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Coupling between Metamorphism
and Deformation

ABSTRACTS

ORAL Presentations

In order of presentation

The challenge of simulating coupled deformation and metamorphism at the grain scale

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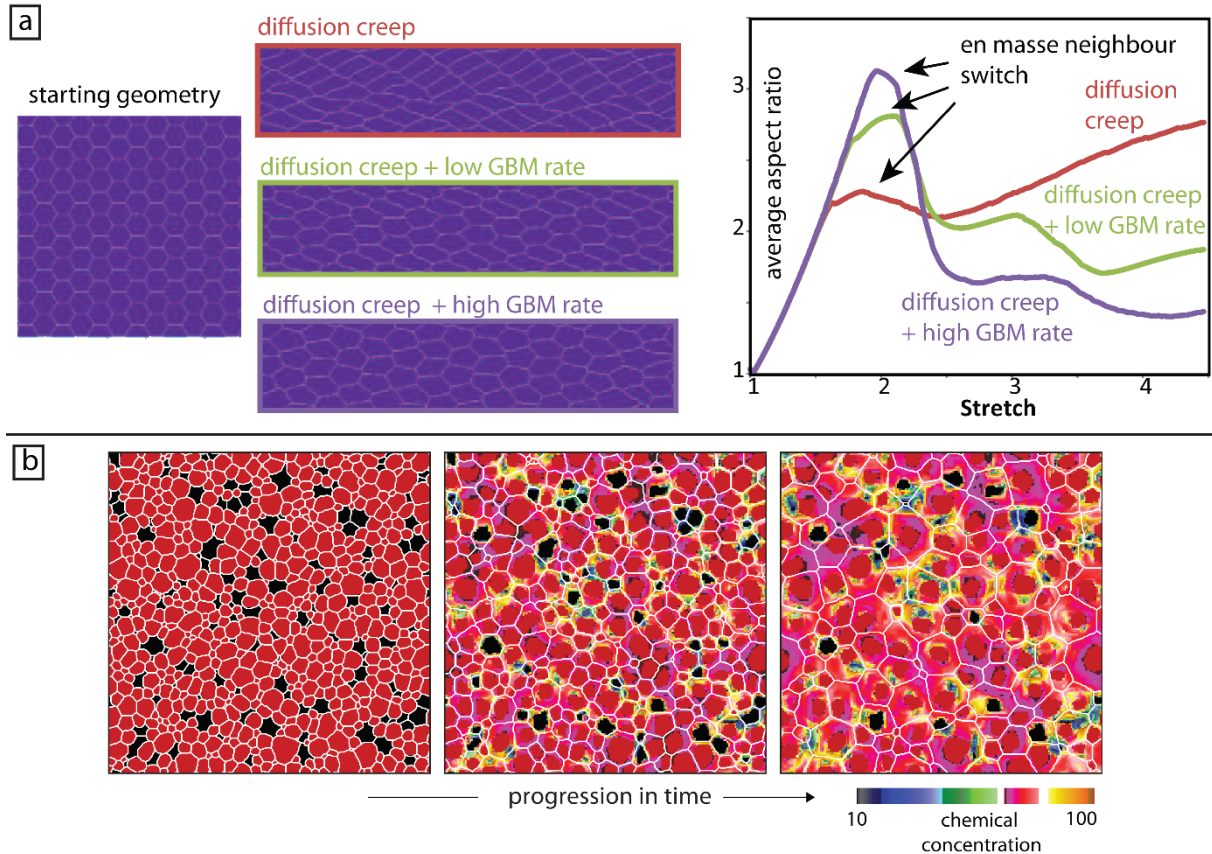
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This review provides an overview of the emergence and current status of numerical modelling of microstructures, with specific reference to the challenge of simulating coupled deformation and metamorphism. We emphasize the general philosophy behind such numerical models and their application to important geological phenomena such as dynamic recrystallization and strain localization from the deformation side of the equation, and the progress made but the real hurdles to developing equivalent simulation techniques for grain-scale metamorphic processes. We focus in particular on the dynamics that emerge when multiple processes, which may either be enhancing or competing with each other, are simultaneously active. We critically assess advances over the last 10 years and current activities in this topic.



Example of new development in microdynamic numerical modelling; preliminary results. (a) Coupling of diffusion creep and surface energy driven grain boundary migration (GBM); (left) starting microstructure; (middle) microstructure at stretch 2; (right) graph showing average aspect ratio versus stretch; note that the microstructure after a significant period of exclusive grain boundary migration is the same as the starting microstructure as no movement occurs as all triple junctions are 120° . Number of grains stays constant for all simulations. (b) Evolution of chemical concentration of an arbitrary element during surface energy driven GBM. The material is a single-phase polycrystalline aggregate with different initial chemical content. This example assumes very low bulk diffusion ($D_{\text{bulk}} = 1e-20 \text{ m}^2/\text{s}$) and fast grain boundary diffusion ($D_{\text{boundary}} = 1e-8 \text{ m}^2/\text{s}$), hence grain boundary diffusion dominates. Colour code indicates chemical concentration and white lines represent grain boundaries.

