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Rock alteration in the upper Crust:
Element mobility and concentration

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ABSTRACTS

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Weathering, regolith-landscape evolution and element mobility

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Deeply weathered regolith profiles are widespread in the inter-tropical belt, particularly on the continental landmasses between latitudes 35°N and 35°S. The depth of weathering may be as much as 150 m but varies considerably and fresh outcrop may occur in any part of the landscape. In parts of Australia, Africa, India and South America the regolith has been forming continuously for over 100 million years in a variety of climates and, hence, is an expression of the cumulative effects of this long weathering history. Deeply weathered regolith profiles, consisting of weathered rock, with a cover of transported overburden of various ages, are widely distributed in Australia. Differential erosion, deposition and chemical modifications have added to their complexity.

An idealised profile commonly comprises fresh bedrock, grading upwards into saprock and saprolite, commonly bleached towards the top, especially on felsic or sheared mafic rocks. This is overlain by a clay-rich and/or quartz-rich zone, a mottled zone and a ferruginous, bauxitic or siliceous upper zone. These horizons are formed by a combination of weathering and landscape processes. Weathering profiles on different lithologies reflect the bedrock. Landscape processes would have been continuous throughout the weathering period as weathering proceeded, with major environmental changes triggering particular erosional and depositional events. Thus, upper horizons, mottled zone, ferruginous duricrust and silcrete have developed in residuum, colluvium and alluvium of various ages.

Weathering is the result of interaction between the hydrosphere, biosphere and lithosphere. During weathering some of the components of primary minerals are leached and secondary minerals are formed as residua. The pathways by which these minerals form are varied and complex. The final product of weathering of all rocks is a mineral assemblage of least soluble minerals (kaolinite, hematite, goethite, maghemite, gibbsite, anatase, boehmite) and the most resistant primary minerals (quartz, zircon, chromite, muscovite and talc). However, neoformation of several generations of hematite, goethite, kaolinite and gibbsite may occur. Poorly crystalline minerals are an important constituent in surface or near surface materials. In addition, the more soluble minerals including carbonates, sulphates and halides, occur in arid environments. These generally form by dissolution, then precipitation upon evaporation.

A combination of long weathering history and variable degree of erosion has resulted a landscape of highly variable and complex regolith. In the present landscape, deeply weathered profiles may be preserved or partly eroded and buried beneath a variety of sediments. Thus, an appreciation of the weathering history is essential for understanding metals mobility in regolith environments. Minor and trace elements, including most ore-associated target and pathfinder elements are fractionated, depending upon the relative retention or dispersion from their primary host minerals, and their adsorption or incorporation into new regolith materials. Understanding the mode of occurrence of these elements is important for prediction of their mobility and dispersion characteristics in different regolith environments. Apart from a few resistates, most minerals are destabilised under surface conditions. Consequently, most minor and trace elements are released and some are trapped in secondary phases. By combining mineralogical and chemical microanalysis of in situ materials, the site of trace elements may be determined in regolith materials.

Mobility (or otherwise) of Ni, PGEs and Au during hydration and carbonation of sulfide-bearing komatiites

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Komatiites are invariably altered, usually to serpentinite or talc carbonate assemblages. Under most circumstances, Ni and the PGEs appear to be highly immobile during these processes, although their mineralogical deportment changes. The accepted idea that Fe-Ni-sulfide mineralogy is entirely controlled by alteration assemblage is not valid; primary sulfide composition plays the major role, although fluid chemistry is important at high fluid-rock ratios. Ni appears to be fixed at mm-cm scale during serpentinisation. The PGEs also appear to be highly immobile, except under some conditions in sulfide-rich environments. The presence of As in hydrothermal fluids greatly increases Pt and (particularly) Pd mobility. Evidence from sulfide ores at metamorphic grades above lower amphibolite suggests that Au is selectively mobilised at deposit scale. The use of background Pt/Au ratios in sulfide-poor mafic and ultramafic rocks may have potential as a regional lithogeochemical tool in Au exploration.

A SIMS Study of Oxygen Isotope Exchange around Veins in Dolomite Xenoliths in Shallow Intrusions

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The large difference in stable isotope composition of the original sedimentary carbonates and fluids interacting with either igneous rocks or surface rocks at high temperatures permits the tracing of even small amounts of fluid flow¹. Unfortunately, the relative short duration of fluid flow stable isotope exchange between non-reactive carbonates and fluid is inefficient. The diffusion of oxygen is slow in dolomite (ca. 1 μm @ 550°C, 10ky) and only somewhat faster in calcite (0.6-100 μm @ 550°C, 10ky). Hence carbonates need to recrystallize for efficient fluid-rock isotope exchange, as has been suggested in the literature. Here we present a detailed petrologic, secondary ion mass spectrometry (SIMS), and cathodoluminescence (CL) study of reactions driven by infiltration of magmatic fluids in carbonate xenoliths of the Bergell and Adamello intrusions (Alps, Italy). Abundant forsterite (*fo*)-calcite (*cc*) veins crosscut large (>50m) dolomite (*do*) xenoliths caught up in the Bergell tonalite. Macroscopic similar veins are found on the border of the Adamello tonalite, in pure dolomites near Paso Bondolo, Sondrio. In each case, a mm-sized central open vein (*cc+fo*) is rimmed by a 1-20cm thick reaction rim of *cc + fo*, with a knife-sharp reaction boundary towards the *do* (\pm *cc*, *fo*) host rock. They formed due to infiltration of silica-rich igneous fluids. Oxygen isotope exchange between *fo* and *cc* yield a formation temperature of 540°C in the case of the Bergell veins. Formation temperatures are estimated to be similar for the Adamello veins. Traditional O and C isotope analyses of *cc*, *fo*, and *do* revealed sharp (sub-mm scale) isotope fronts of several per mil in contact with unreacted dolomite^{2,3}.

We present new SIMS oxygen isotope analysis of *fo*, *cc*, and *do*. Analysis were guided by detailed back-scattered electron (BSE) and CL images. The newly produced *cc* crystals are in isotopic equilibrium with igneous fluids in the reaction zone. Relict grains of *do* in the reaction zone are rimmed by recrystallized *do*, as confirmed by CL-images. The relicts have the isotopic composition of the sedimentary protolith, the reaction rim is equilibrated with the infiltrating fluid.

The macroscopically unaltered host rock was infiltrated along grain boundaries. *Do*-grains in the host rock have recrystallized along the grain boundaries and lobate channels crosscutting individual grains. This texture is visible for distance of several grain sizes (0.5-1cm), measured from the reaction front. Stable isotope compositions range from completely changed to unchanged. They can be modelled as an exchange front, where the isotopic exchange is driven by recrystallization. We are currently working on quantitative models incorporating the driving force for recrystallization.

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Constraints on reaction front propagation rates in serpentinite from Li isotopes

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Serpentinite carbonation represents a natural analogue to in situ CO₂ sequestration, 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 along the basal section of the ophiolite and steep normal faults that represent fluid pathways from the underlying metasediments into the serpentinite. Alteration caused replacement of antigorite by magnesite, talc and minor chlorite (soapstone) and generated sharp alteration fronts that are parallel to the fluid pathways and to the basal thrust. 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. Here we focus on one soapstone reaction selva around a talc filled fracture that propagated 3 m into the host serpentinite. The mass-balance calculation suggests that carbonation front propagation proceeded isovolumetrically and without significant transport of major, non-volatile elements, while bulk rock Li concentration and $\delta^7\text{Li}$ values vary systematically within the soapstone alteration halo and across the soapstone-serpentine replacement interface.

The change in Li concentration and $\delta^7\text{Li}$ appears consistent with an advection-diffusion transport model in a fluid phase^[2]. The model considers measured bulk rock porosity (ϕ) and literature values for Li diffusivity in a fluid^[3], Li mineral-fluid partition coefficients (K_D)^[4] and reaction-induced changes of ϕ and K_D . Based on the best fit of theoretical with measured data, the model suggests a duration of ~200 years for 3 m reaction front propagation and defines a Péclet number of ~22. This rate is comparable to the rate of tectonic plate motion and may have implications for time-scales of mineral deposit formation, rates of natural CO₂ uptake, fluid transport in subduction zones, and rates of metasomatic rock alteration in general.

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^[2] see John et al. (2012); Nat. Geo.

^[3] Oelkers & Helgeson (1988); GCA.

^[4] Wunder et al., (2010); CMP

The effect from solubility on mechanism study of “mineral-hydrothermal solution”: two case studies

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“Water-mineral” or “fluid-mineral” reaction widely occurred throughout the hydrosphere and different layers of the interior of Earth at different scales (Hellman and Wood, 2002). The reaction constructed a geochemical cycle of the Earth material, resulted in the weathering of preexist rock and soil and the accumulation of the useful element then the ore forming. The mechanism of the reaction was well studied and characterized with three important facts: 1) shape and dimension inherited from parent mineral, 2) a moving distinct interface (reaction front), 3) large population of porosity (Putnis, 2002). The “water (fluid)-mineral” might be constrained by the solubility of the minerals in the relevant fluid, however, the solubility and its alteration in a specific fluid were always not known (Putnis, 2002). Two hydrothermal reactions including “sulfuric acid – arsenopyrite (SA)” and “CuCl fluid-pyrite (CP)” were carried out at different temperatures from 100 to 300°C. The solid product was identified as the assemblage of iron sulphates and arsenates (szomolnokite, kornite and parasymplectite etc.) in SA system and the assemblages of copper sulphides and hematite in CP system (Zhang and Cai, 2016), respectively. The products are present either as mixture or obvious zonation. The ferric sulphate and arsenate, such as szomolnokite [FeSO₄ · H₂O] and parasymplectite [Fe₃(AsO₄)₂ · 8H₂O] formed in the SA system (Hu et al., 2016). The szomolnokite was the major component, and its solubility was bigger than the parasymplectite at same conditions. The parasymplectite was reported precipitated from ferrous sulphate solution with a concentration of 0.075 mol/L (Daenzer et al., 2014). Chalcopyrite and bornite, together with hematite were present in the product zones in weak acidic CP system. The zonation was constructed by pyrite→chalcopyrite→bornite. The transformation from chalcopyrite to bornite was reported by Zhao et al. using the hematite as the start material (Zhao et al., 2014). The solubility of chalcopyrite was bigger than the one of bornite, but the first phase of precipitation was chalcopyrite and was attributed to the more difficult nucleation of bornite. To conclude from these two case study, the solubility may not be the most important factor which constrains the daughter phase in “mineral-hydrothermal” reaction.

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Incorporation of Sulfur into Extant Microbialites with Ancient Geological Analogues

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The potential constraints of organics on the mineralisation of sulfide are yet to be established & the $\delta^{34}\text{S}$ of microbial metabolites may help identify the major pathways of S transformation. The $\delta^{34}\text{S}$ of the organosulfur compounds of microbial mats & microbialites will contribute fundamental knowledge on S transformations, identify the primary OS sources in microbialites & potentially establish early diagenetic pathways of S incorporation. Extant microbialites, such as the Shark Bay stromatolites & Lake Clifton thrombolites represent complex microbial consortia. The microbial mat distribution across the hypersaline coastal plain of Shark Bay is attributed to a complex network of physicochemical factors¹. The relationships among internal mat structures (lithification), geochemical conditions, & microbial community structure are only partially understood^{1,2}. S-cycling organisms may make an important contribution to the process of lithification²⁻⁴. Whilst the abundance & properties of organic carbon for microbial metabolism have a well-known influence on the rate of monosulphide formation, the potential constraints of organics on sulphide mineralisation & competing reactions involving the formation of OSCs are yet to be fully understood⁵. These interest areas will be investigated by an integrated biogeochemistry study encompassing compound specific S speciation with microbial metabolism biomarker & intact biolipid analysis of mats, modern stromatolites/thrombolites, & sediment cores^{2,5-7}. Environmental conditions (e.g., pH, conductivity, light, temper, total alkalinity, carbonate alkalinity, major ions) & biogeochemistry (O_2 , sulfide, pH microelectrodes, $^{35}\text{SO}_4^{2-}$ -labelled Ag foil, monobromobimane-fixed samples for inorganic S, tributylphosphine treated samples for OS, petrographic, fluorescence & scanning electron microscopy etc will be determined^{2,5-8}. Biomarker-lipids extracted from microbial mats & microbialites (Garden Point, Nilemah, Shark Bay, W.A. & Lake Clifton W.A.) from environments differing in salinity levels will be studied & a comparison will be made with microbialites from the Bahamas. Additionally, core samples containing both the basinal muds & concretions (carbonate nodules from Canning Basin, WA) *in situ* will be carefully selected for this project through Geological Survey of WA. The S-CSIA data will be integrated with other contemporary organic geochemical analyses (e.g. GC-FPD, GCMS, GC-irMS – for $\delta^{13}\text{C}$ & δD). Integration of the molecular distributions & $\delta^{34}\text{S}$ values of OSCs in these samples will help address depositional & microbial species evolution issues. The specific aim is to link the different morphotypes of microbial mats with their biogeochemistry to better understand their regional occurrence & enhance geological interpretations of their remains.

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Relationship between density, volume and mass transfer during hydration reaction, Bergen Arcs, Norway.

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The interaction between aqueous fluids and dry rocks leads to hydration reactions and in most cases reduces the rock density and tends to increase the solid volume. We are interested about the accommodation of density during a replacement of one mineral assemblage by another. This point is a critical issue and debate on whether metamorphic reaction preserves rock volume has been discussed for over a century. The question addressed about how the system is “open” or “closed” as a function of the spatial scale is fundamental for this kind of reaction because it may generate stress, rock fracturing and mass loss to the fluid. The problem will be discussed with two natural samples from the Bergen Arcs in Norway with hydration of dry granulite into amphibolite-facies conditions.

The first example will be given from studies of the microstructures from which a compelling case can be made for large fluid-rock ratios and significant mass transfer using major [1] and trace elements [2]. The granulitic mineral assemblage is composed of garnet (~55%) and clinopyroxene (~45%) and is replaced pseudomorphically by (i) chlorite, pargasite and epidote, and (ii) hornblende and quartz. Although the bulk composition of both major and trace elements do not change, their gains and losses in replacing garnet are balanced by the opposite gains and losses associated with the replacement of clinopyroxene. Major element and REE indicates around 13% and 20% of the mass of rock lost to the fluid respectively.

The second example will be given by a study of centimetre-sized grains of Al-rich clinopyroxene within the granulitic anorthosites that undergo deformation by micro-shear zones and faults along which fluid has been introduced. The clinopyroxene reacts to the deformation and hydration in two different ways: (i) reaction to garnet plus a less aluminous pyroxene along kinks and fractures and (ii) the replacement of the Al-rich clinopyroxene by chlorite along cleavage planes. Using the Gresens' analysis, the reaction to garnet + low-Al clinopyroxene induces a loss in volume whereas the chlorite formation gains volume. The specific mass evolution associated with both reactions also suggests that they are contemporaneous. Stress variation results in various degrees of undulose extinction in the Al-rich Cpx. Electron backscatter diffraction (EBSD) and mass balance results suggest that the density-increasing reaction to garnet + low-Al clinopyroxene takes place where the strain is highest whereas the density-decreasing reaction to chlorite forms away from the kink where EBSD shows no significant strain. Pseudosection calculations suggest that the thermodynamic pressure of the assemblage within the kink is 15 kbar higher than the pressure conditions for the whole rock for the same range of temperature (~560°C). This result suggests that the deviatoric stress may play a role in determining the reactions that take place during retrograde metamorphism.

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The North West Shelf of Australia: Molecular and isotopic approach to discriminate organic facies; and their potential applications for fluid – source rock correlations

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The North West Shelf of Australia is a world class petroleum system and yet uncertainties still exist around fluid provenance. The fluids in the basins are largely fluids (condensates) that derive from mixed marine/terrestrial sources; additionally, low concentration of key organic compounds and alteration processes (e.g. biodegradation, evaporative fractionation, and water washing) are challenging and limit the discrimination power of traditional biomarker and isotopic methods [1]. A relevant example occurs in the Northern Carnarvon Basin, specifically in the Dampier sub-Basin, where the source of fluid in the Rankin Platform reservoirs remains uncertain. A fundamental investigation has been undertaken to improve our understanding of different petroleum families, both within the known reserves and those yet to be identified, enabling explorationists to evaluate new plays in this region. To assess this, a novel combination of molecular and isotopic parameters has been used to help de-convolute the overlaps between the organic facies (Upper-Triassic vs Middle-Jurassic). The distribution of some higher plant biomarkers and combustion-derived polycyclic aromatic hydrocarbons (PAHs), benzo[*b*]naphtho[*d*]furans, alkylcyclohexanes, alkylbenzenes and certain traditional and novel light hydrocarbons parameters are some of the tools that have helped to better understand the complexity of petroleum systems in the Rankin Platform. This data set is supported by GCMS analysis, GCxGC-TOFMS analysis and compound specific isotope analysis of carbon and hydrogen.

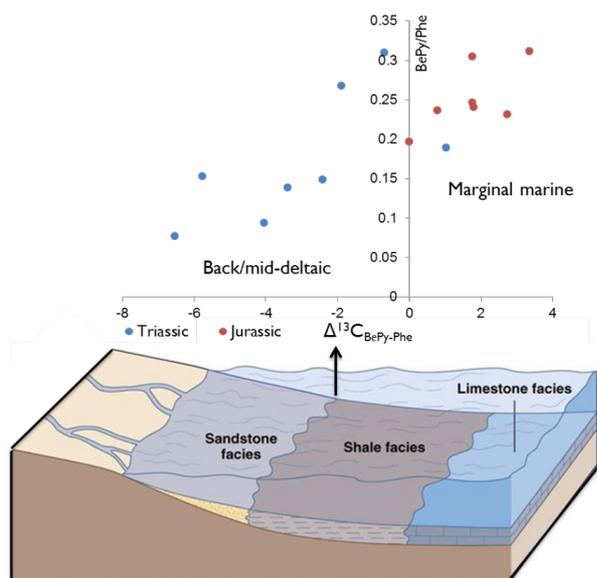


Figure 1. Facies discrimination by implementing the ratio Benzo[*e*]pyrene/Phenanthrene vs the difference in $\delta^{13}\text{C}$ values for the same molecules, in Triassic (Mungaroo and Brigadier Fms.) and Jurassic (Legendre Fm.) source rocks samples.

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Climate oscillations reflected in the Arabian Sea subseafloor microbiome

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Marine sediment contains a vast microbial biosphere that influences global biogeochemical cycles over geological timescales. However, the environmental factors controlling the stratigraphy of subseafloor microbial communities are poorly understood. Using the highest resolved sedimentary metagenomic profile to date together with paleoceanographic proxies, we show that millennial-scale paleoenvironmental conditions correlate with the metabolism and diversity of bacteria and archaea over the last glacial-interglacial cycle in the Arabian Sea. The metabolic potential for denitrification correlates with climate-driven oxygen minimum zone (OMZ) strength and concomitant nitrogen stable isotope fractionation, whereas catabolic potential reflects changing marine organic matter sources across the Last Glacial Maximum¹. These results indicate that the subsisting microbial communities had been stratified to a large extent by paleoceanographic conditions at the time of deposition. As cells are buried in the subsurface, deeply buried populations surviving with weak selection² may provide a genomic record of biogeochemical cycling over long geological timescales, as this phenomenon appears to extend into the deep biosphere³.

