP rim ($2.2 \pm 0.4\text{‰}$, 2σ) (Martin *et al.*, 2014). The very low $\delta^{18}\text{O}$ values recorded in garnet rims, consistent with the $\delta^{18}\text{O}$ signature of the bulk rock (5.5‰), are interpreted as reflecting the interaction of the HT protolith with seawater or fluids equilibrated with mafic or ultramafic rocks.

Eclogite EJ1205b is mainly composed of omphacite, garnet, kyanite, zoisite and white mica. Mm-sized garnet crystals typically record two growth generations: (i) large homogeneous HT Mg-rich garnet cores are surrounded by (ii) Mg-poor rim containing eclogitic inclusions (omphacite and kyanite). Oxygen isotope profiles carried out from the HT cores to the rims suggest only a very small decrease in $\delta^{18}\text{O}$ ($0.3\text{-}0.5\text{‰}$) that cannot be distinguished from analytical error (0.4‰ , 2σ). The absence of oxygen isotope variation between garnet cores and rims can be explained by a low fluid/rock oxygen ratio and/or no significant difference between the $\delta^{18}\text{O}$ of the infiltrating fluid and the $\delta^{18}\text{O}$ of the fluid in equilibrium with the investigated Bergen sample.

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Experimental study of CO₂ sequestration via goethite carbonation

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Mineral carbonation in geological formations is the fixation of CO₂ as stable carbonate minerals, such as calcite (CaCO₃), dolomite (CaMg(CO₃)₂), magnesite (MgCO₃), siderite (FeCO₃) and other carbonate solid solutions. Over geological time the formation of carbonates has regulated the available CO₂ both from the atmosphere and aqueous solutions. This is also one of the promising methods proposed to mitigate increasing atmospheric CO₂ [1,2], principally by the injection of fluids containing dissolved CO₂, into geological formations. Cations released during dissolution would then be available for reaction with the fluid to form stable carbonate minerals.

The objective of this research is to study if goethite (α -FeO(OH)), a mineral found commonly in soils and in several terrestrial environments, could potentially be a material for sequestering carbon dioxide, through the reaction of goethite in the presence of carbonate solutions and replaced to form iron carbonates. To test this hypothesis we have performed a series of experiments with goethite as the starting mineral, using *in situ* Atomic Force Microscopy (AFM) experiments at room temperature, carbonate aqueous solutions such as CO₂-water and NaHCO₃ at different concentrations (1-500 mM) and different pH (4.5-8.5). As well, we have performed similar *ex-situ* hydrothermal experiments under a range of temperatures (25-100°C). After reaction, product phases were characterized using Raman spectroscopy, Scanning Electron Microscopy (SEM) and X-Ray powder diffraction.

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Base and precious metal mineral interactions with aqueous amino acids under oxidising alkaline conditions.

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The minerals of base metals, such as copper, nickel, cobalt, zinc and lead as well as some precious metals, such as gold and silver, have been found to solubilise in aqueous solutions of amino acids in oxidising alkaline environments. The chemistry and leach kinetics of various copper minerals and gold, will be discussed with reference to their interaction with amino acids. The selective dissolution of copper minerals and gold in amino acids, in particular glycine, allows selective recovery as metal glycinate complexes with minimal solution interaction with the surrounding rock matrix so that mineral that would normally react under acidic conditions, such as calcite, dolomite, siderite and various layer silicate minerals, as well as pyrite and arsenopyrite remain unreacted. The lixiviant-mineral interactions, and the benign nature of the reagents, have a significant potential to open up new avenues to extract copper and gold from low grade ore deposits using in-situ, heap or agitated tank leaching. In particular, the role of pH, redox potential, dissolved oxygen, type of pH modifier (caustic soda versus slaked lime), temperature and amino acid concentration and amino acid type on the dissolution of gold, silver, malachite, azurite, cuprite, chrysocolla, chalcocite and chalcopyrite will be discussed in the presence of ubiquitous gangue minerals such as chlorites, sericite and other layer silicates, calcite and dolomite, and pyrite.

Experimental study of the replacement of calcium carbonates by apatite and fluorite: rates and textures

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Understanding how fluids move through and alter low permeability rocks is crucial for understanding many geological processes. In natural rocks, fluids can infiltrate through grain boundaries and/or pre-existing fractures, playing an important role on the rate at which chemical alteration occurs. Permeability can also be generated by the chemical alteration itself. This is the case of coupled dissolution-precipitation reactions, characterized by the generation of porosity that confers increased permeability to the rock/mineral.