Coupling metamorphic reaction rates, fluid flow and microstructures

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Prograde metamorphic reactions producing fluids result in a remarkably complex coupling between mineral dissolution precipitation processes and mechanical instabilities. This complexity relies in the open nature of such systems. A full treatment of the problem would need to account for mineral kinetics, porosity production, dynamic permeability, the rheological properties of the solid matrix and the hydrous fluid phase, and eventually compaction and fluid release. Moreover, metamorphic reactions producing fluids result in a volume decrease of the solid matrix, which is not generally compensated by the volume of fluids produced, thus resulting in transient fluid pore pressure deviating from the lithostatic pressure. A full comprehension of metamorphic devolatilization reactions is therefore hampered given the uncertainty in many of the parameters that are involved, especially at high-pressure conditions. An experimental approach to the problem is appealing but its extrapolation to natural rates necessary requires some sort of validation. The comparison of mineral texture and microstructure between experiments and natural samples could be potentially used to assess the appropriateness of the experimental approach to track this problem. Here, we present new experimental results and natural observations on the serpentinite system to highlight some current developments in this topic.

The transition from hydrostatic to non-hydrostatic conditions during serpentine dehydration is investigated through the use of stress-strain rate sensitive deformation mechanisms in enstatite. Local or homogeneous variations in stress-strain rate results in the inversion of thermodynamically stable orthoenstatite to metastable low-clinoenstatite (Padrón-Navarta et al. 2015; Clément et al. 2018). This shear induced martensitic transformation allows reconstructing the orientation of the main compressional stress that it used to give some constraints on the compaction scales prevailing in the natural record.

The effect of foliation on fluid flow anisotropy is investigated by comparing the textural record of rocks from the contact aureole of the Bergell intrusion in the Malenco area (N. Italy) with those produced experimentally at similar pressure conditions. Oriented samples over a 1 km transect approaching the pluton were investigated by the EBSD technique and compared with structural data. There is a remarkable development of metamorphic olivine CPO associated to the main dehydration reaction; which is consistent over more than 400 m. This remarkable CPO, where [010] axes of olivine are clustered normal to the former serpentine foliation plane, are experimentally reproduced in “open” system experiments of serpentine cores in an internally heated gas apparatus (Paterson apparatus at Géosciences Montpellier, France). We demonstrate experimentally that foliation has a control on olivine textural development that can be linked to the anisotropy in permeability of the serpentine protholith.

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High temperature, chemisorption-induced, crystal lattice transformations in mineralised skarns

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The role of the fluid phase in metamorphism and deformation has enjoyed considerable discussion and not a little controversy for many decades. Part of the problem is that the question that it relates to is rather ill-defined which makes it difficult to find inter-disciplinary solutions. From a purely chemical perspective it is important to understand the **kinds of chemical reactions** that are at play in the PTX space involved and how these relate to imposed stress. We also need to know the phase state of the fluid (liquid or gas) through transient events such as brittle failure¹, who are the players (the molecular and ionic species as well as cluster compounds²) and how exactly they react with solid phases. To do this we need to find examples of reactive mass transfer where reaction kinetics are fast and reaction progress has been frozen in, rather than contexts which suggest they have reached near equilibrium states. And we need to look at the problem at all scales.

Mineralised skarns, such as the giant ~3Ma Ertsberg Cu-Au deposit in Indonesia, provide spectacular examples of the products of reactive mass transport under extreme conditions (< 50 MPa and > 600 °C)³. The principal fluid phase reactant here is SO_{2(g)} through its high dipole moment. This drives **chemisorption reactions** between the fluid phase and the available surface of garnets in contact metamorphosed calc-silicate assemblages extracting calcium to form anhydrite. These reactions establish chemical gradients through the substrate mineral assemblages which then sustain **poly-diffusive**⁴ almandine-grossular to andradite crystal **lattice transformation** via **vacancy-driven reactions**, with anorthite as an intermediate product. At the larger scale the whole rock material composition and its physical properties change progressively through these coupled processes and feed back into its response to deformation. In other open system geological contexts, such as perhaps fault zones, dipolar H₂O and H₂O clusters or their dissociation product ions drive chemisorption reactions and crystal lattice transformations in substrate minerals with consequent changes in physical properties of the rock material.

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Equilibrium thermodynamics for non-hydrostatically-stressed systems

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Thermodynamic calculations, applied under the assumption of local equilibrium and hydrostatic stress, have enabled quantitative interpretation of natural rock observations and insights into the pressure and temperature structure of Earth. Yet common features within rocks, such as preferred mineral orientation, record processes that did not occur under hydrostatic stress. While an approach under the conventional assumptions provides a simple and robust explanation for patterns observed in metamorphic belts, features that record non-hydrostatic conditions raise the question --- what additional knowledge can be gained if the assumption of hydrostatic stress is set aside?