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Incorporation of indigenous microorganisms increases leaching rates of Rare Earth Elements from Western Australian Monazite

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Rare Earth Elements (REEs) are an essential component in most modern technologies and play a key role in medical technology, environmental protection, energy efficiency, digital technology and defence. Decrease in global supply and ever increasing demand for REEs provides Australia, and in particular Western Australia, with an opportunity to become a major player in the REE industry. Conventional REE processing methods are complex, costly, use aggressive reagents and they are harsh on the environment. As an alternative to this approach this study investigated the use of phosphate solubilising microorganisms (PSMs) to liberate REEs from REE phosphate minerals. Numerous microbial species are capable of transforming insoluble forms of phosphate to soluble forms and are applied in agricultural settings (Igual et al., 2001). This study applied the use of known PSM's to the leaching of REEs from a Western Australian monazite ore.

Monazite was added at a 0.5% pulp density to PVK media (Nautiyal , 1999) and REE levels in the leachate analysed by ICP-EOS. Of twenty five known PSB tested the best performer, a *Penicillium sp.* successfully released bound REEs (Ce, La, Nd and Pr) preferentially over potential 'contaminants', thorium and iron, from the sterile monazite into the leachate, at a total concentration of 12.32 mg L⁻¹. These microbial isolates leached REEs from the MWM in quantities significantly greater than was recorded with abiotic dissolution of the ores alone. Indigenous microorganisms present on unsterilized monazite leached the REE's at very low levels 0.9 mg L⁻¹ however, inoculation of unsterilized monazite with the previously tested phosphate solubilisers, enabled us to increase the levels of REE released into the leachate four fold. A synergistic effect of between indigenous and inoculant microorganisms was demonstrated.

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HSE mobilisation in subduction zones: insights from high-pressure serpentinites and ‘hybrid’ rocks from Alpine Corsica

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HSEs are interesting tracers of geological processes and of economic importance but their mobility in many environments is poorly understood. Subducted serpentinites have the potential to carry HSEs to great depths or transfer HSE to the sub-arc mantle upon devolatilisation [e.g. 1]. The sub-arc mantle is considered to be enriched in Pd and Pt relative to IPGE [2] and therefore transport of these elements via high pressure fluids is deemed possible. However, HSE cycling in subduction zones is poorly understood. A combination of analytical techniques was used to trace the HSEs in serpentinites through the subduction cycle. Comparison of bulk HSE concentrations to primitive mantle and abyssal HSE concentrations provides an insight into large scale HSE transfer, mineral paragenesis work constrained the timing of sulphide growth (the major host of HSE), LA-ICP-MS determined the concentration of HSE hosted in sulphides in high-pressure serpentinites, and high resolution feature mapping provided a method to detect PGE-bearing alloys. The bulk concentrations of HSE in the subducted serpentinites are no different to HSE concentrations of primitive mantle and abyssal serpentinites, therefore no large scale transfer of HSE occurred, with the exception of a slight Pd and Au enrichment in one sample. However, hybrid samples show evidence for Au, Re, Ir and Ru fractionation, hence mixing with other lithologies may have significant implications for HSE fractionation in the subduction channel. In the serpentinite samples, millimetre to centimetre scale mobilisation is proposed from sulphides to alloys and between sulphides. Sulphide HSE concentrations and sulphide parageneses provide complementary tools to assess redox conditions throughout the subduction cycle.

¹Foustoukos et al., 2015, *Geochim. Cosmochim. Acta.*, 150, 11–25

²McInnes et al., 1999, *Science*, 286(5439), 512–516

Hydrotalcite Formation for Trace Element and Radionuclide Removal from Uranium Mine Barren Lixiviant: Beverley ISR Uranium Mine

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Hydrotalcite (HT) formation as a method to neutralise acidity and remove trace elements and radionuclides was assessed using barren lixiviant from Heathgate Resources' Beverley and Beverley North In-Situ Recovery (ISR) uranium mines, South Australia (Douglas, 2004; 2009; 2015; Douglas et al, 2014). Batch-scale studies demonstrated proof of concept for the neutralisation of acidity and concomitant removal of a range of contaminants from the barren lixiviant using a range of Mg and/or Al salts.

A HT-dominated precipitate was formed during the neutralisation (Fig. 1), hosting a range of elements including substantial uranium (~1% U) and rare earth elements (~2% REE). High U (99%) REE (99%) and radionuclide (92-99%) recovery from barren lixiviant after hydrotalcite precipitation indicates a potential to both remediate barren lixiviant prior to aquifer re-injection and to offset remediation costs. Alternatively, HT precipitates formed during barren lixiviant neutralisation may be further stabilised facilitating the formation of minerals potentially amenable for inclusion in a long-term waste repository at the cessation of mining, should this be required.

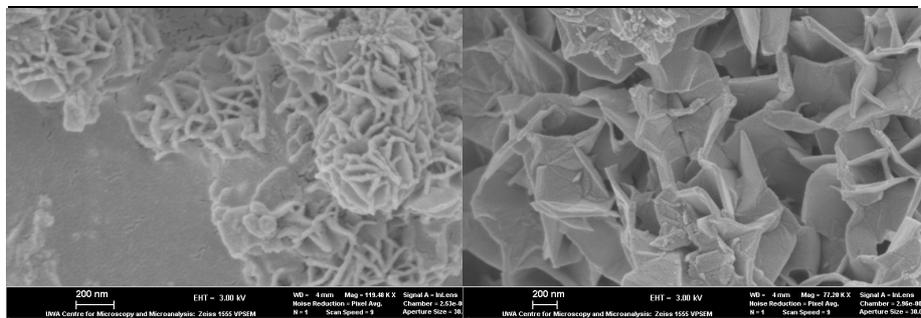


Figure 1. Botryoidal hydrotalcites aggregates (l) and detail of aggregate structures (r). Scale bars 200 nm.

A residual Na-SO₄ brine formed during lixiviant neutralisation creates the option to use electrolysis to generate H₂SO₄/NaOH for mine site use and to further offset lixiviant remediation costs. Importantly, the water quality of the neutralised barren lixiviant produced via HT precipitation is similar to that of existing groundwater. Whilst the ionic composition of Beverley/Beverley North's barren lixiviant would mean easier application of this technology, there is potential to apply it to other uranium mines with suitable addition of reagents. A HT-based remediation technology, after scale-up and performance validation, allows for the prospect of a fully integrated ISR mining, processing and lixiviant remediation strategy consistent with stringent environmental and mine closure standards.

More recently, HT precipitation was used to remediate 56 ML of acid, metal-rich mine pit at the Baal Gammon mine pit in Queensland (Douglas, 2014). Following a combined HT and reverse osmosis treatment approximately 50 ML of water was discharged after meeting environmental release standards.

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Hydrothermal alteration textures and REE mineralisation in the Cummins Range Carbonatite Complex, Kimberley region, W.A.

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The Cummins Range Carbonatite Complex was emplaced at the southern end of the Paleoproterozoic Halls Creek Orogen at approximately 1009 ± 16 Ma (Downes et al. 2016). The complex consists of a composite, subvertical to vertical zoned stock comprising a clinopyroxenite that was intruded by calcite carbonatite and dolomite carbonatite dykes and veins that contain variable proportions of apatite–phlogopite–magnetite \pm pyrochlore \pm metasomatic Na-Ca amphiboles \pm zircon (Andrew 1990; Downes et al. 2014). Downes et al. (2014) identified various intrusive phases of carbonatite within the complex including early high-Sr calcite carbonatite and high-Sr dolomite carbonatite that were cut by thin, late-stage dykes of high-REE dolomite carbonatite. Trace-element geochemistry suggests that the carbonatites have affinities to rift-related carbonatites and generally are not greatly enriched in the REEs. Where REE-enrichment does occur within the primary carbonatite it is restricted to thin, late-stage dolomite carbonatite dykes (~ 3.43 wt% TREO) and shear zone-hosted hydrothermal apatite-monazite-(Ce) and monazite-(Ce)-talc rocks (≤ 25.8 wt% TREO). The apatite–monazite-(Ce) rocks comprise complex intergrowths of apatite and monazite-(Ce) that are overprinted by veins of talc–amphibole–pyrrhotite–dolomite. Hydrothermal and metasomatic processes also produced widespread dolomitization of the carbonatites that resulted in low-Sr dolomite carbonatite with vugs that is weakly mineralised in REEs. Deformation of the carbonatites and clinopyroxenite occurred within vertical–subvertical shear zones (trending ~ 315 – 330°) that focused hydrothermal fluid flow and high-grade REE mineralization within the complex. The complex has undergone a prolonged deformation and alteration history including a thermal event at ~ 900 Ma, during the intracratonic Yampi Orogeny, that reset the K-Ar and Rb-Sr isotopic systems. Furthermore, U-Th-Pb dating of monazite-(Ce) from strongly foliated dolomite carbonatite produced dates ranging from ~ 900 – 590 Ma that reflect a long history of post-emplacment hydrothermal alteration/recrystallization (Downes et al. 2016).

Mechanical concentration of primary magmatic–hydrothermal REE mineralization within the carbonatite during weathering and deflation has produced a monazite-(Ce)-apatite-rich secondary ore overlying the primary carbonatite. Secondary monazite-(Ce) and apatite, along with minor bastnäsite-(Ce), crandallite-group minerals and trace churchite-(Y) occur in the regolith, but secondary REE enrichment is subordinate in importance to concentrations of residual primary monazite-(Ce) and apatite (Sweetapple and Downes 2010). This oxidized zone REE ore body has an inferred resource of 4.90 Mt at 1.74 % total rare earth oxide (TREO), 11.2 % P_2O_5 and 145 ppm U_3O_8 (Kimberley Rare Earths 2012).

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Geochemical and spectral vectors for metamorphosed and deformed VMS-style mineralisation in the Quinns district, Yilgarn Craton, Western Australia

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Volcanic-hosted massive sulphide (VMS) occurrences in the Quinns district are hosted mainly by ca. 2814-2800 Ma banded iron formation (BIF) within a sequence of rhyolite, basalt, and minor siltstone. The VMS occurrences and their surrounding rocks are folded, metamorphosed, and deeply weathered and variably covered by transported regolith. This study uses an integrated petrological and geochemical approach to map gradients in synvolcanic mineral and element abundances, with the aim of understanding the effects of post-volcanic processes on Archean VMS ore bodies. Throughout the Quinns district, rhyolite-dominant footwall rocks and BIF record kilometre-scale gradients in alteration mineral patterns and geochemistry. Distal alteration assemblages in rhyolite include quartz–white mica ± chlorite. Approaching known VMS prospects in the eastern half of the district, the rhyolite grades into a 2 km by 1 km, zone of coarse-grained andalusite ± kyanite ± garnet rhyolitic schist. This broad Al-rich silicate alteration zone envelops two discrete 1 km by 500 m, proximal alteration zones in rhyolite defined by chlorite ± talc, with minor disseminated magnetite, pyrite, and chalcopyrite. The northern-most proximal alteration zone lies stratigraphically below a BIF-hosted Cu-Zn-rich gossan. At the Austin deposit in the western part of the district, abundant talc and anthophyllite with minor cummingtonite and hornblende are associated with mineralisation in BIF, with neighbouring rhyolite altered to chlorite in proximal zones. These mapped alteration mineral patterns mirror bulk rock geochemical gradients in rhyolite and BIF. Proximal alteration zones in rhyolite are enriched in Cu, Zn, Ag, Au, Bi, Fe₂O₃, In, MgO, Mo, S, Se, and Te, with local enrichments in As, Cd, MnO, Pb, and V. These rocks are depleted in Ba, K₂O, Li, Na₂O, and Rb relative to least-altered rhyolite. Rhyolite located in more distal zones up to 100 m from proximal alteration zones is enriched in Ag, Fe₂O₃, In, K₂O, MgO, S, and V. In comparison, BIF hosting massive sulphides is enriched in Cu, Zn, Pb, Ag, and Sn, with local enrichments in Bi, In, and MgO. Positive Eu anomalies are associated with mineralised BIF in the Austin VMS deposit and contrast with the mostly flat REE slopes for BIF sampled from less mineralised areas in the district. The kilometre-scale gradients in hydrothermal alteration minerals and bulk rock geochemistry in rhyolite and BIF are interpreted to be mostly controlled by synvolcanic hydrothermal alteration related to the development of VMS-related hydrothermal fluid pathways. The proximal zones resulted from the interaction between synvolcanic, Mg-rich fluids and rhyolite footwall at the time of VMS mineralisation and BIF deposition. In contrast, outer zones of andalusite ± kyanite ± garnet suggests the removal of silica and alkali elements and residual concentration of aluminium in rhyolite footwall by acidic synvolcanic hydrothermal fluids prior to peak regional upper-greenschist facies metamorphism. The defined alteration mineral and geochemical gradients in the Quinns district demonstrates their use for detecting ancient fluid alteration pathways related to VMS systems in complexly deformed and metamorphosed districts, such as those in the Yilgarn Craton of Western Australia and the Abitibi subprovince of Canada.

The geodynamic setting of serpentinisation: does it matter?

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Up to 13 billion tonnes of serpentinised mantle are subducted every year. This material carries oxidised iron, carbon, sulphur, plus fluid-mobile elements such as chlorine, deep into the Earth, with consequences for the oxidation state of sub-arc mantle and the genesis of arc-related ore deposits. However, there is a lack of consensus on the role of subducted serpentinised mantle lithosphere in earth system processes. One of the reasons for this uncertainty is that subduction fluxes of the relevant elements are poorly constrained. Most subducted serpentinised mantle is serpentinised on the ocean floor in slow and ultra-slow geodynamic settings. Yet this material is poorly represented in the literature because it is so inaccessible. Indeed, the entire body of knowledge that relates to abyssal serpentinites is based almost exclusively on samples from the Kane fracture zone, the 15°20' fracture zone, the Atlantis Massif, and the Logatchev hydrothermal field, which are all on, or close to, the Mid-Atlantic Ridge. Large volumes of accessible serpentinite, on the other hand, are available in ophiolite complexes. This material is serpentinised in quite different geodynamic settings, and by different fluids, than the bulk of subducted material, so it is necessary to assess if ophiolite serpentinites are a good proxy for seafloor serpentinites.

Serpentinites from the 15°20' Fracture zone, sampled during ODP cruise 209, were compared with serpentinites from New Caledonia. The 15°20' serpentinites were serpentinised by modified seawater in a shallow hydrothermal seafloor setting. The New Caledonia serpentinites were serpentinised in a supra-subduction zone setting (SSZ) by slab-derived fluids. Thus serpentinising fluids and the local stress environment would have been quite different in the two geological settings. Petrological, whole rock, and mineralogical analyses were combined to compare the two sample sets.

Petrologically, the evolution of serpentinisation was close to identical in the two environments, with the same sequence of vein types and similar apparent lengthscales of equilibration. These similarities suggest that fluid infiltration and control of critical chemical parameters such as silicon and oxygen activity are controlled within the serpentinite, and are characteristic of the rock type rather than the environment.

However, mineralogically, a greater proportion of oxidized iron was present in serpentine of any particular vein type from the 15°20' serpentinites relative to serpentine in the same vein type in the New Caledonia vein types. Further, the Cl, S and C contents of the 15°20' serpentinites, though heterogeneous, were significantly higher than those from New Caledonia.

Given these observations, the use of serpentinites from different geodynamic settings as a proxy for seafloor settings must be undertaken with caution. Values for subduction zone fluxes of redox budget and fluid mobile elements obtained from SSZ serpentinites are potentially minimum values. However, aspects of serpentinisation controlled by the rock itself such as fluid infiltration geometry and small scale hydration reactions can be studied effectively in serpentinites from a range of geodynamic settings.

Metal and Sulfur cycle in the deep continental crust: insights from the Ni-Cu-PGE sulfide deposits of the Ivrea Zone (Italy)

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The lower continental crust represents a chemical and physical threshold between very diverse Earth reservoirs. At different times throughout the geodynamic evolution of any terrain, the lower crust can act as an impermeable barrier that prevents mixing and physical interaction between the subcontinental lithospheric mantle and the upper continental crust; alternatively, it may be a gateway that permits the injection of mantle-derived melts into the continental crust, with their associated cargoes of metals and volatiles that can fertilise the notably dry lowermost parts of the crust. In the lower crust, these magmas may form localized orthomagmatic nickel-sulfide mineralization, or else pond, fractionate, evolve and form the roots of porphyry copper systems, which would ultimately be emplaced in the upper crust. However, the rate and dynamics of metal and sulfur transfer from the upper lithospheric mantle into the deep continental crust is poorly constrained.

The Ivrea Zone, northwest Italy, is a natural laboratory to study this knowledge gap because it provides a unique snapshot into the architecture and composition of the mid to lower continental crust and subcontinental lithospheric mantle. In fact, the Ivrea Zone represents a section of the lower continental crust and subcontinental lithospheric mantle exhumed during the alpine Orogeny. Throughout this section, a number of mafic and ultramafic sills and pipes outcrop at various structural levels and contain Ni-Cu-PGE mineralization, which varies in texture, composition, grade and tenor. Therefore, the Ivrea Zone provides unparalleled insights into the magmatic processes that lead to the formation of orthomagmatic nickel-sulfide mineralisation in the deep continental crust.

The nickel-sulfide occurrences documented in this study are associated with Ni-Cu-PGE mineralized sills and pipes emplaced from the Permian to the Lower Triassic. New data from this study show that the timing of emplacement of these deep seated magmatic bodies may extend over at least ca. 40 million years. Field and laboratory data indicate that magmatism shifts from an earlier sill-like style event, characterized by the emplacement of dry and relatively metal tenor-poorer magmas, to later pipe-style magmatic activity, made up of volatile-rich and relatively metal-rich magmas. While the basal sills display clear sulfur isotope evidence of crustal contamination, reflected in mixed signatures between mantle-like values and known heavy sulfur enriched crustal sulfides that occur in the host stratigraphy ($\delta^{34}\text{S}$ up to +10), the pipes display on average much lighter sulfur isotope values, which cluster at $\delta^{34}\text{S} \sim +1.34$. We propose that deep seated mineralised magmatic systems such as the ones exposed in the Ivrea Zone play a crucial role in transferring metals and sulfur from the subcontinental mantle up to the overlying continental crust, contributing to its geochemical and isotopic make up.

Catalysing Mineral Recrystallisation at Low Temperature: A New Pathway to Unlock Metals from Laterites?

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Nickel laterites are highly-weathered soils formed over ultra-mafic rocks, which contain over two-thirds of global nickel deposits. Because the Ni in laterites is often in solid solution with crystalline iron oxides (e.g., goethite), processing these resources is challenging and typically requires mineral dissolution in acidic solutions at elevated temperature (~100-250°C). Our recent work has shown that dissolved Fe(II) in aqueous solution rapidly and, in some cases, completely exchanges isotopes with structural Fe(III) in iron oxide phases (i.e., goethite and hematite),^{1, 2} as well as Fe(III)-bearing clay minerals,³ at ambient temperatures (22°C) and circumneutral pH. Dissolved Fe(II) effectively acts as a catalyst to recrystallise these ‘stable’ minerals. Such recrystallisation increases mineral-fluid interaction and element mobility, and promotes the release of Ni (and Co) into solution.^{4, 5} These findings suggest that Fe(II)-catalysed recrystallisation may be a low-cost strategy to extract critical metals from laterites but the efficiency of this process on complex natural laterites that contain variable mineral assemblages and compositions is unknown. Here, we react ore-grade Ni laterite samples in ⁵⁷Fe-labeled aqueous Fe(II) solutions at 22°C to 1) quantify the extent of recrystallisation of iron-bearing minerals and 2) measure the yields of Ni and Co that are released to solution. This study is a crucial first step at developing inexpensive techniques to process Ni laterite resources and also provides fundamental information regarding mineral reactivity and metal mobility in iron-rich sediments.