Different salts in solution may also alter the kinetics of chemical reactions involving mineral replacement (Jonas et al., 2013), however these were yet poorly explored.

The replacement of calcium carbonate by calcium phosphate and by fluorite were used as model systems to explore replacement rates, porosity generation, and fluid preferred pathways at different fluid compositions.

Small Carrara marble cubes and single crystals of around 2 mm³ were treated in hydrothermal reaction vessels at different times and temperatures using phosphate and fluorine bearing solutions with and without the presence of chloride salts. Mounted and polished cross sections of the reacted samples were examined by scanning electron microscopy, electron microprobe analysis and X-ray diffraction to characterize the product phases and explore the resulting microtextures. Results show that changes in the chemistry of the fluid seem to influence the replacement thermodynamics and kinetics, but also determine whether the reaction front is more effective through the grain boundaries towards the centre of the grains, or through the developing porous structures towards the centre of the rock. Moreover, the micro-porosity of the replaced product also shows significant dependence on the solution composition, varying from being very heterogeneous as reported by Jonas et al., (2013), to a more uniform micro-porosity distribution as observed in this study.

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The Lost Samples of the Golden Mile: New Data Sheds Light on the Depth and Temperature of Emplacement of this Giant Gold Deposit

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Historical ore specimens from the Golden Mile greenstone-hosted gold deposit, Kalgoorlie, WA, have been obtained from the Western Australian School of Mines museum. With mine coordinates and sample depths corresponding to open space within the Fimiston Super Pit, these samples provide information that is not otherwise available.

Ore textures in the museum samples, such as banded and brecciated veins and open space fill, are indicative of emplacement within a brittle deformation regime. Fragmented bands of pyrite from the Ivanhoe Mine (Fig. 1A), which occur within a brecciated, banded quartz vein, are suggestive of a decompressive explosion breccia involving a volatile-rich ore fluid. This brecciation event clearly post-dates the pyrite bands, yet the pyrite contains elongate inclusion trails of gold, sulphides and tellurides parallel to the fragmentation axes (Fig. 1B), as well as gold-telluride boundary replacement. These observations contrast markedly with evidence of ductile shear-zone hosted mineralization at the Golden Mile, suggesting that a late stage of gold-telluride mineralization occurred at shallow levels, perhaps during uplift-related decompression.

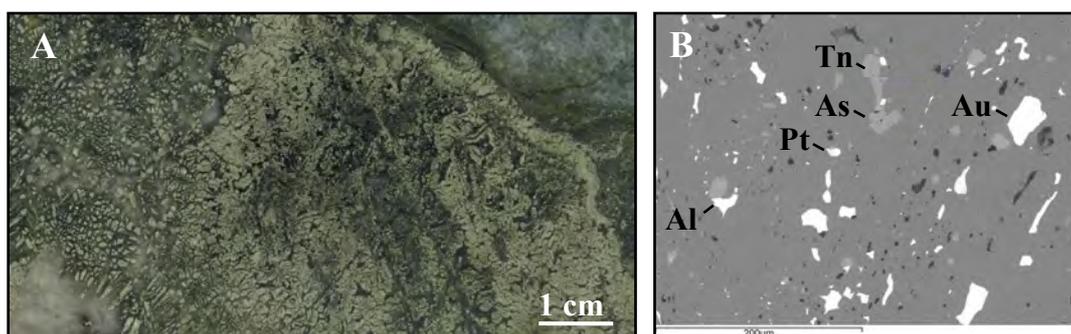


Figure 1 – A. Hand specimen photograph of fragmented bands of pyrite within a brecciated vein. B. Backscattered electron image of inclusions within the pyrite in (A), where Au = gold, As = arsenopyrite, Tn = tennantite, Al = altaite and Pt = petzite.

Complex intergrowths of telluride minerals and gold observed in the museum specimens can help constrain the temperature of ore formation. Tellurides have been characterized using scanning electron microscopy – electron dispersive X-ray spectroscopy (SEM-EDS) at Curtin University, and include the more commonly observed coloradoite (HgTe) and calaverite (AuTe₂), as well as altaite (PbTe), tellurantimony (Sb₂Te₃), an unknown arsenic telluride (AsTe₂) and several Ag-Au tellurides (petzite, AuAg₃Te₂, sylvanite, AuAgTe₄, and stützite, Ag_{5-x}Te₃). Absolute maxima for ore formation can be established from the melting temperatures of telluride phases; that of calaverite and sylvanite are 464 ± 3°C and 354 ± 5°C, respectively¹. A lower bracket is provided by multi-telluride intergrowths in a sample from the Associated Gold Mine containing the assemblage stützite-tellurium, which may be produced through the breakdown of empressite (AgTe) at 210°C². As no empressite has been reported at the Golden Mile, the deposition temperature of these intergrowths must be above 210°C. Cabri (1965)'s geothermometer for the Au-Ag-Te ternary has been applied to the calaverite and sylvanite in this sample, further narrowing the temperature range: Sylvanite contains 10.5-12.9 wt% Ag, corresponding to 320°C-230°C (T decreases with increasing Ag), and calaverite with 2.3-3.1 wt% Ag corresponds to 370°C-320°C. A further constraint on