A range of approaches can be applied to explore this question, with differing degrees of mathematical tractability and physical realism. Here, we describe the first steps towards a viable approach that allows the incorporation of non-hydrostatic thermodynamics into the local equilibrium approach. Issues to be covered include justification for the local equilibrium assumption, the application of a Gibbsian passive resistance to enable attainment of equilibrium in non-hydrostatically-stressed systems, applications that become possible if such an approach is adopted, and limitations to the approach.

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The backbone of the transpressional Yilgarn Orogen

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Structural analysis of shear zones and shear zone patterns plays a fundamental role in estimating deformation evolution and the bulk shape of the strain ellipsoid of deformed regions (Gapais et al., 1987, Fossen and Cavalcante, 2017), and for unravelling the tectonic evolution of crustal blocks juxtaposed by such high-strain zones (e.g. Means, 1995; Butler et al., 1997; Molli et al., 2006). Structural investigations on Archean shear zones are considerably more challenging, since the geological record becomes progressively more fragmented as we go back in time. Furthermore, we currently face a general lack of consensus about Archean geodynamics (Hamilton, 1998; Bédard et al., 2013), and about the role and tectonic significance that large-scale shear zones might have played during fragmentation and assembly of Archean cratons (e.g. Bédard and Harris, 2014). Therefore, the study of large-scale shear zones plays a critical role in unravelling the tectonic evolution of Archean crustal block, and in improving our understanding of Archean tectonics.

Structural studies mainly focused on the Dharwar Craton (India) suggest that some peculiar tectonic processes that dominated the Early Earth were the consequence of the overall low integrated strength of the continental lithosphere (Chardon et al., 2002), which is intrinsically linked to global, secular changes in fundamental physical parameters, such as mantle temperature and density (Labrosse and Jaupart, 2007). The high temperature of the Archean Moho would have therefore facilitated the syn-convergence flow of the weak Archean lithosphere, suppressing strain localization and accommodating the bulk of the deformation in wide, hot orogens through distributed horizontal shortening and lateral flow (Chardon et al., 2009; Cagnard et al., 2011). Whether such a tectonic style was dominant during the Archean, or whether there was a wide variety of tectonic styles in different geological settings, is still a matter of vibrant debate (Perchuk et al., 2016).

In the Yilgarn Craton of Western Australia, a 2950–2750 Ma period of lithospheric thinning accompanied widespread mantle-derived magmatism and the development of a thick, deep-marine greenstone sequence. Significant crustal thickening, the inception of large-scale thrusting and the appearance of syntectonic clastic deposits marked the onset of the Neoproterozoic Yilgarn Orogeny at c. 2730 Ma (Zibra et al., 2017a). Granite magmatism accompanied major shortening events until c. 2660 Ma, when a major transpressional pulse culminated with the exhumation of high-grade greenstones and the development of a second cycle of regional-scale, synorogenic clastic deposits (Zibra et al., 2017b). Overall, the tectonic evolution of the Yilgarn Orogen therefore contributed to the progressive strengthening of the continental lithosphere, when the secular change in tectonic style provided the transition from Archean-type to modern-type orogens (Rey and Coltice, 2008; Condie and O'Neill, 2010).

This contribution details the structural evolution of the Ballard shear zone, a major transpressional shear zone exposed in the core of the Yilgarn Orogen. Structural data show that a large-scale, high-temperature shear zone (5–20 km-wide and >200 km-long in map view) developed during emplacement of an elongate granite pluton, and was partially overprinted by lower-temperature fabrics. The comparison between the structural evolution unravelled here for the Ballard shear zone, with that of other four known transpressional shear zones exposed in the western part of the orogen, allows the formulation of a two-step tectonic model for crustal-scale shear zone development during the Yilgarn Orogeny.

The onset of transpressional shearing along each of these structures is coeval with the emplacement of syntectonic granitic magma (stage 1a), which focused strain and partitioned the strike-slip component of deformation, producing broad, crustal-scale structures containing high-temperature gneissic fabrics and migmatitic greenstone slivers. Greenstone belts flanking the shear zone are deformed heterogeneously, and generally accommodated the bulk of the coaxial and dip-slip components of the three-dimensional deformation.

Stage (1b) offers transition to medium-temperature mylonitic fabrics, with 1–2 km-wide high-strain belts typically developed along one flank of, and with the same geometry and kinematics as the structure (1a). Stage (1b) reflects the cooling of the system to ambient temperatures at the end of magmatism along the actively deforming corridor.

During stage (2), the shear zone system froze, as the main deformation front stepped to a relatively weak adjacent structure injected by granitic magma. The older structure kept deforming, but at lower temperature (greenschist to sub-greenschist facies conditions), with deformation typically focused within greenstone belts, controlled by the rheologically-weak lithologies and exploiting lithological boundaries.

The geometry stage (2) structures is profoundly influenced by stage (1) ones, while kinematics along stage (2) structures are not necessarily linked to the kinematics of the older, higher-temperature structures.