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Things go faster with water: New experimental findings on exsolution microstructures in hydrothermally synthesised Cu-Fe sulphides

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Bornite (Cu_5FeS_4) and digenite ($\text{Cu}_{8.52}\text{Fe}_{0.11}\text{S}_{4.88}$) are common and economically-important sulphides occurring in a wide range of geological environments, and have been the subject of numerous experimental studies since the late 1950's. They form a continuous solid solution above 265°C, and on cooling, rapidly exsolve into mixtures of the end-members [1]. Annealing of intermediate compositions at sub-solvus temperatures results in coarsening of the exsolved end-members into distinctive 'basketweave' textures, identical to those seen in natural ores.

Previous studies on exsolution microstructures in the bornite-digenite solid solution have utilised starting materials synthesised under dry conditions using the evacuated silica tube technique [2,3]. These were annealed at various subsolvus temperatures for up to 6 months, producing a range of similar exsolution textures. More recently, bornite-digenite solid solutions have been hydrothermally synthesised via interface coupled dissolution reprecipitation using natural chalcopyrite as a starting material [4]. Three different solid solution compositions ($\text{Bn}_{60}\text{Dg}_{40}$, $\text{Bn}_{80}\text{Dg}_{20}$ and $\text{Bn}_{87}\text{Dg}_{13}$) were obtained by varying reaction temperatures and durations [5]. Micro-textures in these solid solutions were examined following three different cooling and annealing regimes, and were compared to textures obtained by dry synthesis and subsolvus annealing. The results indicate that, in the presence of a fluid phase (water trapped in micropores and fluid inclusions), coarsening of exsolution lamellae is driven by recrystallization associated with healing of the open porous microstructure in the sulphide causing fluid migration to grain boundaries. Importantly, the coarsening of exsolution lamellae occurs 2,500 times faster in the presence of water compared to the equivalent dry system [5]. As a result, the final microstructure and the kinetics of textural coarsening depend upon the crystallisation history of the parent mineral. Such fluid-driven textural evolution may be a major mode of reaction in ore systems, and is likely to affect oxide and silicate systems alike in the presence of aqueous fluids.

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Preservation and evolution of life across ocean anoxic events

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Oceanic anoxic events (OAEs) are sediments that contain high amounts of organic matter that were deposited under oxygen-depleted conditions and form an excellent archive for the reconstruction of ancient environments. Often OAEs coincide with mass extinction events (e.g., Grice et al., 2005). Concretions are often preserved in sediments and can contain encapsulated fossil remains (e.g., bones, soft tissue). Concretions formed under highly reduced conditions allow for exceptional preservation of soft tissue and biomolecules (e.g., cholesterol Melendez et al., 2013a, 2013b). Concretions were formed over long geological time spans, but have never been studied in sufficient detail by organic –inorganic approaches that we have applied here (e.g. Plet et al., 2016). With access to concretions from several worldwide Lagerstätte locations (e.g., Lower Jurassic Posidonia Shale, NW Germany; The Devonian Gogo Formation, Western Australia) and the surrounding sedimentary shales- organic (biomarkers, biomolecules and stable isotopes, inorganic geochemistry and morphology by imaging) reveal the extent of preservation of cholesterol and the entire diagenetic continuum (Melendez et al., 2013 a and 2013b) as-well as exceptionally well preserved cells from sediments deposited under photic zone euxinic (PZE) conditions (unpublished data). Where molecules and cells meet modern technologies the possibilities for providing significant insights into the development and evolutionary biology and chemistry of early life are extraordinary.

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Lord Howe Rise deep stratigraphic drilling: tectonics, climate and ancient life

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The Lord Howe Rise (LHR) is an elongate ribbon of submerged and extended continental crust that separated from Australia during the Late Cretaceous. The LHR is concealed beneath the Tasman Sea in water depths of 1000–3000 m, so current knowledge of LHR geology is based only on widely-distributed marine and satellite geophysical data, limited dredge samples, and sparse shallow (<600 m below-seafloor) drilling into Cenozoic pelagic sediments.

Existing data provide a broad understanding of the LHR's crustal structure, sedimentary basin architecture and resource potential. However, building more detailed knowledge of LHR geology, and the geological evolution of the southwest Pacific more broadly, requires drilling into rocks that record the >100-million-year geological, tectonic and climatic history of the region. To this end, Geoscience Australia and the Japan Agency for Marine Earth Science and Technology (JAMSTEC) are leading an international effort to drill a deep (up to 3500m below the seafloor) stratigraphic hole through a LHR rift basin that will core Cretaceous and older sediments and potentially basement rocks. Two shallow holes into basement horst blocks may also be drilled.

A proposal for the drilling using the JAMSTEC drilling vessel CHIKYU is in review with the International Ocean Discovery Program (IODP) (Proposal 871-CPP). The objectives outlined in this proposal are to: 1) define the role and importance of continental crustal ribbons, like the LHR, in plate tectonic cycles and continental evolution; 2) recover new high-latitude data in the southwest Pacific to better constrain Cretaceous paleoclimate and linked changes in ocean biogeochemistry; and 3) test fundamental evolutionary concepts for sub-seafloor microbial life over a 100-million-year timeframe.

Deployment of an automatic treatment system to accelerate mineral carbonation in mine tailings at Woodsreef Chrysotile Mine, New South Wales, Australia.

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Carbon mineralisation is being investigated as a potential climate change mitigation strategy. This technology utilises the natural process of silicate weathering to remove carbon dioxide (CO₂) from the atmosphere and store it in the structures of carbonate minerals. Here, we present preliminary results from a field-based trial of enhanced weathering in mine tailings.

Ultramafic mine tailings are an ideal material for carbonation since they contain an abundance of reactive minerals with high cation contents, such as olivine [(Mg,Fe)₂SiO₄] and serpentine [Mg₃Si₂O₅(OH)₄], and their surface area and reactivity have been further enhanced by crushing [1]. The current challenge is to accelerate carbonation rates in mine tailings while minimising economic and energy costs of treatment. The mining industry also produces large amounts of acid generating materials, which have been investigated as a potential source of acidity to accelerate tailings dissolution and carbon mineralisation [2]. There are several environmental and economic benefits to this approach: acid mine drainage is neutralised, dissolved metals are immobilised, and silicate mineral dissolution is enhanced, thereby accelerating CO₂ sequestration.

We have developed and deployed an automatic treatment system to accelerate CO₂ sequestration in mine tailings at Woodsreef Mine in New South Wales, Australia. This mine has previously been identified as a site of ongoing passive tailings carbonation [3]. This system delivers water or dilute sulfuric acid to treatment plots via a sprinkling system. Soil moisture is regulated via soil moisture probes, and maintained within an optimal range of 20 – 40% pore water saturation, in line with Assima *et al.* [4]. Key advantages of this system are that it is solar powered, designed to operate independently, and consists mainly of readily available and inexpensive materials; such that it could be scaled up and incorporated into existing tailings management strategies. The experimental treatments were delivered for two weeks. After 6 weeks, treatment plots were cored and profiled for analysis using quantitative X-ray diffraction, and X-ray fluorescence.

Key findings of this experiment are that Mg-carbonate minerals re-precipitate after being dissolved by acidic solutions, indicating resilience to acid exposure. Secondly, the existing carbonate mineral content of tailings at Woodsreef inhibited the effectiveness of acidic treatments; which would be better applied to fresh tailings. Thirdly, we identified rapid formation of the mineral pyroaurite [Mg⁶Fe³⁺₂(CO₃)(OH)₁₆·4H₂O] in the acid treatment, which may represent a novel way to kick start carbon sequestration in ultramafic materials.

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Ilmenite breakdown and rutile - titanite stability in metagranitoids: natural observations and experimental results

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Despite recent improvements on in situ geochronological and geothermometric methods applied to accessory minerals such as rutile and titanite, the pressure-temperature stability domains of these mineral phases, commonly forming by replacement of ilmenite in metamorphic rocks, remain poorly known. Field observations in exhumed orthogneiss massifs from the Western Alps indicate that, in most cases, titanite is stable below 1 GPa while rutile seems to dominate within rocks recrystallized under higher pressures (above 1 GPa). We herein investigate phase relationships for four granitic compositions (Ti-NCKFMASH system) showing variable CaO content at medium to high-pressure conditions (0.7–1.6 GPa, 450–650 °C) with a focus on ilmenite breakdown and Ti-bearing species formation. Our piston-cylinder experiments show that, in the investigated P-T range, ilmenite reacts during metamorphism above 1.2 to 1.4 GPa to form rutile. Below this pressure, titanite is the dominant Ti-bearing species for most granitoid compositions. Importantly, we show that the position of this reaction curve is strongly influenced by the availability of whole rock Ca. In either case, the ilmenite is partially to totally replaced by either rutile or titanite or both via a fluid-aided coupled dissolution-precipitation process as evidenced by the textures. For a Ca-depleted composition, rutile may be stable down to 0.7 GPa (and below) within the partially replaced ilmenite pseudomorphs while titanite stability may extend at pressures > 1.3 GPa for Ca-richer compositions. Both species may be co-stable in one single sample depending on local gradients in the Ca activity. The finding of metamorphic rutile within Ca-bearing metagranitoids (i.e. higher than c. 2 wt.% CaO) can be considered, under certain conditions, as a reliable indicator of high-pressure metamorphism. The results from this study also highlight the importance of improving our knowledge of the phase relationships between rutile and titanite as a function of P-T-X in order to better interpret the textural and tectonic history in natural samples as well as the meaning of age values yielded by rutile and titanite geochronometers.

The impact of evolving mineral–water–gas interfacial areas on mineral–fluid reaction rates in unsaturated porous media

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The distribution and evolution of mineral–water–gas interfacial areas exert a fundamental yet poorly documented control on mineral–fluid reactions in the unsaturated zone. Here, we explore the impact of changing mineral reactive surface area, water content, and gas distribution on mineral reaction rates in unsaturated porous media using a variety of flow-through column and batch experiments of different scale and water content. Our experiments show that the extent of mineral–gas reaction is limited by the abundance of water available to facilitate precipitation of secondary minerals. Conversely, at high bulk water saturation, the development of preferential gas flow paths limits the exposure of reactive minerals to CO₂ and reduces the overall extent of reaction. Finally, the entrainment of reacting mineral particles by the mobile water–gas interface dramatically alters the relative abundance of reactive mineral surface area to fluid reservoir volume. This ratio, which directly influences reaction rate and reaction progress, was observed to vary by two orders of magnitude as evaporation progressed in the experiments. Its dynamic evolution may have a correspondingly large impact on mineral–fluid reaction in Earth’s shallow subsurface. We predict that spatial and temporal variability of pore-scale reaction rate will be significant during evaporation, imbibition, or drainage in the vadose zone, with implications for chemical weathering, soil quality, and carbon cycling. Current research is aimed at better defining the controls on element flux and secondary mineral precipitation in the unsaturated zone as a function of water saturation and evaporation-recharge cycles.

Trace element and organic matter interaction in karst systems

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Trace element enrichments in speleothems are hierarchical (Y > Zn, Cu and Pb > P and Br), detectable at an annual or subannual resolution, and driven by seasonal (normally autumnal) flushes of dripwater from the overlying soil and vadose zone (Borsato et al., 2007; Blyth et al., 2016). Although trace element data from speleothems can be used in isolation to investigate hydrological, temperature and crystallographic factors (Fairchild et al., 2010; Wynn et al., 2014), the chemical association of trace elements with natural organic matter (NOM) in the soil and vadose zone offers the additional potential to use high resolution trace element records as a proxy for organic matter type, movement and input (Hartland et al., 2012; Blyth et al., 2016). This is of considerable value to future palaeoenvironmental research as the analysis of organic matter in speleothems is difficult at high temporal resolutions due to the very low levels of organic carbon present in the samples (Blyth et al., 2016)

Transition metals ranging from vanadium to zinc show an association with colloidal particles in a range of aquatic systems (e.g. Stolpe et al., 2005), including karst waters (Hartland et al., 2012). Although colloidal material can be organic or inorganic, evidence suggests that in cave waters it is the NOM phases that complex with the trace elements (Hartland et al., 2011). Furthermore, data indicates that ratios of trace metals can reflect the composition of the organic matter (Hartland et al., 2012) – for example, a correlation between Cu:Ni and dissolved organic matter molecular weight (Rutledge et al. 2014). This is supported by evidence from other freshwater systems (Wu et al., 2004).

To fully utilise trace element profiles as a proxy for organic matter it is necessary to obtain a better understanding of how colloidal OM and trace metals are captured by speleothem carbonate, and in particular, identify any partitioning that occurs. This area of research is relatively limited, as the majority of the literature on trace metal partitioning in mineral systems focuses on inorganic processes (Prieto and Stoll, 2011). Evidence indicates that the high affinity of divalent cations for calcite mineral surfaces will create a stable sink for trace metals on the speleothem surface (Blyth et al., 2016 and references therein). However, comparison of related cave drip-waters and speleothems (Hartland et al., 2012; 2014) indicates that partitioning of NOM:trace metal complexes occurs during speleothem formation, meaning that a correction to diagnostic ratios will be required before proxy time-series are developed. Notwithstanding this, the exploitation of trace metal ratios to investigate organic ligand composition within karst systems is now feasible.

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Open system behaviour within the sediments of the Corsican Schistes Lustrés

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It has not yet been determined whether subduction zone carbonates act as closed or open systems. Thermodynamic models suggest little to no decarbonation occurs within dry carbonate rocks and basalts. However, calcite veins found within metagabbros and metabasalts from the Schistes Lustrés surrounding sedimentary units provide evidence that the sediments are behaving as an open system. This is corroborated by stable isotope data that show the origin of the veins to be the calcschist. If the sediments are behaving as an open system on a large scale then it will have implications for CO₂ cycling within subduction zones.



$\delta^{34}\text{S}$ of Organic Sulfur Compounds and the Sulfur Cycle of Petroleum Systems

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This study makes use of recently invented Compound Specific Sulfur Isotope analysis (CS-S-IA) to investigate the incorporation and fate of sulfur in petroleum systems. Sulfur is usually incorporated into fossil fuels via secondary processes (Peters et al., 2005), most significantly by thermochemical sulfate reduction (TSR). The $\delta^{34}\text{S}$ of organo sulphur compounds (OSCs) in oils can be significantly influenced by TSR, as well as by other factors such as depositional environment and thermal maturity. Bulk $\delta^{34}\text{S}$ values of petroleum can vary over a wide range (8 to 32‰; Faure and Mensing, 2005) and have traditionally proved quite useful for oil–oil correlations (see e.g., Gaffney et al. 1980). CS-S-IA has already been applied to several S-rich oils from different parts of the world (Amrani et al., 2009; 2012; Greenwood et al., 2014; Li et al., 2015; Cai et al., 2015; Gvirtzman et al., 2015) with the $\delta^{34}\text{S}$ values measured ranging from -15 to +40 ‰, and with co-occurring OSCs in a single oil varying by as much as 30 ‰ – reflecting the impact of different controls that would not be resolved by bulk $\delta^{34}\text{S}$ analysis. A more sophisticated understanding of the $\delta^{34}\text{S}$ relationships of specific S-sources and alteration events, however, requires further CS-S-IA research and application to a variety of petroleum samples

We are conducting a CS-S-IA study of oils from the Tarim Basin (W. China) to help resolve the controversy about the source of deep oil in the Tarim Basin. CS-S-IA has already been used in correlation studies of oils from the Tarim Basin (Li et al., 2015; Cai et al., 2015), but a clear distinction of a Cambrian or Ordovician source of these oils was often not established. We aim to use $\delta^{34}\text{S}$ signatures to help resolve the respective contribution of these sources, as well as provide a more comprehensive evaluation of the $\delta^{34}\text{S}$ values and relationships with TSR which have significantly impacted a number of deep (>6000m) Tarim Basin oils.

We are also interested in the potential $\delta^{34}\text{S}$ dynamics associated with the biodegradation of oils by microbial communities. Biodegradation is a common and detrimental alteration process in petroleum systems when the temperature in reservoirs is cooler than approximately 80 °C. A number of molecular based biodegradation scales based on the different vulnerability of aliphatic and aromatic hydrocarbons to biodegradation have been defined from many organic geochemical studies (e.g. Volkman et al., 1984; Grice et al., 2000; Larter et al., 2012), and are now commonly used to assess the extent to which crude oils have been biodegraded. Biodegradation can also lead to varied ^{13}C and D fractionation of different hydrocarbons, and $\delta^{13}\text{C}/\text{dD}$ based biodegradation parameters have also been defined (Asif et al., 2009). The vulnerability of OSCs to biodegradation, however, has attracted very little previous attention. We plan to evaluate the abundance and $\delta^{34}\text{S}$ relationships of the OSCs to biodegradation through the analysis of S-rich reservoir oils exposed to different levels of biodegradation and also by simulating the biodegradative processes on selected oils under laboratory controlled conditions. The outcome of this CS-S-IA based research will shed further light on biogeochemical S cycles, help contribute to the discovery and more efficient utilisation of new natural energy resources, and provide a better appreciation of S species and hydrocarbon reaction mechanisms during eogenesis.

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Investigation of Ni Sequestration during Manganese Oxide Mineral Recrystallization using X-ray Absorption Spectroscopy (XAS)

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Manganese oxide minerals are regarded as highly reactive metal scavengers and major sinks of trace elements in the environment. Interaction between Mn(III,IV)-oxides and manganese-reducing microorganisms results in the release of aqueous Mn(II) caused by reductive dissolution of the solid phases. The oxidative arm of biogeochemical manganese cycling involves the oxidation of aqueous Mn(II) and the re-precipitation of solid-phase Mn(III,IV) oxides. Consequently, both the oxidation and reduction of manganese results in coexisting aqueous Mn(II) and solid-phase Mn(III,IV) oxides that abiotically back-react to recrystallize the mineral, as evidenced by recent isotopic tracer experiments (Elzinga, 2016; Frierdich et al., 2016). During this process no significant mineral phase transformation was observed despite that most of the solid phase manganese atoms exchanged with dissolved manganese in solution. The role of such dynamic recrystallization on trace element (e.g. Ni) uptake by manganese oxides is unknown.

In this study, we used synchrotron-based X-ray absorption spectroscopy (XAS) to assess the speciation of Ni after reacting manganite (γ -MnO(OH)) in Ni(II) solutions in the absence and presence of aqueous Mn(II). The experiments were conducted as a time series from 1 to 51 days for different solution pH values (5.5 & 7.5) under strictly anoxic conditions. The concentrations of aqueous Mn(II) were also varied between 0.0 mM and 1.0 mM with a fixed concentration of 0.2 mM Ni(II) in all experiments. Our results suggest that Ni; (a) forms stable sorbed surface-species and; (b) can be incorporated into the manganite mineral structure, with incorporation promoted by Mn(II)-catalyzed mineral recrystallization. These findings have implications for trace element availability and scavenging in aqueous systems and for the fate of contaminants in polluted soils.

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A demonstration of rapid SO₂-glass reactions and their mechanisms

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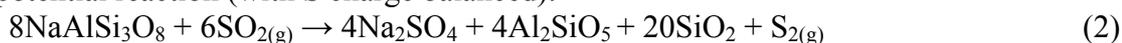
Evidence for gas-solid reactions is found throughout the solar system; for example, in early solar system condensates (e.g., Ebel and Grossman, 2000), secondary phases coating lunar pyroclastic glasses (Renggli et al., 2015) and on Venus (Fegley and Prinn, 1989). On Earth, the products of gas-solid reactions are documented in volcanic systems (Ayris et al., 2012), metalliferous mineral deposits (Henley et al., 2015), impact craters, and on dust or meteorites after passage through the atmosphere (e.g., Court and Sephton, 2011). To understand the chemical dynamics of gas-solid reactions, we are undertaking a large systematic experimental investigation and thermochemical modelling (Renggli, PhD in progress).