temperature is provided from the assemblage sylvanite-stützite-tellurium (calaverite absent), which has a maximum stability of 330°C¹.

Overall, observation of these samples indicates that, while earlier veining and mineralization at the Golden Mile likely occurred under ductile conditions, later gold-telluride ore was deposited in a shallower, brittle regime. Temperature constraints provided by telluride minerals correspond to earlier estimates.

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BaSO₄ crystallization in the presence of polymers: evidence of barite crystallization via non-classical pathways

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Barium sulphate is widely known for being a problematic and costly scale-forming mineral in industrial processes. In oil recovery, barite forms when injection water which is sulfate rich and barium-containing formation water interact downhole. Scale minerals can clog formation pores near the wellbore reducing porosity and permeability of the reservoir and they also can form a thick deposit in production pipes. A common strategy aimed at reducing scale formation is the addition of organic additives (usually phosphonates or carboxylates) to the water injected into the reservoir (threshold treatment, *Shakkthivel et al.*, 2006).

Thus a better understanding of the mechanism of barite formation from aqueous solutions and the role of organic macromolecules on such a process may be relevant for the design and optimization of treatments to prevent scale formation. Here, we investigate the initial stages of barium sulphate precipitation from pure and polymer-containing aqueous solutions. Barium sulphate was precipitated at room temperature by combining equimolar Ba²⁺-bearing and SO₄²⁻-bearing solutions. The precipitation process was quenched at different times by the addition of ethanol or quick immersion in liquid nitrogen and subsequent freeze-drying, and the precipitates were studied by various analytical methods, XRD, TG/DSC, FESEM, ESEM and TEM. As well, precipitation experiments (with and without polymers) were performed by the slow addition of 10 mM BaCl₂ solution to a 1 mM Na₂SO₄ solution. During these experiments, the Ba²⁺ potential, pH, conductivity and turbidimetry were continuously monitored and allowed to get better insights into interactions between copolymers and prenucleation species before nucleation occurs (*Gebauer et al.* 2009).

AFM growth experiments were additionally carried out. Observations of the nanostructure evolution indicate that barite forms by two-levels of oriented aggregation of nanosized particles. In pure solutions, most of the porosity in the micron-sized aggregates formed in the second step is annealed, resulting in perfect single crystals. However, in the presence of polymers, this step is retarded and BaSO₄ mesocrystals are commonly observed. Furthermore, evidence supporting the existence of liquid and solid amorphous precursors that precedes the formation of the first solid (primary) particles is given.

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The chemical oscillator: A new perspective on fluid flow and permeability in the ductile crust

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There is abundant evidence that faults and shear zones act as fluid pathways through the crust, playing an important role in hydrothermal processes including the formation of mineral deposits and the evolution of geothermal systems. Consequently, faults and shear zones are typically assigned high permeabilities in simulations of crustal fluid flow, which in turn may be used to make predictions about the rates and volumes of fluids passing through such structures. However, very little is known about the permeability of these structures, particularly in the ductile regime. Furthermore, the episodic nature of seismicity associated with faults and shear zones suggests that their permeability varies with time. To predict the permeability evolution of a ductile shear zone one must understand the mechanical, thermal and chemical mechanisms that control its behaviour. Recent work (Alevizos et al. 2014; Poulet et al. 2014a; Poulet et al. 2014b; Veveakis et al. 2014) has revealed a mechanism, described as a chemical oscillator, that provides a plausible explanation for the episodic behaviour of ductile shear zones, and provides insight into their permeability evolution.

The chemical oscillator works as follows. Slow, ductile creep on the shear zone results in shear heating, which raises the temperature inside the shear zone. This continues until the heat is sufficient to trigger an endothermic fluid-release reaction, such as dehydration of serpentine, or decomposition of carbonates to form oxides and CO₂. These fluid-producing reactions result in an increase in fluid pressure, which in turn triggers a fast slip event. Fluid release continues until the reactants have been consumed, then the heat dissipates, the reverse reaction consumes the produced fluid, and the cycle starts again.