The spatial extent of metamorphic events is proportional to the size of the syntectonic plutons, so that higher-temperature conditions and highest finite strains occur in pluton aureoles, where the main metamorphic assemblages are generally synkinematic, grading to greenschist-weakly-deformed fabrics away from such plutons.

For each crustal domain, the regional tectonic grain established during stage (1a) represents the backbone that determined the orientation of younger, lower-temperature structures. This field-based tectonic model therefore emphasizes the role of syntectonic crustal magmatism in determining the bulk of the crustal structure in Precambrian orogens, and bears implications for our understanding of the spatial distribution of finite strain and metamorphic isograds in Archean granite–greenstone terranes.

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Microstructural and microchemical study of low to medium-grade metamorphic rocks along the Ballard Shear Zone.

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The geological record from the Archean Eon to the present preserves petrological, structural, geochemical and isotope evidence of significant changes in Earth processes through time. Understanding the way in which these processes have changed is paramount to our understanding of the secular evolution of the Earth's lithosphere. Most geodynamic processes are controlled by the physicochemical properties of rocks, which in turn directly depend on the chemical reactions experienced during their metamorphic evolution. Metamorphic rocks fortuitously preserve textures and petrology that often act to record orogenic processes. Deciphering orogeny depends critically on reading these patterns of microstructure and mineral composition in order to better constrain metamorphic conditions and their evolution in time (t) and pressure (P)–temperature (T) space. Here we utilize metamorphic petrology techniques to assess the interpretation of metamorphic textures and their implications for determining the P – T – t evolution of a suite of layered metamorphosed mafic and sedimentary rocks, and for interpreting larger-scale geodynamic processes operating in the Neoarchean–Mesoarchean from the margin of the Eastern Goldfields Superterrane, Yilgarn Craton, Western Australia.

The Ballard Shear Zone is a crustal-scale structure exposed adjacent to the Ida Fault, a terrane boundary that separates the Archean Youanmi Terrane from the Archean Eastern Goldfields Superterrane. The Shear Zone defines the eastern margin of the Ullaring Greenstone Belt (UGB) adjacent to the syntectonic 2680–2660 Ma Riverina Gneiss within the Eastern Goldfields Superterrane. The area of study represents a high-strain segment of the UGB lying between the Riverina Gneiss (2674 ± 3 Ma; Dunphy et al., 2003) to the west and the Copperfield Monzogranite to the east. The mafic–ultramafic greenstone sequence exposed along the UGB most likely belongs to the 2720–2690 Ma Kalgoorlie Group (De Paoli et al., 2017). Farther to the north, at Maroon Hill, slices of amphibolite and metasedimentary units also occur as km-scale xenoliths within the Riverina Gneiss. The region of the UGB selected for study was identified based on intriguing reports by Goscombe et al. (2009) describing garnet-bearing amphibolite and kyanite-bearing mica schist, for which P – T conditions of 7–8 Kbar at ~600 °C were estimated. Given the dearth of reported high- P metamorphic assemblages or occurrences in Archean terranes, one of the aims of this study is to test the extent to which such high-grade rocks exist along the Ida–Ballard tectonic zone.

Low to medium-grade metabasites with interfingering metasedimentary rocks form most of the Archean greenstones within the UGB. However, P – T constraints are sparse and the nature of the greenschist- to amphibolite-facies metamorphism is poorly characterized throughout. This study will provide new P – T estimates and descriptions of the petrological characteristics of metamorphosed mafic–ultramafic rocks through to sedimentary/volcanoclastic and intrusive rocks of the UGB across the Copperfield area. We intend to apply an integrated approach grounded in detailed observations at map, hand sample and thin section-scales, together with inverse and forward phase equilibria modelling to enhance our understanding of the tectonometamorphic evolution of Archean greenstones in the UGB.

Application of geothermobarometry and phase equilibria modelling, in conjunction with petrographic observations, indicates a range in metamorphic conditions from greenschist to lower-amphibolite facies conditions within the Copperfield study area. The area is cored by a zone that comprises interfingering-to-layered, garnet-bearing pelitic mica schist and andalusite-bearing micaceous psammite, through to garnet-staurolite-bearing micaceous semipelitic

schist. This zone records at least two mesoscale, steeply dipping fabrics; a penetrative NNW-trending, layer-parallel foliation (S_1) and an overprinting, locally developed, axial planar to differentiated crenulation cleavage or foliation (S_2). The lineation (L_1) plunges moderately south, while a dextral shear sense prevails along the whole section. The S_1 and S_2 foliations are defined by at least two metamorphic assemblages indicative of: (S_1) high- T , low- P ($\sim 450^\circ\text{C}$, ~ 3 Kbar) conditions; and; (S_2) higher- T , high- P conditions related to progressive loading that is probably associated with transpression along the Ballard Shear Zone (Zibra, this volume). Metabasites, metagabbros and serpentinitized ultramafic schists on either side of the interlayered core zone record comparable metamorphic conditions, schistose fabrics and shear sense. Micro- and mesostructures indicate that porphyroblasts of garnet and andalusite have mostly dextral synkinematic sense-of-shear with respect to S_1 within the core zone, whereas both dextral and sinistral fabrics (typically wrapping sheared plagioclase phenocrysts), are present in the adjacent mafic-ultramafic sequence.