We previously showed that Ca-bearing materials – labradorite, feldspar glass and anorthosite (rock) – rapidly react to form anhydrite in a vertical gas-mixing furnace at 800 °C and 1 bar, with 20 sccm SO₂ (Henley et al., 2014). The experiments produce anhydrite as clusters of crystals that, in some cases, extend from the substrate forming precarious 'towers', fill cracks, displace minerals and create porosity. Anhydrite growth is sustained at high temperature by SO_{2(g)} adsorption and bonding through a δ- charge on oxygen to the Ca-bearing substrate. Ca migration to the substrate's surface creates a δ+ charge, and migration is accelerated by increased bond lengths, and in some cases phase separation. Significantly, SO₂ (S⁴⁺) disproportionates to form both oxidized sulfur (as anhydrite, S⁶⁺) and a reduced sulfur species (written as S₂, but could be a S* radical ion) following:



In nature, the reduced sulfur may react with gas phase Fe, Zn and Cu cluster compounds to form metal sulfides. This is observed at the scale of kilometres through the formation of co-existing anhydrite and sulphide in porphyry copper deposits on Earth (Henley et al., 2015).

We undertook further SO₂ reactions at 600 °C for 10 minutes with two endmember glass substrates: anorthite (An) and albite (Ab). The anorthite glasses produced a uniform fine-grained coating, whilst the albite glasses produced larger and more scattered crystals, in some cases with an annealed texture (triple point boundaries). The albite experiment was designed to test the potential reaction (with S charge balanced):



Chemical profiles of the reaction products were obtained using a Cameca 6f at Arizona State University. Analyses were made in a depth profiling mode through the coating into the glass on a rastered spot over a range of cycle lengths (depths). Charge compensation (offset) was automatically adjusted based on either ⁴⁰Ca or ²³Na. Analyses were performed both at low mass resolving power and also higher mass resolving powder that was sufficient to separate ³²S from ¹⁶O₂ and ⁴⁰Ca from ²⁴Mg¹⁶O.

Anorthite glass: The surface coating is enriched in Ca and S, consistent with forming CaSO₄ (reaction 1), with some Na and K also present. Ca shows a significant depletion below the glass surface and then increases to levels slightly above that of the substrate before returning to substrate levels; indicating significant diffusion. Sulfur decreases into the substrate. Several elements are highest just below the interface with the sulfate coating: Al, Si, are higher than the substrate and show no depletions at depth, consistent with Al and Si components forming below the interface following the mechanism in reaction 1. Sodium and K are significantly higher than the substrate glass and show slight depletions with depth before returning to substrate levels; suggesting that Na and K are migrating towards the surface.

Albite glass: The surface coating is enriched in Na and S, consistent with forming Na₂SO₄ (reaction 2), with some Ca also present. However, there is no enrichment in either Si or Al at or near the surface, instead concentrations of these elements gradually rises with depth in

the glass. This suggests that although albite reacts with SO₂ to form Na₂SO₄ in 10 minutes at 600 °C, the reaction is either incomplete or that reaction 2 is incorrect.

These short experiments demonstrate the rapid conversion of SO₂ and silicate substrates to sulfate coatings. The coating type and therefore chemical distribution depends on the availability of cations (Ca and Na) and their diffusion through the substrate. Ongoing experiments in the Ab-An-Di system aim to further illuminate the reaction mechanisms and kinetics.

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Distinguishing In Situ Stromatolite Biosignatures from Silicification and Dolomitisation using Short Wave, Visible-Near and Thermal Infrared Spectroscopy: A Mars Analogue Study.

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The search for life on Mars has relied on infrared spectroscopy from orbit and in-situ rovers to detect chemical signals akin to those found within stromatolites on Earth. Carbonate and hydrothermally altered mineral signals were detected on small rock units within the Nili Fossae region, and in small concentrations within the Gusev Crater region, but these minerals were likely a product of dolomitisation rather than an indicator of stromatolitic precipitation. To date, no studies have been undertaken to investigate the effect of weathering processes such as dolomitisation and silicification, which may obscure mineralogical signals that may be associated with stromatolites during *in-situ* spectroscopic detection. This study investigates the capacity that short-wave, visible-near, and thermal infrared spectrometers have in detecting minerals in the oldest known and heavily weathered stromatolites of the Pilbara Craton, Western Australia. A diversity of mineral signals in stromatolitic samples can be distinguished from dolomitisation and silicification in even the oldest rock units, when fresh surfaces are scanned multiple times by a short-wave infrared capable spectrometer, with a minimum spectral resolution of 7 nm. It is expected that this approach will significantly inform and direct the interpretation of carbonate signals within the heavily weathered Noachian rock units on Mars.

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. Copper deposit solution chemistry and its importance in in-situ recovery applications

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In-situ recovery (ISR) (also referred to as in-situ leaching or solution mining) refers to the recovery of valuable metals from ore deposits by the circulation of a fluid underground via a number of injection and recovery wells. The fluid contacts and dissolves value and gangue minerals, and metal contents are recovered from the fluid at the surface. ISR shows promise for the leaching of copper oxide minerals in fractured, permeable deposits; although no commercial processes exist currently for the in-situ recovery of copper, demonstration plants are being planned to utilise this technology (for copper recovery from oxide ores) in Arizona, USA. A greater challenge presents for the ISR of copper from sulfide minerals, because of the lower recoveries and difficulties in accessing mineral values. Besides the potential significant economic advantages associated with reduced mining and rehabilitation costs, an in-situ environment offers potential advantages for metal recoveries, such as improved reaction kinetics with increased subterranean temperatures. However, in-situ operation may present challenges related to lixiviant/oxidant system stabilities and leach product behaviour. We will discuss some of the advantages and challenges of the in-situ environment and their effect on solution chemistry for copper recovery by in-situ means.

Anomalous sulfur isotope signatures preserved in the Proterozoic Capricorn Orogen: linking fluid-driving tectonic processes and ore genesis at craton margins

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Proterozoic cratonic margins are structurally and magmatically complex areas of the Earth's crust, having undergone one or more orogenic cycles and consist of newly formed and/or reworked crust. The Paleoproterozoic Capricorn orogenic belt, situated between the Archean Pilbara and Yilgarn cratons, preserves mineral deposits and occurrences of various commodities (Au, Cu-Au, Pb-Zn) that are under-exposed and remain poorly understood. A majority of these mineral systems are sulfide-rich, utilizing sulfur for the transport and precipitation of metals. In situ and bulk multiple sulfur isotope systematics are a robust and powerful tool for fingerprinting spatially and temporally anomalous signatures found in the crust. When combined, $\delta^{34}\text{S}$ and $\Delta^{33}\text{S}$ have the potential to link physical processes of formation with the age of the sulfur-bearing mineral. To demonstrate how these two chemically conservative tracers can lend insight into tectonic processes related to recycling, transfer, mobility and focussing of sulfur we present a case study from the Proterozoic Prairie Downs Zn-Pb-Ag deposit situated at the margin between the Pilbara craton and Capricorn orogenic belt. At the Prairie Downs deposit, Proterozoic sulfide mineralization (including sphalerite, galena, chalcopyrite, pyrite, pyrrhotite) yield bulk and in situ multiple sulfur isotope data that clearly demonstrate mixing between underlying Archean banded iron formation ($\delta^{34}\text{S} = 2\text{‰}$; $\Delta^{33}\text{S} = 0.8\text{‰}$) and Proterozoic seawater ($\delta^{34}\text{S} = +12\text{‰}$; $\Delta^{33}\text{S} = 0\text{‰}$). Broadly, this study demonstrates how multiple sulfur isotope systematics can be used to map the localization of fluid and metal pathways to investigate the spatial and temporal evolution of lithospheric architecture, and better understand how sulfur can be transported from metal-endowed Archean cratons and accumulated in younger orogenic belts at their margins.

High Temperatures Recorded in Quartz-Anhydrite-Sulfide Veins from the Giant Grasberg Porphyry, Papua.

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Sulfur isotope analyses of coexisting sulfide-sulfate pairs from Grasberg veins yield temperatures ($>800^{\circ}\text{C}$) much higher than current models allow. Gas reactions will be presented that may explain such temperatures. However, quartz-hosted fluid inclusions from deep in the Grasberg System have been identified that homogenise by vapour disappearance at temperatures (up to 1300°C), well above the hottest measured fumaroles. These inclusions contain 20 – 40 vol.% vapour, three or more transparent crystals and one or two dark to opaque solid phases and less than 10 vol.% water. The largest crystal is usually halite while sylvite, anhydrite, hematite, pyrite and chalcopyrite have also been identified by Raman spectroscopy. Similar inclusions have been reported from porphyry copper occurrences in the Metaliferi Mountains, Romania (Pintea, 2014), the Zaldívar Deposit in northern Chile (Campos et al., 2006), and the Duobuza porphyry copper–gold deposit, Northern Tibet (Li et al., 2011) These inclusions may hold the key to porphyry formation but their role remains obscure.

These fluid inclusions may not be the result of trapped fluids. The high salt, sulphate and iron concentrations present in these inclusions may represent salt melts. One explanation is that salt melt was exsolved first, as homogeneous salt globules during the primary and secondary boiling processes, and was overprinted by fluid/melt-rock interaction during mafic magma mingling/mixing (e.g. Cloos, 2001). It is clear that the salt melt is a metal solvent solution because in the micro-thermometric runs, both the transparent salts and opaque minerals dissolved during heating and re-precipitated on cooling. An alternative explanation for these uncommonly (ridiculous?) high T-P trapping conditions of the salt melt inclusions could be related to post-entrapment modifications or heterogeneous trapping, as suggested by Lerchaumer and Audetat, 2012 (and references therein).

Overall, there are many lines of evidence that point to high temperature gases and melts in porphyry deposits. It is therefore timely that these high temperatures be re-evaluated in the context of current models.

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Speciation and thermodynamics of HCl in hydrothermal fluids up to 700 °C and 60 kbar by molecular simulations

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HCl is one of the most significant volatiles in the Earth's crust. It is well established that chloride activity and acidity (pH) play important roles in controlling the solubility of metals in aqueous hydrothermal fluids. Thus, quantifying the dissociation of HCl in aqueous solutions over a wide range of temperature and pressure is crucial for the understanding and numerical modeling of element mobility in hydrothermal fluids. However, significant discrepancies exist in the dissociation constants for HCl(aq) determined from various experimental studies, especially at low temperatures (up to 6 log units difference at 25 °C). Here we conducted ab initio molecular dynamics (MD) simulations to investigate the mechanism of HCl(aq) dissociation and to calculate the thermodynamic properties for the dissociation reaction at 25 to 700 °C, 1 bar to 60 kbar. Ab initio MD simulations for HCl(aq) were conducted using Car-Parrinello molecular dynamics, and thermodynamic integration was used to calculate the free energy of the dissociation reaction by performing series of distance-constrained ab initio MD simulations.

Our results predict that HCl(aq) tends to associate with increasing temperature, and dissociate with increasing pressure. In particular, HCl(aq) is highly dissociated at extremely high pressures, even at high temperatures (e.g., 60 kbar, 600-700 °C). At 25 °C, the calculated logKd values are close to the value recommended by IUPAC (International Union of Pure and Applied Chemistry). At 100-250 °C, our predictions are in reasonable agreement with some previous thermodynamic extrapolations (within 1-2 log units). At temperature of 300 – 700 °C, up to 5 kbar, the logKd values in this study show good agreement (within 1 log unit) with values derived from previous experimental and thermodynamic extrapolations. Hence, the MD simulations provide an independent check that helps to resolve the discrepancies of the dissociation constants for HCl(aq) from different experimental studies. We also provide new logKd data at extreme high pressure (up to 60 kbar), where experimental data are not available. The new thermodynamic properties based on the MD results allow prediction of the role of HCl in controlling element mobility in deep earth hydrothermal systems, down to ultra-high pressure metasomatism associated with subduction zone fluids.

Metal mobility in ore-forming fluids: insights from molecular simulation and geochemical modelling

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Metals are transported within the deep Earth at high pressure and temperature by fluids possessing a complex chemical makeup. The hydration and complexation of metals in hydrothermal fluids are key processes controlling the mobility of elements in the Earth's crust, leading to the formation of ore deposits from which the World's supply of Fe, Mn, Ag, Au, Pd, Cu, Zn, Co, Pb, U, Mo is mined. Therefore it is crucial to understand the nature and thermodynamic properties of metal complexes in hydrothermal fluids.

Ab initio molecular dynamics simulation provides a means to determine the nature and stabilities of metal complexes under conditions that are beyond experimental practicality. In the last five years, we have tested this approach on Cu^[1,2], Au^[2,3], Zn^[4,5], and Pd^[6] complexing in chloride- and sulfur-rich ore fluids under extreme P-T conditions and achieved encouraging agreements comparing with experiments. The simulations also helped to resolve some uncertainty in the interpretation of experimental data. Coupled with experimental studies, the simulations gave molecular-level insights into the chemical processes responsible for the formation of ore deposits and enable us to explore the P-T regimes where experiments are impractical. The numerical modelling of chemical reactions was also constructed to understand metal transport in the fluids and ore formation in the nature and man-made systems^[7].

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Virus-plankton interactions during long-term changes in Monsoon-controlled oxygen minimum zone (OMZ) expansion in the Arabian Sea

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Oxygen minimum zones (OMZ) occur when the respiratory oxygen demand during degradation of organic matter exceeds oxygen supply in the ocean. Rise in the sea surface temperature results in the OMZ expansion and is predicted to continue due to global warming^{1,2}. The most extensive OMZ is observed in the northern Arabian Sea where intensity of the OMZ is largely triggered by Monsoon-influenced surface-water productivity^{3,4}. The sedimentary record from the Arabian Sea offers a long-term time-series of past changes in OMZ expansion due to natural climate variability^{5,6}. Information on how OMZ intensity affects marine planktonic and benthic communities is mainly based on recent observations and modelling experiments⁷. Such models also do not account for the role of viruses in causing mortality and regulating marine food webs. As viruses and the majority of planktonic taxa lack diagnostic features preserved upon fossilization, we are applying palaeontological-independent methods (i.e., ancient DNA stratigraphy⁸ and organic and isotope geochemistry⁹) to reconstruct ecosystem-climate and ecosystem-virus interactions in the Monsoon-impacted NE Arabian Sea. For this analyses a 13 m-long sediment core from the classical OMZ coring location off the Indus Canyon spanning key climate intervals of the last 52,000 years has been collected. Here we present preliminary data that shows long-term effects of OMZ variability on changes in the distribution of oceanic planktonic and benthic ecosystems and to what extent these ecosystems were controlled by paleoenvironmental conditions vs. viral stress.

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Magnesite forms from CO₂ released during decomposition of hydrated Mg-carbonate phases

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Carbon mineralisation is a promising technology for combating global warming. It enhances natural weathering processes to promote CO₂ capture within the structures of carbonate minerals. Although environmentally benign magnesite (MgCO₃) is highly stable over geologic time periods, and ideal for long-term storage of atmospheric and industrial CO₂, its precipitation from solution is kinetically inhibited at Earth's surface temperatures. To optimise carbon mineralisation as a strategy to mitigate CO₂ pollution, a fundamental understanding of MgCO₃ formation pathways is required. This includes exploring the stepwise decomposition of hydrated Mg-carbonate precursor phases, such as nesquehonite (MgCO₃·3H₂O) and hydromagnesite [Mg₅(CO₃)₄(OH)·4H₂O], to MgCO₃ under a range of environmental conditions.

In this study we couple *in-situ* X-ray diffraction (XRD) with thermogravimetry and differential scanning calorimetry (TG-DSC) to investigate MgCO₃ formation during thermal decomposition (30–600°C) of hydrated Mg-carbonates under varied CO₂ partial pressures. The structural collapse of nesquehonite and hydromagnesite produces a poorly-ordered solid phase with 70 and 57 % mass loss respectively. Interestingly, an external CO₂ source was required for MgCO₃ to crystallise from this near-amorphous decomposition product in open-system conditions, while in a closed system MgCO₃ precipitates in the absence of an external CO₂ source. This suggests that CO₂ generated during the decomposition of hydrated Mg-carbonate minerals can be reincorporated back into the solid mass to be trapped in the MgCO₃ crystal structure. This provides important mechanistic information for tailoring CO₂ capture to promote formation of stable carbonate products for long-term CO₂ storage.

Hydrothermal chloritization processes of biotite in the Toki granite, Central Japan: Singular value decomposition analysis of reaction relations and the temporal variations in fluid compositions

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Biotite chloritization process in the Toki granite, Central Japan, shows temporal variations in chemical characteristics of hydrothermal fluid responsible for the chloritization during the subsolidus cooling of the pluton. Singular value decomposition (SVD) analysis was employed to survey the reaction relations in the chloritization systematically. The condition of volume constant replacement was incorporated into the analysis by adding a row consisting of molar volumes of minerals into the composition matrix used in the SVD analysis. In the nine component system Si - Ti - Al - Fe - Mn - Mg - Ca - Na - K, the closure conditions for arbitrary components and the solid volume were searched for eight sets of reactant (biotite) and products (chlorite and associated minerals). The resultant eight reactions indicate the temporal variations of chemical characteristics of hydrothermal fluid; the progress of chloritization results in gradual increase of Si^{4+} , K^+ , and Cl^- and gradual decrease of Ca^{2+} and Na^+ with temperature decrease. The variations in physicochemical parameters of the hydrothermal fluid are also observed such as a gradual decrease of pH and a gradual increase of redox potential as progress of chloritization. The chloritization comprises two different mechanisms: chlorite formation mechanism (CF) 1 and 2. The CF 1 mechanism is characterized by small volume decrease and inflow of cations such as Al^{3+} , Fe^{3+} , Mn^{2+} , and Mg^{2+} from the hydrothermal fluid, whereas the CF mechanism 2 is by large volume decrease and large outflow of cations. Chlorite produced with CF 1 mechanism dominates over that of CF 2 mechanism. The biotite chloritization and resultant temporal variations of chemical and physicochemical characteristics in hydrothermal fluid triggered for the successive dissolution - precipitation process of a granitic rock (Yuguchi et al., 2015).

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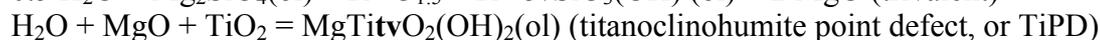
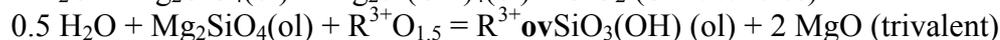
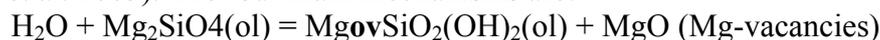
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Problems caused by multiple substitution mechanisms of trace elements in crystals

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In principle, the substitution of a particular trace element into a mineral may not be limited to one mechanism. Good examples are the substitution of H in Nominally Anhydrous Minerals, where infra-red spectroscopy has shown that many mechanisms co-exist in olivine (Berry et al. 2005). The four main mechanisms are:



where **ov** and **tv** stand for octahedral and tetrahedral cation-site vacancies, respectively. The H concentrations controlled by each of these four equilibria will respond differently to temperature and pressure, and to chemical environment, specifically, to the activity of silica (a_{SiO_2}), and the availability of trivalent cations and Ti. Importantly, the stoichiometry of the substitution mechanisms implies that they should also respond differently to $f(\text{H}_2\text{O})$. Experiments conducted at high $f(\text{H}_2\text{O})$ may be addressing different substitution mechanisms to those important in natural situations where $f(\text{H}_2\text{O})$ is low. The different substitution mechanisms lead to differing diffusion rates (Padrón-Navarta et al. 2014), causing asymmetry in rates of hydration compared to dehydration, and potentially resulting in misleading estimates of original H contents in dehydroxylated olivines. This phenomenon has been documented in olivine from a mantle xenolith, where it was shown that H incorporation was a metastable process controlled by the availability of suitable sites for substitution (Tollan et al. 2014). This completely obscures any quantitative connection of H contents with $f(\text{H}_2\text{O})$.