It has been shown that this chemical oscillator can explain episodic tremor and slip in subduction zones (Poulet et al. 2014a) and characteristics of major orogenic structures such as the Glarus Thrust (Poulet et al. 2014b). Here we consider the implications of the chemical oscillator for the permeability and fluid flow characteristics of ductile shear zones. Questions to be considered include: What is the time-averaged permeability of a shear zone controlled by a chemical oscillator? What happens if such a shear zone is connected to a fluid reservoir? What happens in the case of more complex chemistry, e.g. multiple fluid phases? Could this mechanism concentrate or remobilise metals? How does this process interact with regional metamorphism? These questions are the focus of ongoing research, which will contribute to our understanding of hydrothermal processes in the Earth's crust.

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The Presence of Sphalerite in Pyrite Framboids

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Unusual framboids containing intimately intergrown of pyrite and sphalerite microcrystals are reported here for the first time, to our knowledge. Common framboidal pyrite, which is usually found in sedimentary rocks and present as spheroidal clusters, consists of discrete pyrite microcrystals (Rickard, 1970; Love, 1984; Schoonen, 2004; Ohfuji and Rickard, 2005). Framboidal pyrite has been attributed to biogenic processes in natural samples, but can be synthesised under experimental conditions without bacterial activities (Rickard, 1970; Love, 1984; Schoonen and Barnes, 1991; Wilkin and Barnes, 1997; Donald and Southam, 1999). Framboids from prehnite-pumpellyite facies samples from the Otago Schist, New Zealand (Hu et al., 2015, in preparation) has been investigated via nano-scale chemical mapping. A combination of Zn mapping, which is used as a proxy for sphalerite distribution, and Fe mapping, which is used as a proxy for the pyrite distribution, shows intimate growth of these two minerals in one framboid (Figure 1A). All the microcrystals are equidimensional, with the diameter of 0.3~1 μm for each microcrystal. Sphalerite microcrystals are rare but present in other framboids in the sample. Maps of organic carbon and nitrogen (CN) produce high counts on the boundary of the microcrystals, but low counts within the microcrystals (Figure 1B), and may indicate microcrystals growing within the organic frame (Wacey et al., 2015). Sphalerite found in organic biofilms has been suggested to be related to sulfate reducing bacteria activity, and sphalerite coating on organic structures has been recorded, whereas pyrite is usually found in interstices rather than in direct contact with organic surfaces (Maclean et al., 2007; 2008). The findings in this study may provide evidence of sulfate reducing bacteria activity during the formation of these framboids and may provide information on the formation conditions of the sulphides and their subsequent modification by metamorphism. However, the detailed mechanisms of these processes need further investigation.

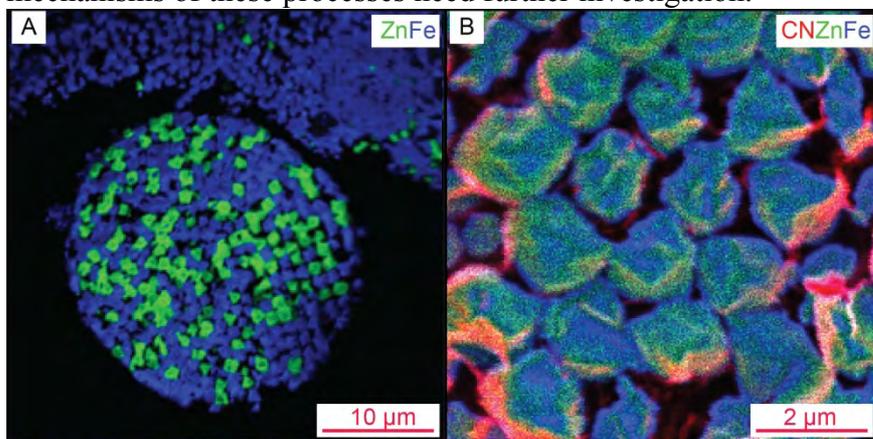


Figure 1 (A) Zn and Fe mapping of one framboid. (B) CN, Zn and Fe mapping of part of another framboid.

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Hydration through Melt-Rock Interaction triggers Local Partial Melting in the Lower Crust: Example from Fiordland, New Zealand

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Patchy partial melting within compositionally homogeneous rock units is commonly observed in lower crustal rocks. Such local variations in melt production cannot be due to temperature or pressure variation, and another process is inferred.