Preliminary fieldwork along the Ida Fault and Ballard Shear Zone, and detailed structural mapping in both the Copperfield and Marron Hill areas, has resolved several thin, metasedimentary layers within a dominantly mafic-ultramafic greenstone sequence. This metasedimentary layering was locally observed to contain abundant garnet, andalusite and associated staurolite porphyroblasts within a dominant metamorphic fabric defined by chlorite-muscovite in pelitic compositions, and muscovite-quartz in psammitic compositions. A metasedimentary rock located 28 kilometres to the south but along strike of the study area was sampled for geochronology, and gave a maximum depositional age of 2695 ± 5 Ma (Wingate et al., 2010). This provides a maximum age on metamorphism and is at least 30 Ma younger than the main high-grade metamorphic event reported along the Waroonga Shear Zone, approximately 150 kilometres farther north in the Waroonga Gneiss by Zibra et al. (2017).

Ultimately, this work will be integrated into a new regional-scale interpretation, which will refine important constraints for the tectonometamorphic evolution of the margin of the Eastern Goldfields Superterrane and the adjacent Youanmi Terrane. In a holistic sense, the data from this study will provide insight into the processes and relationships between metamorphism, regional deformation and granite emplacement in Neoarchean-Mesoarchean granite-greenstone terranes.

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Thermodynamics for metamorphism and deformation

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Metamorphism and deformation forms interesting patterns in space and time which can be attributed to multi-scale reaction-diffusion equations of heat, fluid flow and chemistry. This type of equation has been a playground for physicists and mathematicians interested in pattern formation with main applications in theoretical physics, quantum mechanics, chemistry, heat and biological phenomena. The theory is robust and transferrable to geoscience problems where quantitative analyses are sparse and no consensus exists about the appropriate thermodynamic framework for these far from equilibrium processes. The problem lends itself to explicit forward simulations. Unprecedented insights into the physics of metamorphism and deformation may be deciphered from the observed patterns, if we can harness the available compute power. Here we present the first steps in terms of a formulation of a basic approach which allows a scientific evaluation of the predicted patterns. This basic approach combines classical thermo-mechanics [Collins and Houlsby, 1997] with uncertainty evaluation and upscaling [Regenauer-Lieb et al., 2013a; Regenauer-Lieb et al., 2013b].

We consider a series of metamorphic reactions with multiple dissolution-precipitation reactions and fluid flow paths as in the model microstructure Fig. 1 by Wheeler [2014]. This system can be treated by two scales: a microscopic view of individual reactions and fluid flow and macroscopic thermodynamic view based on energy and entropy flows (Figure 1). Extending classical thermo-mechanics, we can write the rate of mechanical work for metamorphism and deformation as:

$$\dot{W} = \dot{\Psi} + T\dot{S} + T\tilde{S}^{irr} \quad (1)$$

where W is the work done through the applied stress, Ψ the Helmholtz free energy, T the absolute temperature and the total entropy $S = S^{rev} + S^{irr}$ is decomposed into a reversible processes transferring entropy from one portion to another of micro-system but not generating entropy and irreversible processes generating entropy [Tolman and Fine, 1948]. An over-dot specifies a complete time derivative and an over-tilde an incomplete time derivative.