Problems due to multiple substitution mechanisms are also demonstrated by experiments to study the diffusion of Al into synthetic forsterite, with $a_{\text{R}_{\text{SiO}_2}\text{R}}$, $a_{\text{R}_{\text{MgO}}\text{R}}$ and $a_{\text{R}_{\text{Al}_2\text{O}_3}\text{R}}$ buffered (Zhukova et al., in preparation). The main substitution mechanism of Al in olivine, from previous equilibrium studies, is the coupled substitution of 2 Al for Mg + Si, giving the stoichiometry MgAl_2O_4 ; but diffusion of Al by this mechanism is likely limited to unobservably small distances in the experiments by the extremely slow diffusion of tetrahedrally coordinated Al^{3+} , by analogy with the slow diffusivities of Si^{4+} and P^{5+} . Instead, the experiments show fast diffusion of low concentrations of Al. The apparent interface concentrations of Al, obtained by extrapolating the diffusion profiles to the crystal/buffer interface, were only a fraction of those expected at equilibrium, and varied among the differing buffer assemblages according to $(a_{\text{Al}_2\text{O}_3})^{1/2}$ and $(a_{\text{SiO}_2})^{3/4}$, pointing to the substitution of Al by a secondary mechanism involving the octahedral-site, vacancy-coupled component $\text{Al}^{3+}_{4/3}\text{vac}_{2/3}\text{SiO}_4$. In this case, neglect of this secondary mechanism would produce relatively minor errors in inferring equilibrium temperatures from Al-in-olivine geothermometry, but orders-of-magnitude errors in any inference from transport phenomena like diffusion.

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Understanding natural analogues of mineral carbonation to inform the development of industrial CO₂ storage

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Natural examples of mineral carbonation, the conversion of Mg-silicate to Mg-carbonate and silica, are common in ultramafic rocks throughout the world and reflect the thermodynamic instability of Mg-silicate minerals in the presence of CO₂. However, the industrial implementation of mineral carbonation as a means of safely storing CO₂ in the form of carbonate minerals is hampered by slow kinetics and the cost associated with heat-activation and carbonation reactors at high pressures and temperatures^[1,2].

In the Great Serpentine Belt, New South Wales, Australia, natural carbonation occurs in the form of weathering-derived magnesite deposits, carbonate crust on ultramafic mine tailings and hydrothermal silica-carbonate alteration. At Attunga, low temperature (10 to 50 °C) meteoric waters have altered serpentinite to typical cauliflower-like magnesite nodules and veins, usually accompanied by late stage amorphous silica. Consistently low $\delta^{13}\text{C}$ and small radiocarbon contents point to overlying soil as the source of carbon in the magnesite^[3]. Textural observations suggest carbonation progressed via fractures and porosity created by weathering of the host-rock, producing intermediate phases with decreased Mg/Si ratios in the process. For the mine tailings of the Woodsreef Asbestos Mine a relationship between textures, mineral content and isotopic fingerprint indicates that carbonate crusts covering the tailings formed from evaporating meteoric fluids, which absorbed CO₂ directly from the atmosphere^[4]. Rate estimates based on the carbonate content and time since closure of the mine indicate that carbonation of the mine tailings proceeds at much higher rates than background uptake of CO₂ by chemical weathering. Lensoid masses of silica-carbonate rock and magnesite veins at the Piedmont magnesite deposit formed by hypogene replacement of serpentinite at temperatures between 165 and 225 °C^[5]. The magnesite is usually Fe-rich, indicating reducing conditions during formation, and often accompanied by dolomite and quartz with alteration fluids ascribed to hydrothermal and magmatic sources^[5].

Each of the above processes created a distinct set of textures, minerals and isotope-geochemical signatures which reflect conditions and mechanisms favourable for carbonation, but also the associated limitations that need to be overcome for industrial implementation. A better understanding of natural analogues to mineral carbonation informs the development of accelerated carbonation processes for large scale industrial storage of CO₂ in carbonate minerals.

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Microstructural Evidence for Copper Remobilisation in IOCG Deposits

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Mineral deposit formation requires transport, concentration, deposition and preservation of anomalous quantities of otherwise rare elements. As enriched fluids flow through the crust their often disequilibrium character, with respect to the host rocks, leads to significant fluid-rock interaction, deposition and alteration of the surrounding rocks. However, continued fluid flow can also lead to removal of existing mineralisation. In conventional studies of mineral deposits, less attention is paid to the evidence for this remobilisation and removal but it can potentially make or break an exploration target.

The Emmie Bluff prospect in the Olympic Dam District of South Australia contains economically significant amounts of Fe-Oxide, with lesser Cu and Au mineralisation, hosted in the metasedimentary rocks of the Wallaroo Group. Fe-Cu-Au mineralisation is associated with hematite-chlorite-sericite alteration with chalcopyrite commonly replacing pre-existing pyrite. With the use of cutting-edge Synchrotron X-ray Fluorescence Microscopy and scanning electron microscopy we shown for the first time that subeconomic IOCG mineralisation in the Olympic Dam district was affected by a late fluid event, which resulted in partial dissolution of Cu mineralisation and transport of Cu in the form of chloride complexes.

The porous chlorite-sericite matrix associated with the late alteration of chalcopyrite hosts a Cu-Cl-OH phase previously undescribed in IOCG rocks, which was identified as atacamite, $\text{Cu}_2\text{Cl}(\text{OH})_3$. Thermodynamic modelling shows that atacamite is produced during dissolution of chalcopyrite by an oxidized, Cl-bearing fluid. An acidic environment is produced within millimetres of the chalcopyrite grains during oxidation driving chlorite recrystallization. The recrystallization is recorded by incorporation of Zn from the chalcopyrite and Mn from the fluid into the newly formed chlorite. Late removal of Cu mineralisation has been arrested at Emmie Bluff but the trace element halo in the chlorite left behind has the potential to be used to track late-stage fluid pathways in areas of protracted fluid-flow.

Chemical and thermal evolution of subduction zones: Insights from trace-element distribution and Lu–Hf geochronology in HP oceanic rocks, Halilbağı Complex (Central Anatolia)

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High-pressure/low-temperature (HP/LT) oceanic rocks exposed at the Earth's surface record a wide range of processes taking place in subduction zones. In the last few years, natural and modelled zoning patterns of HP/LT garnet have been used to investigate fluid production and circulation, and element recycling in subduction zones. However, whereas lawsonite–garnet blueschist and lawsonite eclogite are predicted to have been widely formed in Phanerozoic subduction zones, surprisingly still little is known about the distribution of trace elements in lawsonite- and garnet-bearing parageneses. The same applies to the thermal history of subduction-channel complexes, though it plays a crucial role in the chemical- and mechanical evolution of the plate interface.

We inspected the distribution of trace elements (mainly REE+Y) and performed Lu–Hf geochronology on garnet- and/or lawsonite-bearing mafic samples from the Halilbağı subduction complex, Central Anatolia, to gain insight into the linkage between the chemical and thermal histories of the subduction channel. Samples include pristine lawsonite blueschist, lawsonite–epidote (epidote)–omphacite blueschist, lawsonite–epidote–glaucofan eclogite, epidote eclogite, and garnet amphibolite (from the overlying sub-ophiolitic metamorphic sole).

Our trace element analysis reveals that, with respect to chondrite, lawsonite is typically enriched in medium rare earth elements (REE) over light- and heavy REE. Lawsonite that grew in absence of garnet or epidote have higher heavy- or light REE concentrations in their cores, respectively. Garnet has heavy REE–rich cores, but also displays a second, rimward enrichment in medium- and heavy REE associated with the replacement of titanite by rutile. Rare earth element partitioning coefficients (K_D) were calculated between lawsonite and garnet in cases where a textural equilibrium was unambiguous. The $K_D(\text{lawsonite/garnet})$ values are generally 10^{-2} – 10^{-1} but up to ~ 1 for prograde lawsonite–garnet associations.

Lutetium–hafnium geochronology was carried out on 3–4 garnet and 2–3 lawsonite separates of each sample. In each sample, 2–4 garnet batches yielded similar two-point matrix–garnet dates whereas one batch, if any, yielded an older date. The outliers consistently have higher $^{176}\text{Lu}/^{177}\text{Hf}$ and $^{176}\text{Hf}/^{177}\text{Hf}$ ratios than the other batches from the same sample, and no correlation exists between Hf element concentration and isotopic composition. We interpret the scatter to be geologically meaningful, reflecting minimal garnet growth intervals. In addition, lawsonite fractions from three samples were analysed for Lu–Hf geochronology. For prograde lawsonite blueschist, two-point matrix–lawsonite isochrons yielded dates from 83.6 ± 2.0 to 77.5 ± 2.5 Ma, which are distinctly younger than garnet dates for this sample (89–86 Ma). Two-point matrix–lawsonite isochrons calculated for the two other samples (lawsonite–epidote blueschist/eclogite) yielded geologically inconsistent dates (between 49.7 ± 2.5 Ma and 12.3 ± 3.4 Ma).

The metamorphic evolution of the samples may be interpreted in the light of the petrological observations, Lu–Hf garnet dates, and REE distribution patterns in garnet. Our results indicate that LP/HT metamorphism at the bottom of the ophiolite took place at ca. 109 Ma, “warm” HP metamorphism (epidote eclogite facies) culminated at ~ 93 Ma, and “cold” HP metamorphism (prograde and retrograde lawsonite blueschist facies) followed from 89 to 86 Ma. Garnet dates thus reveal the progressive, active cooling of a former subduction interface,

from its inception to a steady thermal state over ca. 15–20 Myr. Long-lived thermal equilibration of the subduction interface suggests that the thermal structure of many modern subduction zones might be transient, and not precisely reflect the slab parameters.

Low temperature magnesite formation: Implications for carbon sequestration

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Magnesite (MgCO₃) deposits and mineralization pathways are of renewed interest in the context of *ex situ* and *in situ* CO₂ sequestration strategies.¹ The kinetic inhibition of magnesite precipitation at low temperature has hindered our understanding of natural magnesite formation and restricted mineral carbonation technologies that store CO₂ within magnesite to costly high temperature and pressure systems. Thus, there is a need to better understand the fundamental geochemical processes of low temperature magnesite formation over long timescales and devise novel reaction pathways for accelerating magnesite formation. Hydromagnesite-magnesite playas host a complex assemblage of carbonate minerals including abundant magnesite, up to 86 wt.%.² Within the playas, there is a propensity for hydrated Mg-carbonate minerals to transform to less hydrated, more stable forms (lansfordite → nesquehonite → dypingite → hydromagnesite);³ however, stable, radiogenic, and clumped isotope⁴ data in concert with electron microscopy demonstrate that magnesite forms by direct precipitation from aqueous solution in the shallow subsurface at low temperature (~3-10 °C). Magnesite particle size distributions, mineral abundance data, and estimated precipitation rates (25 °C)⁵⁻⁷ suggest that magnesite formation in the playas is nucleation limited with long induction times. Magnesite crystal morphology varies with depth indicating variable crystal growth mechanisms and precipitation rates. We estimate rates of magnesite formation (nucleation + crystal growth) in the range of 10⁻¹⁸ to 10⁻¹⁶ mol/cm²/s. In microcosm experiments aimed at accelerating magnesite formation, carboxylated polystyrene microspheres caused desolvation of Mg²⁺ ions, minimizing the rate limitation and inducing magnesite precipitation at room temperature over 72 days. In comparison to natural magnesite formation, this is an acceleration of several orders of magnitude without requiring energy input. Incorporating surfaces with carboxylated surfaces into *ex situ* mineral carbonation processes and the use of such ligands for deep geologic CO₂ storage may offer novel and economically viable strategies for permanent carbon storage.

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Fluid induced microstructures in granulites from the Reynolds Range, central Australia.

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Fluids play a major role in the evolution of the Earth's crust, where fluids can change the physical properties of rocks, facilitate transport of heat and matter, and drive metamorphic reactions. How and whether fluids affected shear zones present in intraplate orogens and shear zones in general is of interest in order to understand the relation of fluid-driven rock weakening and deformation. Understanding fluid-rock interaction is of special interest in the tectonic reworking of continental interiors. Here we present preliminary observations from the Aileron Shear Zone (ASZ) a reworked major crustal-scale fault in the Reynolds Range, central Australia, last reactivated during the Palaeozoic Alice Springs Orogen (ASO).

This study focuses on the effects of fluids on the mineralogy and mineral chemistry of deep crustal rocks collected from a transect running through the ASZ. The ASZ is thought to have been of major importance during exhumation of the ASO. It exhumes a partly retrogressed suite of granulite facies meta-pelitic and felsic gneisses. Hydration reactions associated with retrogression resulted in the partial replacement of orthopyroxene and K-feldspar by biotite, magnetite and quartz. The development of myrmekites in association of epidote mineralogy is also attributed to hydration contemporaneous with deformation.

In undeformed samples, a (hydration) reaction between orthopyroxene ($\text{En}_{56}\text{Fe}_{44}$) and K-feldspar (Or_{87}) produced a corona of quartz and biotite ($\text{Phl}_{70}\text{Ann}_{30}$), opx boundary sub-parallel rims of magnetite and biotite \pm quartz. Deformed samples show various types of dynamic recrystallization textures changing in mechanism from subgrain rotation to grain boundary migration. Dynamic recrystallization of quartz can be recognized in a fine grained foam texture of quartz defining the foliation together with biotite. With increasing strain, the mineralogy is dominated by quartz and minor biotite.

The presence of fluid-driven mineral replacement reactions in undeformed samples suggests that hydration predates shearing and exhumation, and furthermore, that strain may have been localized in areas of intense hydration and rock weakening. Retrograde reactions and myrmekite textures suggest the availability of a silica-saturated fluid. Additional mass-balance calculations will be applied to constrain the composition of the alteration fluid, and to gain further insight into mass-transport related to rock weakening and shear localization.

The creation and healing of porosity in Coupled Dissolution- Reprecipitation Replacement Reactions

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The creation of porosity during fluid-mediated coupled dissolution reprecipitation reactions seems to be universal and essential feature of these processes. It plays an essential role in the mass transport between the bulk fluid and the reaction interface through the product mineral. Without porosity (or more correctly permeability) the reaction will stall, as we see in the case of armouring or passivating layers. The generation of porosity and healing of porosity has been studied in some details such as the replacement of KBr by KCl (Putnis et al 2005, Raufaste et al 2011). We report the results of long term studies on the healing of the porosity and the formation of fluid inclusions. Such replacement systems allow us to probe the relationship between fluid inclusion composition and the bulk fluid composition and thus probe the validity of fluid inclusion studies in minerals. The driving force for generation of porosity and its coarseness do not seem to be well understood. On the other hand the healing process seems to be driven by a reduction in surface energy which drives recrystallization. It appears that this recrystallization can drive and accelerate the other mineralogical processes such as the coarsening of exsolution. In the bornite-digenite system (Cu_5FeS_4 - Cu_8S_5) the coarsening for exsolution has been found to be some 2500 times faster, than the equivalent solid state process.

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Control of silicate weathering processes at the mineral-fluid interface

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The mechanism of surface coating formation (the so-called surface altered layers [SALs] or leached layers) during weathering of silicate minerals hinges on understanding the saturation state of the fluid at the dissolving mineral surface¹. In-situ data on the evolution of the interfacial fluid composition during dissolution of wollastonite (CaSiO₃), obtained using interferometry and micro pH and ion-selective electrodes is already published^{2,3}. New experimental results obtained from the dissolution of labradorite will be presented. Steep concentration gradients develop at the mineral interface as soon as it makes contact with an aqueous solution. This interfacial fluid becomes supersaturated with respect to amorphous silica that forms a surface coating, limiting fluid access to the mineral surface and hence affecting the dissolution rate. The thickness of the supersaturated zone and the precipitated layer depends on the relative rates of mass transport and surface reaction in the system. This effect could contribute to the discrepancy between dissolution rates measured in the field and in the laboratory. As well, our results have implications for predictions of silicate weathering rates and hence climate evolution, as different assumptions on dissolution mechanisms affect calculations on CO₂ drawdown during weathering and consequent effects on estimates of global mean temperatures.

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Tracing geochemical mobility, alteration and mineralisation with LA-ICP-MS mapping

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Laser ablation–inductively coupled plasma–mass spectrometry (LA-ICP-MS) is conventionally used to quantify major and trace element (wt%–ppb) content in a wide variety of geological materials via spot analysis. However, its utility as an imaging tool has recently emerged to allow 2D mapping with excellent detection limits (ppb) over a wide isotopic range (⁷Li to ²³⁸U), with minimal sample preparation required. This is achieved by rastering of the focused laser beam in linear transects, which are then stitched together by post-acquisition processing to form a quantified image of the element distribution. Large suites of isotopes can be collected concurrently, including multiple isotopes of the same element, providing access to substantially increased geochemical information from analysed samples.

We outline a technique for the routine acquisition of high-resolution trace and rare earth element (REE) maps by LA-ICP-MS, and introduce an extension of the software package *XMapTools* for rapid processing of LA-ICP-MS data in order to visualise and interpret compositional zoning patterns. These methods form the basis for investigating the mechanisms controlling geochemical mobility, alteration and mineralisation. Along with other case studies presented, a key example is given from the Peaked Hill shear zone, Reynolds Range, central Australia, which exhibits contrasting trace element distributions in garnet that can be linked to a detailed sequence of growth and dissolution events. Trace element mapping is employed to place garnet evolution in a specific paragenetic context and derive absolute age information by integration with existing U–Pb monazite and Sm–Nd garnet geochronology. Ultimately, the remarkable preservation of original growth zoning and its subtle modification by subsequent re-equilibration is used to ‘see through’ multiple superimposed events, thereby revealing a previously obscure petrological and temporal record of metamorphism, metasomatism and deformation.