We investigate in detail a low-strain exposure of the lower crust, the Pembroke Granulite, exposed in Pembroke Valley, northern Fiordland, which exhibits partial melting in patches (~ 100 m²). Detailed field mapping and whole rock chemical analyses show that exposed migmatites and protolith gabbroic gneisses have gradational boundaries rather than sharp, igneous contacts, and are indistinguishable in terms of rock chemistry. Gradational boundaries are characterised by increased replacement of pyroxene by symplectitic amphibole and quartz into migmatized rocks. The progressive replacement is attributed to melt-rock reaction occurring as a consequence of porous melt flow focussed in tens of metre wide zones throughout the bulk of the Pembroke Granulite. As such, porous melt-rock interaction results in local hydration of an otherwise largely anhydrous two-pyroxene gabbroic gneiss, governing later incipient partial melting in the most hydrated zones.

P-T pseudosections indicate that the melt-rock reaction producing a locally hydrated gneiss occurred at conditions above the solidus, where aqueous fluids are unstable. Our observations suggest that these changes are evidence for an episode of diffuse porous melt flow in the Pembroke Granulite. Variably focussed in time, at scales of tens of metres rather than throughout the complex, melt flow was reactive and cumulatively pervasive, hydrating gabbroic gneiss leading to patchy partial melting. This model implies a metasomatic origin for the observed patchiness in melt production in the study area, previously interpreted as a result of primary compositional differences due to igneous differentiation.

Tourmaline $^{40}\text{Ar}/^{39}\text{Ar}$ geochronology of the Illaara Greenstone Belt, Yilgarn Craton

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$^{40}\text{Ar}/^{39}\text{Ar}$ ages and Boron isotopes are presented from hydrothermal fluid-related tourmalines cross-cutting the Hadean zircon-bearing metasedimentary rocks from the Illaara Greenstone Belt, Western Australia. Concordant $^{40}\text{Ar}/^{39}\text{Ar}$ plateau ages on the tourmalines at Mt. Alfred give a weighted mean age of 2935 ± 9 Ma (95% confidence) and provide a minimum depositional age for this sequence, placing constraints on the deposition age of detrital Hadean zircons to between 2930 and 3250 Ma. These results are the first reported Archean $^{40}\text{Ar}/^{39}\text{Ar}$ ages obtained on tourmaline.

The 2930 Ma tourmalines occur as a quartz-tourmaline intrusion with associated stratiform layers and veins, inferred to have grown during a hydrothermal fluid circulation event. The tourmalines, about 0.1 to 0.8 mm in size, are randomly oriented within a quartz matrix. The main intrusion exhibits evidence of recrystallization along the margins, as well as a second generation of tourmaline growth often aligned with the foliation fabric and associated with younger quartz veins.

A younger generation of tourmalines from the Brooking Hills, 30km south of Mt. Alfred has a concordant $^{40}\text{Ar}/^{39}\text{Ar}$ plateau age of 2622 ± 20 Ma. These tourmalines occur as aligned crystals, about 0.5 to 3 mm in size, within and along the margins of post-kinematic quartz veins, parallel to the foliation fabric. The age of these tourmalines marks the end stage of high temperature metamorphism within the Illaara Greenstone Belt at 2630 Ma.

The retention of 2930 Ma tourmaline ages within the Illaara Greenstone Belt shows that the K/Ar system of tourmaline remained closed throughout repeated upper-greenschist to mid-amphibolite metamorphic events between the ages of 2930 to 2630 Ma. This is in agreement with an Ar closure temperature of >700 °C experimentally determined in this study, suggesting that tourmaline is one of the most Ar-retentive minerals identified so far.

Further characterization of the K/Ar system in tourmaline is ongoing, with studies looking at further samples from the central Yilgarn Craton, and of gem-quality tourmalines from well characterized localities throughout the Adirondacks, NY.

Striation development during fault slip depends on temperature under hydrothermal conditions

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We have deformed silica discs embedded in synthetic gouge under hydrothermal conditions to examine i) if there is any relationship between striation morphology and P, T, or shear strain, and ii) what processes and deformation mechanisms accommodate striation development. The experiments were performed using the hydrothermal rotary shear apparatus at the HPT laboratory, Utrecht University (Niemeijer et al. 2008) at 100 or 450°C, $\sigma_{\text{neff}} = 100$ MPa, $P_f = 100$ MPa to shear strains in the range $2.02 < \gamma < 8.25$.