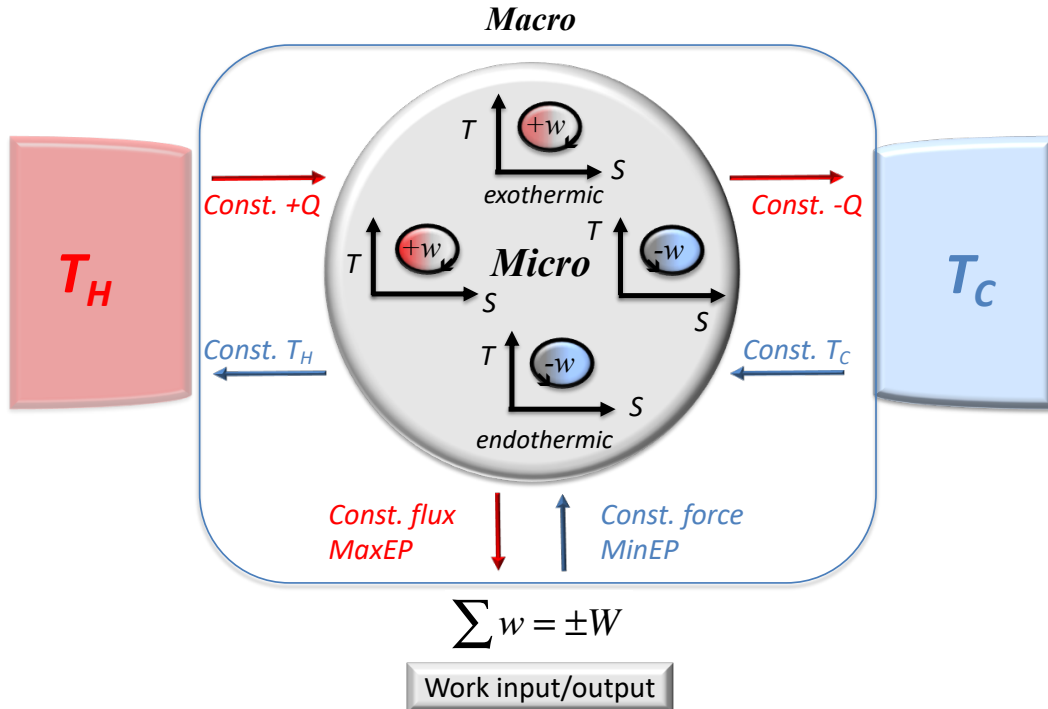


Figure 1 Thermodynamic abstraction of the model microstructure by Wheeler [2014]. The various dissolution-precipitation reactions are here depicted as exothermic or endothermic micro-engines, up- or downgrading entropy.

The distinction between complete and incomplete time derivatives is mathematically important as it introduces uncertainty in the macroscopic description. An integration of an incomplete time derivative features path dependence. In thermo-mechanics it is common practice to ignore the uncertainty from the incomplete derivative and assume a maximum of the entropy production [Ziegler, 1983]. This maximum entropy production principle can be derived from the fluctuation theorem [Evans and Searle, 2002]. The fluctuation theorem encapsulates the notion that the probability of positive entropy production over negative entropy production increases exponentially with time. Thus, for infinite time steady state is achieved, which is defined by a maximum of dissipation. This implies that the thermodynamic flux (heat flux in the example given in Figure 1) from the hot source into the micro-system is equal to the heat flux coming out of the system and the system is isothermal allowing to drop the second term in Eq. (1).

An alternative bound of the irreversible entropy production can be calculated if the system is driven by a sudden application of a constant thermodynamic force (a difference in temperature in the example given Figure 1) inducing time-dependent behaviour. In this case the system needs to be investigated using the concept of finite time thermodynamics [Andresen *et al.*, 1984]. It can be shown that the application of a constant thermodynamic force on the microsystem yields a lower bound of entropy production [Regenauer-Lieb *et al.*, 2010]. The above discussed uncertainty of the metamorphic system between upper and lower bounds hence becomes a problem where the uncertainty is attributed to a given time and length scale. For sufficient thermodynamic forcing the lower bound of the reaction-diffusion equation can trigger travelling wave solutions which create complex dynamic metamorphic patterns.

An independent derivation of the applicability of the simpler time-independent maximum entropy production limit can be derived if the time and length scale of the system is systematically increased. Entropy production of both upper and lower bounds converge when approaching large scale and ultimately coincide at the maximum entropy production (infinite time) limit of thermo-mechanics [Regenauer-Lieb *et al.*, 2014]. At infinite time the wave speed of the developing patterns can be equated to zero and standing waves are predicted for critical parameters. These standing waves produce more regularly spaced metamorphic patterns than their time-dependent siblings. This approach is strictly analogous to particle physics, where wave equations of subatomic particles incorporate the concepts of quantization of energy (micro-engines in Fig. 1), wave-particle duality (not discussed here), uncertainty principle and correspondence principles (recovering the classical geomechanics). We will illustrate a number of dissipative patterns that can be interpreted using the above described thermodynamic concepts and discuss how the entropic bounds can be used for thermodynamically based upscaling methods.

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Metamorphic reactions and the mechanics of compositional layering and lineation formation.

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The synchronous and diverse operation of different deformation mechanisms in aggregates of newly formed mineral phases of differing grain sizes during metamorphism can be analysed using a thermodynamically consistent generalised mixing model which takes into account chemical composition, grain size distributions and topological features of the microstructure. As the grain size for an individual mineral composition increases during grain growth the deformation mechanisms can change from bulk diffusion to grain boundary diffusion to various forms of grain boundary sliding to dislocation creep. The constitutive parameters such as activation energies, stress exponents and pre-exponential factors evolve during grain growth and as the composition changes. Once the grain size reaches a critical value grain size reduction processes operate driven by coupled grain boundary migration/grain boundary shear processes. The synthesis of all of these processes enables the construction of generalised deformation mechanism maps in which the evolution of flow stress during mineral reactions and grain size evolution is expressed as a function of grain size distribution, mineral chemistry, strain rate and temperature. The resulting stress strain curves at a constant strain rate have localised “bumps” arising from strain hardening and correspond to the introduction of new deformation mechanisms or chemical compositions. This means that the Helmholtz energy of the evolving deforming-reacting system is non-convex and the energy of the system can only be minimised by the formation of inhomogeneous microstructures including spot like clusters of like mineralogy, or compositionally defined layering and/or lineation. The generalised mixing law enables the Helmholtz energy to be defined as the grain size distribution and chemical composition evolves. We explore Cahn-Hilliard and Swift-Hohenberg representations of the Helmholtz energy to understand the conditions for formation of spot-like aggregates of like mineral, mineral lineations and mineral foliations in terms of the extent of mineral reactions, the relative proportions of various mineral phases, strain-rate, temperature and the type of deformation. We illustrate the approach using a natural example where a quartz-alkali feldspar rock deforms to produce an albite-oligoclase-K-feldspar-quartz-muscovite mylonite.