Continental-scale correlation of regolith trace elements with iron

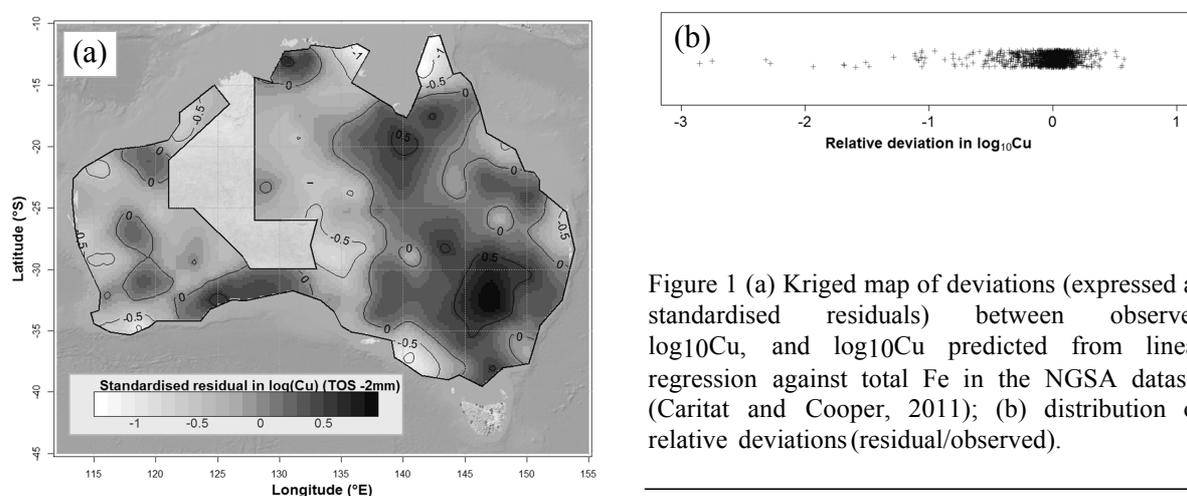
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The concentrations and behaviour of trace elements in regolith materials such as soils represents important information for mineral exploration, soil pollution, and micronutrient supply to biota. While it is common knowledge that many trace elements in unpolluted soils occur in association with iron mineral phases (McQueen, 2009), particularly crystalline iron oxides (see Li *et al.* 2003), the extent and predictive capability of any such relationships have received less attention (*e.g.* Hamon *et al.* 2004).

Public domain regolith geochemical data from Australia (Caritat & Cooper 2011), USA (Grossman *et al.* 2004), and Europe (Salminen *et al.* 2005) were used to assess continental-scale relationships between total concentrations of a range of trace elements and iron in soils and surface sediments. Statistical analyses used R (R Core Team, 2015) and the ‘geoR’ package (Ribeiro and Diggle, 2015) was used to investigate and map spatial relationships.

Robust regression and multivariate (PCA, LDA) analyses identified the existence of significant relationships between a range of elements and Fe. Across all three continental datasets, iron was a significant and accurate predictor of the concentrations of several trace elements, including As, Ce, Co, Cr, Cu, Mn, Ni, Pb, and Zn (see example for Cu in Figure 1). In multiple regression models following stepwise refinement, Fe was commonly the major element with the greatest contribution to predicted trace element concentrations.



The consistency and accuracy of prediction afforded by many of the relationships found is strong additional support for the global role of iron phases in retaining an extensive suite of trace elements in regolith materials. In addition, these apparently globally consistent relationships represent a variable baseline against which more rational assessments can be made of (a) soil contamination, and (b) signatures of concealed mineralisation. Contamination and mineralisation can be inferred from offset regression relationships (see Morgan *et al.* 2012), or by analysis of regression residuals (*cf.* Figure 1).

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Geobiology in Exploration: Using Bioindicators and Biosensor in Australia

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The discovery of new world-class mineral deposits is becoming increasingly difficult, because worldwide many un(der)explored regions are covered by thick layers of *in situ* and/or transported weathered materials. An on-going revolution in molecular biology now offers the prospect of using the microbial signatures and biomolecule to explore for underlying deposits [1].

Weathered materials (soils, sediments and deeper regolith materials) are highly active zones of the environment hosting large microbial communities of commonly $>10^9$ cells g^{-1} . These communities are primary drivers of C-, N-, S- and P- cycling. They also drive metal cycles, because many metals are used as micro-nutrients and for energy generation. If contents of mobile heavy metals, e.g., Ag, Cu, Au, Ni, Pb, U and Zn, exceed certain thresholds, metals become cytotoxic. This changes the microbial community composition; while some species thrive others decline. Generally, thriving species display increased capability in dealing with metal toxicity by expressing more genetic metal-resistance determinants. This allows them to detoxify their immediate cell environment, and is commonly also linked to the immobilisation of metals via the formation intra- and extra-cellular biominerals.

Modern molecular techniques have enabled the generation of highly detailed profiles of composition and functions of microorganisms inhabiting these metal-anomalous zones, as well as understanding of the genetic pathways that enable organisms to survive in metal enriched environments. Using advanced statistical modelling allows us to link the genetic profiles to geochemical/geological parameters of underlying deposits. In a number of recent Australian studies of soils overlying VMS-, Au-, Pt-, Cu-Au-U- and base deposits microbial community compositions and abundances of metal-resistance genes were closely linked to the underlying mineralisation, demonstrating that pinpointing underlying ore bodies is feasible using these techniques [2, 3, 4]. To provide a dataset against which these anomalies can be compared the Biomes of Australian Soil Environments (BASE) project is currently underway, with 1400 sites across the Australian continent currently in the database. As this database will keep growing and the price of sequencing will decrease even further, these new geobiological tools using easy to obtain surface soils/sediments samples, will provide critical advantages for exploration in covered terrains.

Another approach aims to alleviate a major problem faced by the Au industry. Here the detection of new gold deposits is extremely rare due to the many technical challenges faced during the exploration stage. One reason for this is the large amount of surface sampling and drilling required to find a single world-class ore deposit, which in Australia amounts to approximately 10,000 kilometres of drilling. Each drill hole needs to be sampled multiple times to determine whether the gold is present and delineate if the ore body is economically viable. A main cost and time factor while surface sampling or drilling is the lack of a suitable methodology for detection gold down to the parts-per-trillion/parts-per-billion levels in the field. Currently the only analytical techniques that deliver this accuracy are laboratory based, and these require the exploration sample (e.g., soil, water, rock or plant materials) to be transported from the drilling/sampling localities to a laboratory equipped with suitable

analytical facilities. This is a particularly time consuming and costly task for samples from remote localities in Australia or from developing countries, where many gold exploration and mining companies are strongly engaged. Even in less remote locations, this costs companies time, money and resources, which could be better spent if a field based technique existed.

Therefore, we have developed the capacity to design an ultrasensitive handheld biosensor, which will enable field-based analyses of gold that will complement existing technologies and provide additional information to narrow-down targeting in green and brownfields exploration. The development of biosensors for gold exploration will mean that mineral explorers will be able to instantly obtain information on gold concentrations in samples on site, rather than waiting weeks for laboratory analyses. In addition, biosensor devices may aid in mineral processing, where real-time in-line analysis of specific mineral components of ores can be determined. This enables real-time fine-tuning of the metallurgical process, which will improve recovery and decrease costs.

In conclusion, bioindicators and biosensors will provide a way forward for exploration by tapping into a previously unused/underutilized knowledge.

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Transport of gaseous metals and deposition of metal sulfides and salts in lunar fire fountain eruptions

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Transport of metals in volcanic gases on the Moon differs greatly from their transport on the Earth because metal speciation depends largely on gas composition, temperature, pressure and oxidation state. We present a new thermochemical model for the major and trace element composition of lunar volcanic gas during pyroclastic eruptions of picritic magmas (200-1500 °C, 10^{-9} - 10^3 bar).

Using published volatile component concentrations in picritic lunar glasses, we have calculated the speciation of major elements (H, O, C, Cl, S and F) in the coexisting volcanic gas as the eruption proceeds. The most abundant gases are CO, H₂, H₂S, COS and S₂, with a transition from predominantly triatomic gases to diatomic gases with increasing temperatures and decreasing pressures.

The Cl and S contents of the gas strongly control metal transport because their concentrations respectively control metal chloride gas species and sulfide gas and solid species. We calculate the speciation of trace metals (Zn, Ga, Cu, Pb, Ni, Fe) in the gas phase, and also the pressure and temperature conditions at which solids form from the gas. Chloride gas species promote the transport of metals. During initial stages of the eruption, elemental metal gases are the dominant metal species. As the gas cools, chloride and sulfide species become more abundant. Our chemical speciation model is applied to a lunar pyroclastic eruption model with isentropic gas decompression. The relative abundances of the deposited metal-bearing solids with distance from the vent are predicted for slow cooling rates (< 5 °C/s).

Biogeochemical controls on invertebrate biodiversity and trophic relationships within calcrete aquifers in the Yilgarn Craton, Western Australia.

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Subterranean invertebrate fauna occur in a range of near-surface geological formations including non-karst (e.g. alluvial deposits, sandstones and banded ironstone formations) and karst (calcrete and limestone) systems (EPA, 2012). Subterranean fauna tend towards high biodiversity and short-range endemism, meaning that taxa can be restricted to a single aquifer system. The localisation of taxa means that relatively small and geographically restricted environmental changes, including water extraction for mining or agriculture, single pollution events, or climate fluctuations, can result in extinction.

Western Australia hosts over 4000 species of subterranean fauna, including forty species known to be under immediate threat (EPA, 2012). As well as their intrinsic ecological value, these species are believed to be refugial survivors of the mesic environments of Australia prior to continental aridification (Hancock et al., 2005; EPA, 2012). The impact of the potential loss of these ecosystems is significant, as subterranean fauna provide ecosystem services including the maintenance of groundwater quality; their management is, therefore, of direct social and economic importance (EPA 2012)

The composition and life-modes of subterranean fauna are directly influenced by the geology and hydrology of the systems they have evolved in. Geological discontinuity of aquifers can restrict lateral movement, while hydrological and chemical stratification can influence vertical ranges (Humphreys, 2009). Chemical parameters within subterranean environments are also crucial in regulating the associated ecosystem, including the low levels of nutrients and carbon, pH, oxygen levels, salinity and the availability of trace elements (Schmidt et al., 2007; Humphreys, 2009).

The Yilgarn calcretes sit at the surface of one of Australia's most ancient landmasses, the Yilgarn Craton, a continental mass of igneous and metamorphic rocks, rich in elemental deposits such as gold, and supporting an active mining industry. The calcretes are secondary sedimentary deposits formed by the precipitation of calcium carbonate rocks from shallow groundwaters along the paths of palaeodrainage channels (Leys et al. 2003). The systems sit upstream of salt lakes and so have a strong biogeochemical gradient that is comparable to estuarine systems (Humphreys et al., 2009). Due to the isolation of each calcrete, some ecosystems may have been self-contained for over 5 million years (Humphreys et al., 2009). These systems display the highest level of biodiversity in the world for some fauna types (EPA, 2012), and their biogeochemistry and age allows marine or near-marine tolerant species to co-exist in close proximity to freshwater organisms. However, although these calcrete ecosystems are quite well-studied in terms of taxonomic identification, many of the functional aspects of the ecosystem, such as the trophic relationships and interaction with some physiochemical parameters of the groundwater are poorly understood. It is important that this knowledge gap is rectified as these systems are vulnerable to the impact of climate fluctuations and local mining operations.

The primary focus of this project will be on identifying the energy sources within the ecosystem, and characterising the resultant trophic web. To achieve this, $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ compound specific stable isotope analysis will be applied to amino acids recovered from chitinous tissue of invertebrates. $\delta^{13}\text{C}$ of essential amino acids will allow firm identification of the base carbon source in the system (plant-based, microbially recycled, chemosynthetic etc.), while $\delta^{15}\text{N}$ of different amino acids will allow separation of a "source" and "trophic" signal (Steffan et al., 2013; Ishikawa et al., 2014), providing a quantification of each organism's position in the trophic chain. These analyses can

be complemented by isotopic analyses of other biological molecules to better understand metabolic processes in the trophic system (Grice et al., 1998), and direct assessment of groundwater physiochemical parameters (age, nutrients, carbon content, hydrological pathway, trace elements, pH, salinity, redox etc) to place the ecosystem data within their hydrogeological context.

These geochemical analyses will allow us to accurately characterize biogeochemical interactions within the subterranean ecosystems found in WA groundwater, with the research being initiated in the Yilgarn, but being further applied to geologically very different sites in the Pilbara. This geochemical data framework, which will be integrated with taxonomic, microbiological and genetic analyses undertaken by project collaborators, will then usefully inform future management of these systems for both ecological and social benefit.

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Connecting geochemistry and microbiology in ancient, saline environments at extremes of pH: insights from Western Australian salt lakes

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Isolated inland saline lakes which display extremes of pH over short distances have developed in the ancient (*ca* 3000 Ma) and stable Yilgarn Craton in Western Australia. The causes of acidification plaguing this (and other) deeply-weathered landscapes are poorly understood. Microorganisms play critical roles in the acidification of geochemically analogous mining environments, but have not been investigated in saline waterways. Additionally, the stability and antiquity of deeply weathered, highly saline landscapes and waterways provide an ideal environment in which repositories of novel microbial diversity (species and functions) may develop, which is of particular interest for bioleaching applications. We present the results of a preliminary study identifying the major drivers of microbial community composition across Western Australian salt lakes at extremes of pH, and link these drivers to iron- and sulfur-oxidising activity within communities to evaluate the potential for biologically-driven acidification of saline systems. Environmental tolerances of culturable iron- and sulfur-oxidisers will also be benchmarked against those currently used in bioleaching.

The End Cretaceous Mass Extinction Event - Recovery and Evolution of Life

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The End-Cretaceous Mass Extinction Event was one of the five largest mass extinction events in the Phanerozoic (Wiese and Reitner, 2011) and the only one proven to be associated with a meteorite impact (e.g. Hildebrand, 1991; Schulte et al., 2010). The impact crater at Chicxulub in Mexico is the largest terrestrial crater with a peak ring and a global ejecta area. For the first time the peak ring of the crater has been drilled by the Integrated Ocean Drilling Program (IODP) 364 drilling expedition “*Chicxulub: Drilling the K-T Impact Crater*” in April – May 2016 and the newly obtained samples will be used to study the impact crater with a novel approach. While the impact event has been fairly well studied for fossilising taxa, the post impact recovery and evolution of the majority of “soft-bodied” plankton and invertebrates is largely unknown. In this study molecular fossils will be analysed using organic and isotopic geochemistry parallel to a molecular biological approach. It has been shown that ancient DNA can be preserved for hundreds of thousand years and be used for ecosystem reconstruction (Coolen and Overmann, 2007). For this project, it will be explored to what extent ancient plankton and vegetation DNA can be recovered from Cenozoic marine sediments overlying the Chicxulub impact crater and if this DNA is suitable to study the post-impact recovery and if possibly living bacteria in the Cenozoic record can provide information about post-impact environmental and depositional conditions. Further, the study of microbial metagenomics in the impact breccia and the peak ring below the marine Cenozoic sediments will reveal the diversity and function of microbial communities that at some point in history must have been able to recolonise the fractured impact rocks after the crater had sufficiently cooled down to sustain microbial life. The coupling of the obtained paleogenomic and deep subsurface microbiome datasets with organic, isotopic, and general geochemistry data and in the context of geological data through collaboration with the other IODP 364 science party members will contribute to a deeper understanding of environmental factors that control life in the deep biosphere, its ability to recover and evolve after major extinction events, and the possibility of life to form beyond Earth (Grice et al., 2000; Orsi et al., 2016; Whiteside and Grice, 2016).

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Mineralogy of the Yangibana LREE Deposit, Western Australia

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The Yangibana LREE deposit is hosted within the Proterozoic Gifford Creek Carbonatite Complex (GCCC) of the Gascoyne Province, Capricorn Orogen, Western Australia. LREE mineralisation is hosted in “ironstone” dykes and sills that intrude the rocks of the Durlacher Supersuite and Pooranoo Metamorphic Suite. The “ironstones” are heavily oxidised dykes and sills composed mainly of hematite, quartz, clay minerals, monazite and apatite. Based on field relationships and detailed petrography, we show that the mineralised “ironstones” are actually alteration products of various rock types including ferrocarnatites, phoscorites and hydrothermal assemblages that appear to emanate from the ferrocarnatites. The ferrocarnatite dykes and ironstones are enveloped by K-dominant, fenite alteration of the host metasediments and granites. These fenite alteration zones often have subordinate phosphate mineralisation.

The ferrocarnatite dykes are composed of ferroan dolomite, ankerite, siderite, riebeckite, aegirine, annite–phlogopite, apatite and monazite. The phoscorites are comprised of magnetite, annite–phlogopite, monazite and apatite. The hydrothermal veins vary in composition and mineralogy from riebeckite–aegirine–magnetite–rutile–zircon–columbite–monazite, to riebeckite–rutile–magnetite–ankerite–monazite–apatite, to magnetite–quartz.

Monazite is the dominant LREE-bearing mineral and occurs as large (100–1000 μm) euhedral prisms, often in clusters. Two chemically distinct types of monazite are found at Yangibana:

- 1) Ce-monazite, which occurs in the western deposits and
- 2) Nd-monazite, which occurs in the eastern deposits.

Both types of monazite contain variable amounts of Th (1–5 wt % ThO_2) and U (10–120 ppm).

Fluorapatite occurs as a subordinate LREE-bearing mineral phase in the ironstones and associated rocks, but most often in the fenite halos. It occurs as elongated crystals up to 500 μm in length that often contain small (10–20 μm) inclusions of monazite. Under CL, the apatite crystals contain darker, REE-poor cores with brighter, REE-enriched and texturally complex rims. These variations in monazite and apatite composition appear to be indicative of fluid mobilisation and recrystallisation of the phosphate minerals.

A range in ages (1380–950 Ma) for the rocks at Yangibana suggests that multiple magmatic-hydrothermal events have affected the GCCC. Furthermore, the transition from Ce-monazite to Nd-monazite (moving from West to East) may represent an evolution of hydrothermal fluid(s) throughout the system (Smith et al., 2010). Work is ongoing to determine what factors are controlling this trend in a phosphate-dominated mineral system.

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Bacteria-mineral interactions

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Bacteria play an important role in catalysing a wide array of biogeochemical processes that affect mineral dissolution, aqueous geochemistry and secondary mineral formation. While μm -scale in size, bacterial growth over geological time can produce km-scale features. Importantly, many of these processes have the potential to work over human life spans, and are contributing to the development of applied geomicrobiology.

The biogeochemical cycling of gold is critical to Au exploration. Weathering of Au-bearing sulphides releases Au grains that float, possessing evidence of secondary Au formation, *i.e.*, Au dissolution and Au precipitation. Bacterial transformations of Au (I)-thiosulphate and Au (III)-chloride complexes produce a range of nanophase particles, ranging from colloids to octahedral Au. X-ray Absorption Spectroscopy experiments demonstrated that the reduction mechanism of Au(III)-chloride to elemental Au involves the formation of intermediate Au(I)-organo-S compounds, intuitively glutathione. Ecosystem modelling of a placer system, integrating all of these processes produced mm-scale Au grains, > 5 orders of magnitude larger than the original colloidal material. Overall, these processes provide unique targets that should have application in exploration geochemistry for tracking the origin(s) of Au deposits.

Supergene enriched iron ore deposits are typically protected by a goethite-cemented ferruginous duricrust layer referred to as canga. In these deposits, canga forms extensive deposits blanketing ancient erosion surfaces, is tough, well consolidated, permeable and resistant to erosion and chemical weathering, protecting the relatively soft enriched iron ore below. This protective canga horizon is therefore, essential to supergene iron ore enrichment and formation of high-grade iron ore. Active, biogeochemical Fe cycling is essential for the 'self' healing cementation/re-cementation occurring in canga. Recently, the formation of canga possessing macroscopic 'organic' textures has been linked to the biogeochemical cycling of iron, preserving fossilised bacteria via permineralisation of biofilms. Growth of grasses also suggests that the rhizosphere contributes to canga formation. At the canga surface, these often unique, endemic plants carve out an existence without 'soil'. The formation of canga has been essential for the formation of these iron ore deposits, and will ultimately be required for remediation of these unique ecosystems.