On removal from the sample assembly, the discs were extracted from the gouge powders and examined by SEM. All the disc surfaces are decorated by fine gouge, sometimes arranged in linear trails, and many have ellipsoidal pits. Additionally, only the discs deformed at 450°C, regardless of total shear strain, have smooth grooves with wavelength $< 10\mu\text{m}$ and amplitude $< 0.5\mu\text{m}$ on their surfaces. Many of these grooves extend across the entire disc surface but some terminate in scallop-shapes. We infer these are a type of striation developed parallel to the direction of relative shear of the gouge and the disc surfaces. In places the parts of the grooves below the original disc surface contain scattered rounded beads of silica $\sim 100\text{nm}$ diameter (composition confirmed by EDS). Conversely, close examination of pits in the 100°C experiments reveals they contain angular particles ranging $< 2\mu\text{m}$ diameter.

FIB-SEM allowed extraction of a TEM foil cut perpendicular to the disc surface and inferred slip direction. This cross-sectioned the undulating surface and the rounded particles. There are no significant systematic dislocation arrays in the adjacent disc quartz, but microfractures form an anastomosing array parallel to the disc surface, and are sporadically present elsewhere. Additionally, amorphous silica fills the space between the rounded quartz beads.

We infer that dislocation processes were not important in deformation of the sample surface. Instead, we propose that at both temperatures brittle failure generated microfractures and micro-comminution occurred where gouge particles impacted the disc surfaces. It seems feasible that, at the higher temperature, surface energy-driven(?) dissolution processes resulted in rounding of the beads, and the interstitial amorphous phase was precipitated from this solute. Moreover, calculations of rates of silica precipitation suggest that 100nm diameter crystalline quartz could precipitate in only 100 seconds, well within the timeframe of the experiments. We look forward to discussing the various possibilities for the origin of the beads and the amorphous phase.

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Regional-scale metasomatism in the Hamersley Basin: The source of Australia's Iron Ore?

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The genesis of the world-class banded iron formation (BIF)-hosted iron ore deposits of the Hamersley Basin, Western Australia, is highly debated (Morris & Kneeshaw, 2011). Models vary from gangue removal to iron addition, and from hydrothermal events to supergene processes. All models involving mass transfer require a source and/or sink for transported elements. Banded iron formations of the Hamersley Group are underlain by mafic to intermediate lavas of the Fortescue Group, which forms the lowermost stratigraphic unit of the 100,000 km² Hamersley Basin on the southern margin of the Pilbara Craton. A regional burial metamorphic gradient extends across the basin from prehnite-pumpellyite facies in the north to epidote-actinolite facies in the south (Smith et al., 1982; White et al., 2014a). Replacement of the original igneous mineralogy and texture increases with metamorphic grade. Superimposed on the metamorphic gradient are widespread zones of intense metasomatism, focussed along lava flow tops, interpreted to represent zones of inherent permeability (White et al., 2014a). During hydrothermal alteration metamorphic and relic igneous minerals are progressively replaced to produce a suite of pumpellyite-quartz- and epidote-quartz-dominated assemblages. There is evidence for complex mineral growth, dissolution and regrowth cycles (White et al., 2014; 2014b). The mineralogical changes are driven by intense leaching of alkalis, Mg, and the heavier first transition series metals (Mn-Zn), accompanied by silica addition (White et al., 2014a). Such mineralogical and geochemical trends have been documented elsewhere in mafic igneous terranes where they have been interpreted as the products of fluid-rock interaction with an evolved, highly saline fluid derived from sea water (Galley, 1993; Banerjee et al., 2000; Hannington et al., 2003; Jowitt et al., 2012). Thermodynamic modelling of metasomatic mineral assemblages indicates uniform conditions for metasomatism across the basin of ~275°C, 10 km depth (White et al., 2014b). This is interpreted to represent fluid flow occurring following basin burial and being driven by Ophthalmian deformation in the south (2.1–2.2 Ga). Therefore, it is expected the same regional-scale fluid flow will have affected the BIFs of the Hamersley Group. Specifically, we propose that leaching of Fe from the Fortescue Group lavas contributed, at least in part, a source of iron to the overlying BIFs, resulting in local upgrading to martite–microplaty-hematite ore. Similarly, silica removal from the overlying BIF may provide a source for the silica added to the Fortescue Group. In any case, the impact of the Palaeoproterozoic metasomatic event should not be ignored in any model of iron ore genesis in the Hamersley Basin.

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