The influence of metamorphic reactions on localisation in deforming rocks.

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Mineral reactions during metamorphism produce grain size distributions of the various mineral phases involved. These distributions arise from the nucleation kinetics of individual minerals and evolve differently with time and depend on the nucleation and grain growth kinetics as well as on the mode of deformation. Grain size distributions present the opportunity for different deformation mechanisms to operate depending on the grain size. Typically grain size insensitive mechanisms operate at large grain sizes although in this mode of deformation the flow stress is sensitive to variations in chemical composition so that even though the stress is insensitive to grain size, softening or hardening can occur because of compositional changes. At smaller grain sizes various forms of grain size dependent deformation mechanisms occur involving grain boundary sliding and diffusion. All of these mechanisms can be represented on generalised deformation mechanism maps that incorporate changes on mineral chemistry as well as grain size, temperature and strain rate. The conditions for localisation in such materials are sensitive to the stress level, the hardening or softening modulus and the strain rate sensitivity of the material. Although softening is a necessary condition for localisation in viscoplastic materials it is not a sufficient condition. The critical condition for localisation is influenced by the strain rate sensitivity of the reacting/deforming system and this depends in turn on the microstructure. The conditions for localisation depend not only on the grain size distribution and chemical composition but also on the topology of the current microstructure. We use a thermodynamically based mixing law to explore the progressive evolution of these quantities and the resultant criterion for localisation in reacting metamorphic rocks as the grain size distribution, topology of the microstructure and mineralogy change during metamorphic reactions and deformation. An example is presented for the progressive conversion of a tonalite to a mylonite.

Influences of the elastic anisotropy of minerals on deformation and metamorphism

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What is elastic anisotropy and why is it important? Elasticity is a measure of the resistance of a body to applied force and is a fundamental continuum rheological property. Rocks and minerals exhibit elastic behavior, which is important in geosciences because it controls the transmission of acoustic waves through rocks, and precedes yield conditions for brittle and plastic deformation. Different aspects of elastic behavior are commonly represented by Young's modulus (E), which relates longitudinal stress and strain, shear modulus (G), which relates shear stress and shear strain, and Poisson's ratio (ν), which relates longitudinal to lateral strain. Minerals have directional variations in elastic properties (elastic anisotropy) that relates to their crystallographic structure. Elastic anisotropy is perhaps best utilised by geophysicists in calculations of seismic anisotropy. In structural geology and rock mechanics, minerals are commonly assumed to be elastically isotropic and scalar mean values of elastic moduli are used, and/or elastic strains are assumed to be small relative to plastic deformation and so ignored (e.g., in VPSC code). The effects of mineral elastic anisotropy is generally dismissed as insignificant and ignored in metamorphic petrology. This presentation investigates elastic anisotropy phenomena in minerals to stimulate discussion on their importance in geosciences.

Visualization of elastic anisotropy in minerals is vital in order to fully appreciate their complexity. For elastic materials in 3D, stresses and strains are related by a generalized Hooke's Law. Elasticity described by fourth rank tensors of stiffness and compliance – six by six matrices of elastic constants that relate the Cauchy stress tensor to the infinitesimal strain tensor. Elasticity tensors are not easy to visualize, and even recent studies of elastic anisotropy tend to report just one component of the stiffness (or compliance) tensor. This presentation utilizes an open source toolbox of MATLAB scripts for visualization elastic anisotropy in minerals (AnisoVis). The code produces linked 2D and 3D representations of E , G , and ν from input elasticity data for any mineral to encourage investigation and deeper understanding of directional variations in these fundamental properties. AnisoVis visualizes directional variations as rendered 3D surfaces, colour-contoured stereonet, and plots azimuthal variations along planar projections.

The results reveal complex 3D geometries that carry the symmetric elements of the crystal system but are unique to each mineral. All minerals are elastically anisotropic - even optically isotropic minerals. Typically, the magnitudes of the anisotropy of E , G , and ν are significantly high for most minerals, and many minerals display negative Poisson's ratio (auxetic behavior) in some directions. Examples are presented to show the effects of P and T on elasticity (e.g., quartz, feldspar), the effects of mineral composition on elastic anisotropy (e.g., feldspars, pyroxenes, olivine), the effects of elastic anisotropy on polymorphic phase transformations (e.g., zircon-reidite, Timms et al., 2018), and links to deformation mechanisms (e.g., zircon, Timms et al., 2018). It is clear that the directional variations of elastic properties of rocks and minerals have significant consequences for their physical response to natural or imposed stresses. Yet, the effects on grain-scale processes such as the distribution of intra- and intergrain stresses and strains in stressed rocks in deforming rocks, consequences for deformation mechanisms, and ultimately the effects on metamorphic reactions has not been fully investigated.