Ultramafic mine wastes, rich in magnesium silicate minerals, have an inherent but untapped capacity to absorb and trap the GHG, carbon dioxide. Weathering of ultramafic materials releases magnesium, which can then be utilized in carbonate precipitation reactions, thereby trapping carbon from DIC in stable carbonate minerals and as potentially valuable biomass. A natural playa from Atlin, British Columbia, Canada, that has demonstrated the ability to microbially-accelerate hydromagnesite formation, was easily transferred into an engineered ecosystem model. Subsequent growth of microbial mats from Atlin, in this 10 m long flow-through bioreactor catalysed hydromagnesite $[\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}]$ precipitation under 'natural' conditions. Under optimised nutrient and magnesium inputs, a mass balance calculation using water chemistry data and hydromagnesite resulted in a carbon sequestration rate of 61 t C/ha/year, approx. 3 X average rainforest productivity.

Palaeoenvironmental changes in Ordovician source rocks of the Canning Basin, Western Australia

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The Ordovician Period is well-known for several major global climatic and evolutionary events that strongly influenced biodiversity and source rock development. Extensive epicontinental seas developed during sea-level high stands, driven by an extended greenhouse climate (Munnecke et al., 2010). Marine life was characterized by a drastic increase in biodiversity (Great Ordovician Biodiversification Event (Cooper and Sadler, 2004; Harper, 2006; Servais et al., 2009), and a subsequent major extinction at the end of the Ordovician. Furthermore, the limited ocean circulation and predominant anoxic conditions promoted the preservation of organic matter, resulting in global petroleum source rock deposition. (Klemme and Ulmishek, 1991; Obermajer et al., 1999; Ghorri, 2013).

The Goldwyer Formation (467-462 Ma) of the Canning Basin, Western Australia, is an example of Ordovician sediments with hydrocarbon potential that were deposited in a warm, shallow epeiric sea. The base of the Goldwyer Fm. reflects the onset of a marine transgression across the Canning Basin, resulting in the deposition of shallow marine to lagoonal carbonates and mudstones. Two source rock units are developed within the Lower (Unit 2) and Upper (Unit 4) Goldwyer Fm. (Foster et al., 1986), to which several oil discoveries have been correlated (Edwards et al., 2013).

The aim of this study is to characterize the two main source rock units within the Goldwyer Fm. using molecular and stable isotope analyses, to complement the existing geological framework, whilst providing further insight into Ordovician biodiversity and source rock development in epeiric seas.

Five petroleum wells were sampled on a NW-SE cross section along the Dampier and Barbwire Terraces of the northern Broome Platform, reflecting a distal-proximal trend towards the SE. Molecular proxy analysis revealed that deeper marine environments were characterized by reducing conditions and stratified water column while shallower environments were more oxygenated and contained terrestrial organic matter. High hopane/sterane ratios (>12) in shallower environments indicate a strong predominance of bacteria over eukaryotic algae, consistent with limitation of algal production due to extensive denitrification in oxygen minimum zones (LaPorte et al., 2009; Rohrssen et al., 2013).

The characteristic biomarker signal associated with *G. prisca* (Foster et al., 1986; Hoffmann et al., 1987; Edwards et al., 1997) was identified in the upper part of the Goldwyer Fm., whereas this molecular signal was absent in rock extracts from Unit 2. In this study, palynological and petrological analyses confirmed the presence of *G. prisca* microfossils in selected samples of the Upper Goldwyer Fm. *G. prisca*-rich samples were characterized by oxygenated, poorly stratified conditions, high hopane/sterane ratios, elevated 3 β -methylhopane abundance and depleted carbon isotopic signatures. These results highlight that environmental conditions and possibly salinity changes strongly influenced the occurrence of the microorganism. High 3 β -methylhopane abundance suggests that *G. prisca* could have been utilizing carbon ultimately derived from methane produced by aerobic methanotrophs, resulting in ¹³C-depleted *n*-alkanes.

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Titanite as a monitor of hydrothermal and magmatic processes

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Titanite (sphene) is a common accessory mineral in a range of igneous and metamorphic rocks and is often associated with hydrothermal alteration and ore formation processes. Titanite can accommodate high levels of trace elements (e.g., REE, F, HFSE, U, Th, Sr), so it has potential to be used for geochemical and isotopic fingerprinting of geological processes, and as a U–Pb geochronometer. It is stable to high P and T conditions (>1000° C and >3.5 GPa in some cases), but it is relatively reactive during metamorphism, hydrothermal alteration and erosion. These characteristics offer advantages over other mineral geochronometers such as zircon, in that titanite may be used for dating and characterizing metamorphism and hydrothermal alteration, in addition to igneous crystallisation.

We have characterized a new titanite standard, labeled MKED1, that can be used to calibrate U–Pb ages, and Sm–Nd isotope compositions of titanite from a range of rock types/settings. MKED1 derives from large (several cms) 1518 Ma titanite crystals from calcite-apatite-titanite veins that cut skarn rocks of the Mount Isa Inlier. MKED1 is relatively homogeneous in trace element content and U–Pb and Sm–Nd isotopic composition, and has very low levels of common Pb (see Spandler et al. 2016). It is in plentiful supply, and is available to analytical labs by contacting the lead author.

To demonstrate the potential of titanite to record hydrothermal and igneous events, we present two case studies that examine; 1). The timing and origin of mineralization at the Elaine Dorothy skarn orebody, Mt Isa Inlier, and; 2). The nature, age and origin of cryptic ash units from the Rukwa Rift Basin of the East African Rift (EAR).

The Elaine Dorothy Cu–Au–REE orebody is hosted within a steeply dipping shear structure within amphibolite-grade marble and skarn rocks of the Corella Formation of the Mary Kathleen Fold Belt, Mount Isa Inlier. Titanite intergrown with the Cu sulfide minerals returned at date of ca. 1530 Ma, which we interpret to be the timing of Cu mineralization. This age is consistent with the timing of major granitic magmatism in the region (Williams–Naraku event) and, together with non-radiogenic Nd isotope compositions (ϵ_{Nd} of ~ -6 for titanite), indicates that the mineralising fluid and metals were derived from an upper crustal source (felsic intrusions or metasediments), rather than the mantle.

The Rukwa Rift basin of the western branch of the EAR contains a number of enigmatic weathered ash units that contain pristine titanite crystals. U–Pb geochronology of these titanite grains reveals that volcanism is date to ca. 25 Ma. ϵ_{Nd} values (+1.5 to +2) are consistent with magma derivation from an enriched mantle source. Phonolitic to dacitic glass inclusions hosted in these titanites reveal that the alkaline parental magma underwent a complex evolutionary history involving immiscibility between carbonatite and phonolitic melts, followed by feldspar- and biotite- controlled fractionation, with no significant role for assimilation of upper continental crust.

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New insights into the growth of modern coralline algae and the ‘Dolomite Problem’ from synchrotron micro-diffraction and the chemistry of magnesium-rich minerals

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Crustose coralline algae (CCA) are important calcifying organisms and reef-builders around the globe, forming a substrate for corals and providing habitat for numerous organisms. CCA form massive algal ridges protecting the reef and shoreline from wind and wave energy, and when buried may form important hydrocarbon reservoirs (e.g., Terry and Williams 1969). Despite the economic and ecological importance of CCA, their mineral make-up is enigmatic. It has long been known that the Mg/Ca in the bulk CCA may exceed the Mg/Ca in the skeletal calcite that dominates its mineralogy (Milliman et al., 1971); however, the identity of Mg-rich phase(s) has remained unknown. Candidate Mg-rich minerals in the CCA skeleton have compositions similar to dolomite [CaMg(CO₃)₂], magnesite [MgCO₃] and brucite [Mg(OH)₂] (Milliman et al., 1971; Nash et al., 2011). These precipitates are less well understood due to their sub-micron grain size and poor crystallinity. Any Mg-rich phase(s) would impact the formation and biomineralization of CCA; may affect Mg uptake by CCA in reefs (e.g., ‘calcite’ versus ‘aragonite seas; Sandberg, 1983); and would place limits on models for maturation and diagenesis of CCA. Finally, if Mg-rich phase(s) are present in CCA they would influence the so-called “Dolomite Problem” – an abundance of dolomite in fossil reefs compared to its apparent absence in modern reefs.

This project provides a detailed study of the specific Mg-minerals, their structure and spatial distribution in modern CCA. We collected actively growing coralline algae *Porolithon onkodes* (Heydrich) Foslie from Heron Island, Great Barrier Reef, Australia. Samples were characterised using backscattered electron images collected with scanning electron microscopy (SEM) at the ANU Centre for Advanced Microscopy. Select minerals were analysed using SEM plus energy-dispersive X-ray spectroscopy using known standards. Synchrotron micro-X-ray diffraction (μ-XRD) was performed at the Advanced Light Source (Lawrence Berkeley labs). A ~10 keV beam was focussed to 2 x 5 micron used to collect elemental X-ray fluorescence maps, including Ca abundances. We then used a ~9 keV beam to collect smaller μ-XRD maps within the context of the larger XRF maps.

1. The epithallus (surface layer; Figure 1, 2) is photosynthetically active and dominated by recently precipitated high Mg-calcite (16 ± 2 mol% MgCO₃).
2. The perithallus makes up most of the sample (Figure 1) and contains a framework of high Mg-calcite (16-29 mol% MgCO₃) that contains Mg-rich phases with the following textural relations:
 - a. Within or lining cell walls, we confirmed the presence of *protodolomite* (40-80 mol% MgCO₃) with morphologies ranging from smooth cell linings to well-formed crystals. We show for the first time that the protodolomite is mostly disordered, but some patterns of near-stoichiometric dolomite composition show a *weak ordering* reflection (015). In addition, the high spatial resolution of the micro-diffraction technique revealed *hydromagnesite* (Mg₅(CO₃)₄(OH)₂·2H₂O) as platy crystals in the centers of cells and *Ca-rich magnesite* (80-85

mol% MgCO₃) lining cells. These two minerals have not been reported previously in CCA to our knowledge.

b. Conceptacles, the reproductive organs of the coralline algae (Figure 1, 3a-c) that were originally dominated by organic material (i.e., tetraspores, membranes, extracellular polymeric substances) are mineralized by *protodolomite* (Figure 3a-c) and *Ca-rich magnesite* (Figure 3c). *Hydromagnesite* occurs as void-filling aggregates. Each conceptacle has different ratios of the mineral types and we attribute the variability to the breakdown of the organic material, perhaps mediated by bacteria as suggested by nodular textures (Figure 3c).

c. In areas of damaged crust (Figure 1, 4), *hydromagnesite* (~ 99 mol% MgCO₃) occurs as massive aggregates and is commonly intergrown with *aragonite* (CaCO₃). These areas may be sealed off by elongate hypothallial cells that are dominated by the most Mg-rich protodolomite (nearing 80 mol% MgCO₃) and aragonite (CaCO₃).

3. The hypothallus occurs at the base of the CCA and contains substrate material, elongate hypothallial cells, great variability and complex alteration. Therefore, we did not focus on detailed characterization of the hypothallus.

We definitively show that the Mg-minerals such as protodolomite, hydromagnesite and Ca-rich magnesite precipitate while the CCA crust is still alive. This provides a new pathway for incorporating Mg in reef material. Precipitation of these Mg-rich minerals is likely biomediated and assisted by the presence of organic material (Roberts et al., 2013) and/or microbial activity (Vasconcelos et al., 1995). If there is subsequent dissolution of high-Mg calcite during burial and diagenesis then the Mg-content of CCA structures may increase over time, providing Mg and also future nucleation sites for dolomite (i.e., the ‘Dolomite Problem’).

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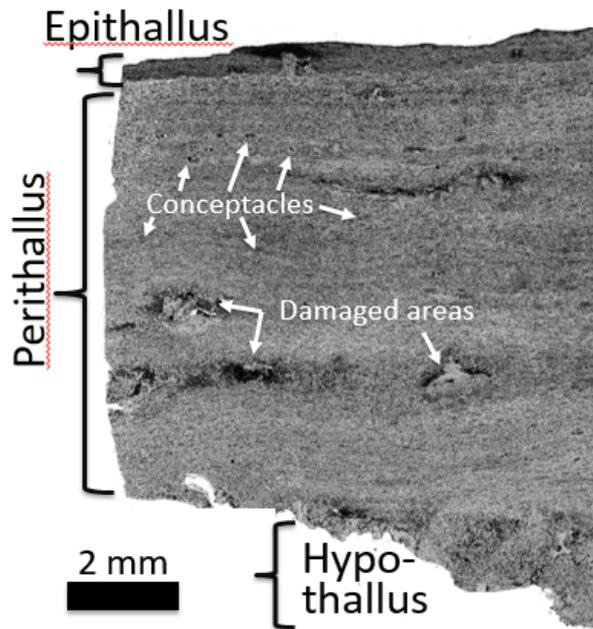


Figure 1: Cross-section through the outer part of a crustose coralline algae with subdivisions.

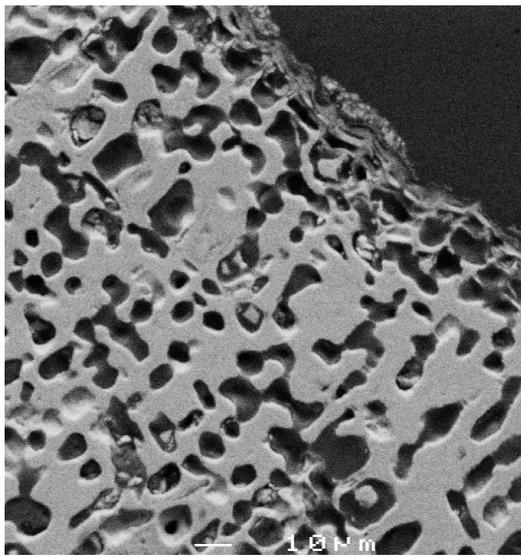
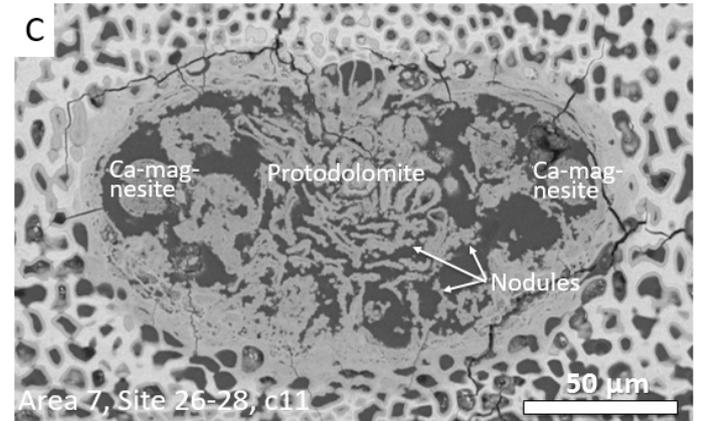
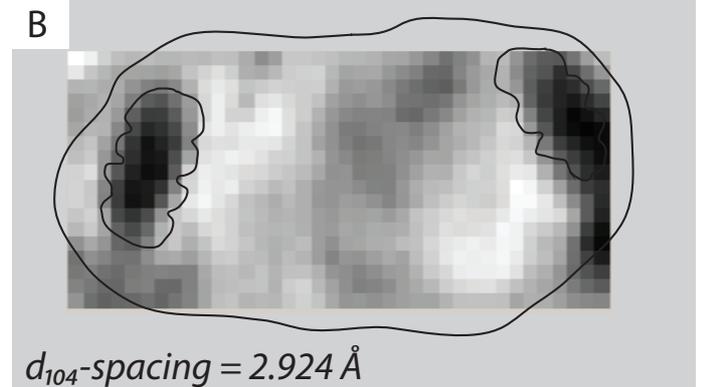
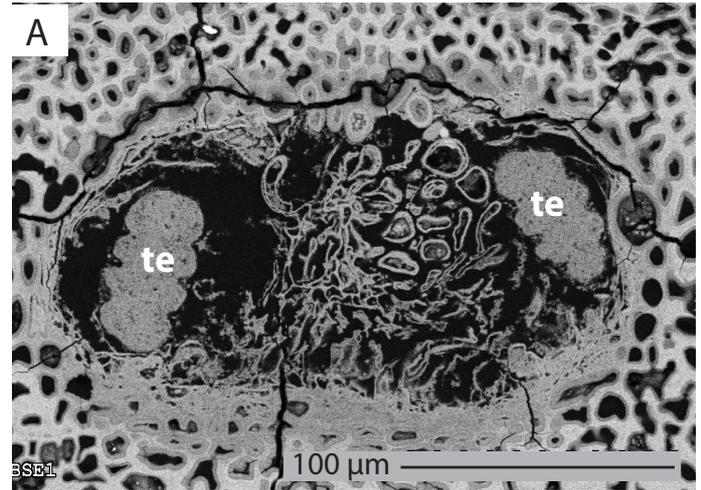


Figure 2: Epithallus (surface layer) with high Mg-calcite.



Hydrotalcites as a carbon sink in serpentinites

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Ultramafic mine tailings are being investigated for their potential to trap and store atmospheric CO₂ via passive carbonation reactions. Hydrotalcite minerals may be a potential carbon sink in many ultramafic tailings piles. Hydrotalcites can trap atmospheric CO₂ in multiple ways: either through the carbonation of brucite, which is present in ultramafic tailings, or through the carbonation of pre-existing non-carbonate bearing hydrotalcite minerals via anion exchange.

Pyroaurite [Mg₆Fe³⁺₂(CO₃)(OH)₁₆·4H₂O], a carbonate bearing hydrotalcite mineral is found throughout the tailings pile at the Woodsreef Chrysotile Mine (New South Wales, Australia).¹ This may represent a second carbon sink, in addition to the hydrated magnesium carbonate crusts that form on the surface of the tailings pile. In order to determine whether pyroaurite at Woodsreef and similar localities is capturing atmosphere CO₂, it is necessary to determine whether it forms in the tailings or was already present ore as a gangue mineral. If the pyroaurite is sequestering atmospheric CO₂, then it becomes important to quantify its modal abundance in tailings. This will allow an estimate to be made of the total amount of CO₂ sequestered in pyroaurite as well as determining the relative contributions to CO₂ sequestration from all carbonate-bearing phases present in the tailings.

Samples were taken from across the tailings pile at Woodsreef to determine the horizontal and vertical distribution of pyroaurite. Quantitative X-ray diffraction (XRD) analysis was used to obtain modal abundances of the constituent minerals. The surface of the tailings is covered by hydromagnesite [Mg₅(CO₃)₄(OH)₂·4H₂O] crusts. Pyroaurite is present throughout the tailings with higher abundances at the tailings surface. A poorly crystalline decomposition product of nesquehonite [MgCO₃·3H₂O] is found deeper within the tailings material. There is an inverse relationship between brucite and pyroaurite abundances with depth, implying that pyroaurite at Woodsreef is forming by carbonation of brucite.

Mineral abundances obtained from XRD data can be combined with tailings density data to estimate the amount of CO₂ sequestered by each carbonate phase in the tailings. For a given cubic metre of tailings, 10.4 kg of CO₂ are sequestered (within the top metre of the tailings pile at Woodsreef). By extrapolating from 1 cubic metre to the entire surface of the tailings pile, we estimate that Woodsreef has sequestered ~13.8 kt of CO₂, with approximately 20% of the CO₂ being sequestered by pyroaurite.

Further research is currently ongoing to use stable carbon and oxygen isotopes to fingerprint the source of carbon in pyroaurite.

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Multiscale petro-structural study of the Malinvern-Argentera migmatite complex in the external collisional Alpine belt

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Eclogite- and granulitic mineral assemblages were previously documented from boudins and lenses of ultramafic, mafic and carbonatic rocks occurring amongst the Variscan migmatites of the Argentera–Mercantour Massif (Maritime Alps) (Compagnoni, Ferrando, Lombardo, Radulesco, & Rubatto, 2010; Ferrando, Lombardo, & Compagnoni, 2008; Malaroda et al., 1970). The continental basement of the Eurasian margin of the Alps thus encloses an early subduction-related history that remains poorly studied, and might offer a window to a segment of the Variscan suture zone.

The study areas are located in the Argentera–Mercantour Massif (Maritime Alps), which is the southernmost of the External Crystalline Massifs of the Western Alps (Helvetic Domain). The Argentera–Mercantour Massif consists mainly of biotite-bearing and amphibole-bearing migmatitic gneiss, diatexite and anatexite produced during the Variscan collision (Compagnoni et al., 2010). Migmatites contain mafic- and ultramafic lenses and boudins, and are intruded by late-Variscan granites (Corsini, Ruffet, & Caby, 2004; Ferrara & Malaroda, 1969; Monié & Maluski, 1983).

A multi-scale structural analysis, aimed to correlate lithostatigraphic, structural and petrographic data, is the fundamental tool to understand the tectono-metamorphic evolution of such a poly-deformed crystalline basement. Mafic boudins and calc-silicates were analysed in detail to explore the geological evolution preceding the partial melting of the country rocks. Structural–geological field mapping at the 1:10,000 scale of the whole study area, and complementarily at 1:50–1,500 scale of key areas with a high density of mafic, ultramafic and carbonatic rocks has been undertaken. To reconstruct the tectono-metamorphic history of the Variscan units, field structural data were combined with micro-structural, micro-chemical analysis and thermobarometry (using empirical calibrations as well as Thermocalc), which allowed P–T estimation of the successive metamorphic stages for eclogitic, granulitic and calc-silicate samples.

Migmatite, which is the dominant lithotype in the mapped area, shows fabrics suggesting different progression of the partial melting (metatexite, diatexite, anatexite). The S1 regional foliation in migmatite is marked by biotite ± sillimanite and is coeval with the boudinage of mafic-, ultramafic- and carbonatic layers. Foliation S1, developed during D1, was folded at various scales during a D2 phase. Mineral assemblages marking S1 foliation suggest that D1 and D2 both developed during partial melting. D1- and D2-related structures are crosscut by granitoid bodies (Central Granite). During D3 deformation stage, the development of a fracture system led to the intrusion of silicic- and mafic dikes in both the migmatites and granitic bodies. Ductile shear zones, defined by chlorite and muscovite, are related to an Alpine-aged D4 deformation that developed at shallow crustal levels.

Mafic layers record a HP stage (M1) characterized by sodic pyroxene (partially replaced by diopside–plagioclase symplectite), garnet, and sodic amphibole. Stage M1 in eclogitic rocks predates partial melting of country rocks, while stage M2 (diopside–Ti-amphibole –plagioclase) seems to correlate with the earliest assemblages observed in granulite (garnet–orthoamphibole–biotite–ilmenite) and calc-silicates (garnet–diopside–quartz–epidote). Empirical thermobarometry yield similar P–T conditions for M2 in the eclogite and the granulitic association, suggesting coeval development, which is consistent with structural data. Amphibolite facies mineral assemblage M3 in the boudins, which is the most pervasive, represents the re-equilibration during partial melting of country rocks. During M4 and M5, boudins underwent a LT/LP imprint during the Alpine collision.

In conclusion, the integration of the presented data allows reconstructing the P–T–d evolution of the Variscan basement of the Eurasian basement of the Maritime Alps. The close association of mafic, ultramafic and carbonatic rocks and the identification of an early HP/LT metamorphic stage in the Argentera Massif point to a Variscan suture zone within the external Alpine collisional belt.

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Biogeochemical Cycle of Silicon and Biosilicification

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Silicon (Si) cycles between plants/algae and soils, although the absolute requirement of Si for plant survival continues to be debated (1, 2). Silicic acid is taken up by a specific transporter (3) in the class Bacillariophyceae (diatoms) and colloidal spheres nucleated by cationic polypeptides (4) are precipitated intracellularly within a specialized vesicle. Through convergent evolution by the angiosperm rice (*Oryza sativa*), Si uptake in root cells is facilitated by silicon transporters of *Lsi1* and *Lsi2* derived from a diverse family of transmembrane aquaporins (5, 6). Silicic acid is then translocated to the shoot by transpirational flow through the xylem, transported out of xylem by *Lsi6* (7), and finally deposited/redistributed into the cell walls or specialized cells, including epidermal cells, silica cells and bulliform cells (8), as hydrated amorphous silica.

Silica is widely used within rice plants and other grasses for structural support and stress resistance (9). In addition to structure-function relationships within individual plants, it is widely appreciated that biosilicification plays a fundamental role in the global biogeochemical cycle of silica over geologic time (10). It is evident that the effects of plants on terrestrial silica cycling date back to their early evolutionary history in the Palaeozoic Era more than 400 million years ago (11). A dynamic biological silica cycle also plays a critical role in carbon cycling, both on the continents and in the oceans through carbon fixation by silica-biomineralizing marine diatoms (12).

Although silica in rice plants exhibits many functions, contributing strength and enabling plants to respond adaptively to environmental stresses, the mechanism of action of biosilicification is largely overlooked due to its multiscale complexity at the tissue, organ, and whole-plant level. Here, we use a simplified single cell system and show a multifunctionality of the silicified cell walls with an enhanced cell strength, and a capability to inhibit cadmium ion uptake into the cells. The multifunctional extracellular biosilicification may have had considerable influence in rice growth and the biogeochemical cycle of silicon over the course of its evolutionary history.

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Are porosity forming reactions an important ingredient in the formation of orogenic gold deposits? An insight from the Mick Adam gold deposit, Yilgarn Craton, Western Australia.

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Orogenic gold deposits require focussing of large volumes of hydrothermal fluids, of magmatic or metamorphic derivation, into upper crustal ore deposit sites. Here we present a study of the Mick Adam deposit, situated within the Castle Hill gold camp of the Kalgoorlie Terrane within the Archean Yilgarn Craton of Western Australia. The Mick Adam deposit is a structurally controlled gold deposit within the Kintore Tonalite pluton. In this work we combine petrology, geochemistry, geochronology, geothermometry and isotope data, to define the fluid-rock interaction processes at play during mineralisation. Using the Mick Adam deposit as an example we develop a new holistic model for gold mineralisation in an orogenic context. This model has further implications for the mechanism of fluid transport in other gold bearing systems. Our findings show that the Kintore Tonalite has undergone two episodes of hydrothermal alteration. The first alteration event causes wide zones of episyenitisation, related to the intrusion of feldspar-phyric porphyry units, with significant porosity (~8-12%) within an altered zone. A fluid of magmatic derivation (High-Ca granite), with temperatures between ~600-700°C, an alkaline signature (pH ≈ 8.5), and XCO₂ between 0.3-0.7 caused the episyenitisation. A second alteration event is related to mineralised quartz vein development adjacent to, and overprinting episyenitised zones. This second alteration and mineralisation event is dated by U-Pb in titanite at c. 2612 ± 28 Ma. Similarly, a fluid interpreted to be of magmatic origin (Low-Ca granite), with alkaline affinity and temperatures between ~620-680°C mineralised the Mick Adam deposit. Porous zones, developed during the first stage of alteration and hydrothermal fluid flow, created permeability pathways for subsequent mineralising fluids, complimenting fracture induced permeability pathways. In this way we propose that hydrothermal alteration chemically prepared previously impermeable rock for the flow of later mineralising fluids.

Distinguishing local- and regional-scale metasomatic systems

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Geochemical alteration in mafic rocks of the Fortescue Group large igneous province around the Prairie Downs Zn-Pb-(Cu-Ag) deposit, Western Australia, is the result of two overprinting metasomatic systems. The first is a regional-scale event, well documented across the Hamersley Basin to the north, and resulted in extensive depletion of alkalis, Mg, and heavier first transition series metals (Mn-Zn) (White et al., 2014a). This drove the progressive formation of epidote/pumpellyite-quartz rocks that successively replaced the pre-existing low-grade regional metamorphic assemblages (White et al., 2014b). The second, localized event was associated with Zn-Pb mineralization and resulted in Ca-loss accompanied by enrichment in a complex suite of metals and metalloids (Zn-Pb-Sn-Ag-K-Ba-Tl-Sb-Ge-U-Th-Cd-Hg-Se-REE) (White et al., 2016). This mineralization-related event was superimposed on the earlier regional-scale system: previously 'least altered' basalts underwent growth of biotite and Zn-bearing chlorite at the expense of epidote and amphibole; regionally metasomatized rocks were replaced by assemblages dominated by quartz, muscovite and baileychlorite (Zn chlorite). In all cases, these altered basalts host Zn within chlorite in a broad (km-scale) halo around the deposit. Recognizing and distinguishing the two separate systems is vital for exploration as some observed chemical zonation around the deposit (e.g. Fe and Mn depletion) are related to the earlier regional-scale system, and not the later mineralizing event. Geochemical modelling with HCh indicates that the observed alteration assemblages can be generated through interaction of rocks with large volumes of saline, Zn-K-bearing fluid (fluid/rock ~1000). This study highlights the importance of understanding the regional geochemical background when investigating local metasomatic systems.

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Tracing fluid channeling in the continental crust

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Much Earth Sciences research is devoted to understanding the interaction between the crystalline phases that constitute the Earth's lithosphere and volatile phases that permeate this lithosphere. Fluid infiltration processes can be studied from the nano-scale, using surface chemistry techniques to basin-wide scales of several tens of kilometers. The focus of the present research is on the larger scale processes.

Fluid inclusions in minerals are often viewed as representing a sample of the fluid phase present in the crust at the time of mineral growth or recrystallization, and traditionally have been used for estimates of P-T conditions during mineral growth, and to determine the composition of the trapped fluid. Fluid inclusions can either be primary, i.e. reflecting the fluid at the time of original crystallization of the mineral, or secondary, i.e. formed or altered during subsequent processes. Distinction between the two is commonly on criteria such as shape or position in the crystal, e.g. confinement to crack-seal planes.

In the present study we focus on trace elements: the noble gas content of the fluid inclusions. We assume closed system behavior for the fluid inside to inclusion. For the present case relevant is the exchange of K, Cl and Ar between the fluid inside the inclusion and the hosting mineral crystal lattice. Minerals that we focused on so far include quartz, garnet and actinolite, which are all low in structural potassium, chlorine, and radiogenic argon.

K-bearing hydrous trapped fluids typically contain signatures derived from three components that can be separated by step-wise crushing: excess ⁴⁰Ar, radiogenic ⁴⁰Ar accumulated in the fluid since entrapment, and an atmospheric argon component. Stepwise crushing neutron irradiated vein-minerals thus allows quantification of ⁴⁰Ar/³⁹Ar timescales of vein formation and hence, fluid mobility. Similarly, stepwise crushing of neutron activated vein minerals allow the quantification of Ca and Cl concentrations in the fluid as both calcium and chlorine produce distinct isotopic signatures in the argon spectrum (³⁷Ar and ³⁸Ar, respectively) of the fluid. With the present study we tread new ground analytically by developing techniques in close collaboration with industry using new-generation high-sensitivity 10¹³ Ohm faraday collector amplifiers and new detector configurations for argon analysis in multi-collector noble gas mass spectrometers.

In a previous study focused on the UHP metamorphic belts of central China we demonstrated that our stepwise crushing approach, when applied to eclogite garnets yielded old ages, reflecting the crystallization of these garnets early in the metamorphic loop, whereas actinolite in a late greenschist metamorphic vein yielded an age that reflects passing through late greenschist conditions in the PT loop, and cross cutting veins yielded post metamorphic ages.

Dissolution–reprecipitation reactions control the stability of CO₂ and transition metal trapping in hydrated Mg-carbonate minerals

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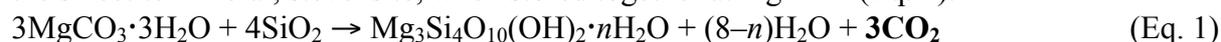
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Carbon dioxide (CO₂) removal technologies, such as carbon mineralisation, may be used to mitigate the adverse effects of anthropogenic climate change. Carbon mineralisation enhances the natural rate of silicate weathering to produce silica and Mg-carbonate phases, the latter acting as long-term sinks for CO₂.

The results of our systematic study of Mg-carbonate mineral precipitation and decomposition show that hydrated Mg-carbonate minerals decompose via the Ostwald step rule to form less hydrated, more stable phases under humid, but nominally dry conditions. At low relative humidities (RH), pristine, unreacted crystals of more hydrated, less stable phases persist to unexpectedly high temperatures. Our observations indicate that Mg-carbonate phase transitions occur via vapour-mediated dissolution–reprecipitation reactions.

Our laboratory- and synchrotron-based experiments also demonstrate that transition metals (Cr, Mn, Fe, Co, Ni, Cu) are rapidly sequestered by hydrated Mg-carbonate minerals and Fe-oxyhydroxides under conditions relevant to carbonation of ultramafic rocks [1]. Greater than 99 wt.% of aqueous transition metals are sorbed to these colloidal precipitates within 5 minutes. These are retained during recrystallisation to form mm-scale, euhedral crystals of nesquehonite (MgCO₃·3H₂O), which suggests there is low risk of metal release during enhanced weathering and carbonation.

Finally, our results show that hygroscopic Mg-carbonate minerals and silica react to produce the smectite mineral, stevensite, when stored together at high RH (Eq. 1).



We find this reaction goes to completion within 7–18 months of storage at ~100% RH and temperatures relevant to Earth's surface (23–75°C). It can occur in the absence of observable liquid water and proceeds via reaction of either hydrated or anhydrous Mg-carbonate minerals with amorphous silica, cristobalite or to a lesser extent quartz.

Our findings indicate that hydrated Mg-carbonate minerals recrystallize to form less hydrous and more stable traps for CO₂ and transition metals when stored at moderate RH, but that they should be separated from silica during storage to prevent subsequent release of trapped CO₂.

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The pathway of mineral replacement of gold tellurides under oxidative hydrothermal conditions investigated by *in situ* PXRD

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Gold tellurides are a group of gold minerals, including calaverite AuTe₂, sylvanite AuAgTe₄, krennerite Au₃AgTe₃, petzite AuAg₃Te₂, montbroyite (Au,Sb)₂Te₃, and muthamannite (Ag,Au)Te. In Nature, gold tellurides react with oxidative hydrothermal fluids, forming porous Au or Au-Ag alloy called ‘mustard gold’, most likely through mineral replacement reactions. Recent mineralogical and microscopic characterization of quenched specimen from hydrothermal experiments suggest a direct replacement of calaverite by Au (Zhao et al., 2009), and krennerite by Au-Ag alloy (Xu et al., 2013), but a complicated multi-step replacement of sylvanite by Au-Ag alloy (Zhao et al., 2013). To further reveal the reaction pathway, this work monitored the same three replacement reactions by synchrotron radiation *in situ* powder X-ray diffraction (PXRD), in which time resolved PXRD patterns were collected over the course of the mineral replacement reactions that were carried out in a quartz glass micro pressure reactor. The results were generally in agreement with the anneal-quench experiments that all the three gold tellurides were eventually replaced by Au or Au-Ag alloy. However, the *in situ* experiments also revealed an intermediate petzite phase in the replacement of krennerite and sylvanite, and the formation of two distinct TeO₂ phases. Hence, the pathways for gold tellurides decomposition under oxidative epithermal condition are: (1) calaverite → Au, (2) krennerite → petzite → Au-Ag alloy, and (3) sylvanite → petzite → Au-Ag alloy.

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Rare earth element behaviour and iron sulfide formation in dredge spoils and adjacent sediments

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Land-based disposal of dredged sulfidic sediments is known to generate coastal acid sulfate soils (CASS), which can generate drainage rich in iron, sulfate and trace elements (Åström et al., 2010). While some studies explore the geochemistry of rare earth elements (REEs) in streams and sediments impacted by CASS (Åström and Corin, 2003, Gröger et al., 2011), investigations on direct association between REEs and iron sulfides is lacking. Chaillou *et al.* (2006) suggest that fractionation of REEs might be a consequence of co-precipitation with Fe-S phases, but acknowledge the need for further research. In this study we investigated REE concentrations and fractionation associated with reduced inorganic sulfur species in sulfuric dredge spoils and sulfidic sediments from an adjacent drain. Consistent with Morgan *et al.* (2012), drain sediments contain abundant iron monosulfide, with acid volatile sulfide (AVS, a proxy for FeS) observed as high as 278 $\mu\text{mol/g}$ (median 79 $\mu\text{mol/g}$), and high concentration of near-total (aqua regia soluble) REEs (median ΣREE 609 mg/kg, range 20–1819 mg/kg). In the dredge spoil, AVS is below detection limits and REE concentrations are much lower (median ΣREE 267 mg/kg, range 0.4–871 mg/kg). We found FeS was stable in the anoxic sediments, with some conversion to pyrite (Fig.1), and that REEs are enriched in the solid phase in waterlogged sediments. Reactive FeS occurs in minor amounts in the dredge spoils, with Fe-sulfide oxidation inducing acidification and resulting in desorption and remobilization of REEs, leading to much lower REE concentrations in the solid phase of the dredge spoil. Scanning electron microscopy (SEM) images of the sediment demonstrates that pyrite is present in a variety of morphologies, including scattered cubic, scattered double pyramid, and framboids (Fig.1 a,b). Framboidal pyrite has diameters ranging from 1 to 20 μm . Morphological variability in framboid morphology may be explained by formation kinetics (Butler and Rickard, 2000) and the oxidation status after formation. No detectable lanthanum or other REEs were found in these pyrite or other FeS phases; instead, the lanthanum compound is found attached to clay minerals (Fig.2 a,c) and has a porous structure (Fig.2 b).

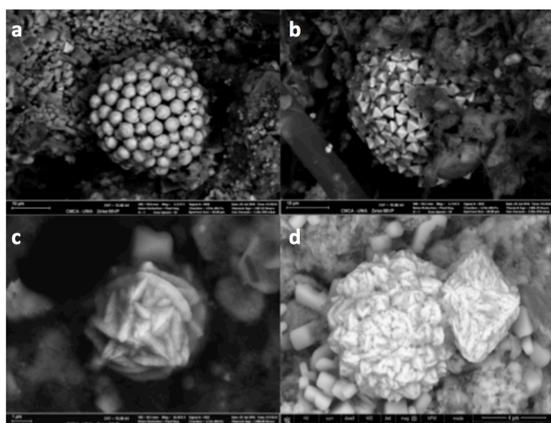


Fig.1 Back scatter scanning electron microscopy images show pyrite in different morphologies

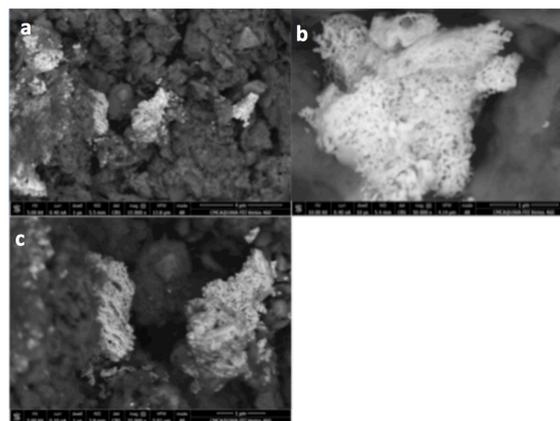


Fig.2 Back scatter scanning electron microscopy images show lanthanum-bearing phase(s)

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