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Modelling the Evolution of Metamorphic Rocks: Effects of Inhomogeneous Pressures

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We describe the chemo-mechanical interactions of rocks which lead to phase transformation and cracking. In particular, we model reaction-diffusion processes that generate physical and chemical changes in metamorphic rocks. Such processes, control the evolution of the metamorphic system by setting the inhomogeneous pressure distribution of quartz inclusions in garnet. A related process is the growth of new minerals along the boundaries between reactant minerals, which yields the rim growth associated with reactive minerals. From metamorphic petrology, we know that the chemical processes in rocks trigger substantial volume changes which induce stresses that lead to cracking. We model chemical interactions in rocks as reaction-diffusion phase-transformation processes. We also relate and model the interleaving between the chemo-mechanical interactions. Finally, we study the fracture formation as a consequence of such chemo-mechanical interactions. Herein, we summarize the main ingredients for the modelling and description of these stages.

Fluid escape structures from reacting and deforming rocks

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The thermodynamic framework of solids during metamorphism and their ductile deformation has been successfully described by thermodynamics and mechanics of fluids and gases. Enigmatic observations at various scales have been often non-critically assumed to be the evidence of an insufficiency of this oversimplified treatment of solids and their related reaction kinetics. I will argue that problems are actually coming from an oversimplified treatment of the relevant fluid dynamics. Reactions and deformation are driven by changes in pressure, P, temperature, T, and composition. P and T are, solely for simplicity reasons, almost universally assumed to follow the hydrostatics of incompressible fluids. Either the system composition or the chemical potentials are usually kept constant in the course of thermodynamic calculations. This simplistic treatment of reacting and deforming fluids eliminates the quantification of well-established fluid dynamics phenomena, such as detonation and combustion waves. Even much slower chemical transformations, for instance related to flames propagation and fluid-gas phase transitions, are often associated with substantial lateral P and T gradients due to the large volumetric and latent heat effects of the transformations. Equilibrium thermodynamic relationships successfully used in these contexts do allow for high spatial and temporal variability of the pressure, temperature and very high reactions rates due to large overstepping of the reaction boundaries. These thermodynamic approaches and similar used in petrology¹ work well regardless if pressure gradients are supported either by inertial or viscous forces and temperature gradients are caused either by the slowness of heat conduction or by boundary conditions. Mathematical models which are coupling compressible fluid mechanics and thermodynamics are well established and validated by experiments. For example, reactive gas-dynamic simulation of meteorite or rocket burning in ‘dense’ atmosphere would not demand completion of all chemical reactions to be able to utilize the concept of ‘local thermodynamic equilibrium’. Very slow geological processes may be well treated by incompressible hydrostatics and equilibrium phase diagrams. Much faster coupled reaction/deformation processes -up to earthquakes time scales- must be first studied by well-established approaches of reactive fluid dynamics. I will present several case studies of thermo-hydro-mechanical-chemical (THMC) coupled models demonstrating robustness of classical thermodynamics to allow for highly dynamic and spatially variable P, T and other state functions. HM model² investigates non-lithostatic solid and non-hydrostatic fluid pressures. Local equilibrium HC³ and HMC⁴ models deal with reactive density and porosity changes in non-isobaric systems. Allowing for reaction kinetics revealed⁵ new fluid escape mechanism in HMC model. Allowing for melting overpressure and temperature rise due to shear heating results in crustal model for ultrafast eclogite formation⁶.

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Why an understanding of diffusion creep is key to the debate about the effects of stress on chemical change in rocks

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As the conference title indicates, stress and chemical processes in rocks are linked. I have created an internally consistent framework for how this may be understood (Wheeler, 2014; Wheeler, 2018) which remains controversial. For me it is self-evident that one manifestation of the link is the process of diffusion creep (or the “wet” equivalent, pressure solution). In this, differential stresses give rise to different normal stresses on different interfaces, which give rise to different chemical potentials for the stressed phase(s), which drive diffusion. Even if diffusion is sluggish, the stress-related driving force is always there. Some works critical of mine pay no attention to diffusion creep, or mention it without acknowledging its significance. These works then make assertions incompatible with the existence of diffusion creep as a process; examples follow.

- It is assumed that there will be an equilibrium in a stressed system, a claim which despite being incorrect has triggered great effort to characterise such an equilibrium. Diffusion creep tells us that a phase *is not even in equilibrium with itself* in a stressed system, so I cannot conceive of how a multiphase global equilibrium can be postulated. Pressure solution and diffusion creep can be explained using *local* equilibria, in the absence of *global* equilibrium.
- It has been proposed that the mean stress can be used in place of pressure to make calculations related to equilibrium in stressed systems. Imagine a uniformly stressed grain of quartz. In such a scenario the mean stress is the same everywhere, and the chemical potential will be the same everywhere so there is no driving force for pressure solution or diffusion creep. How can this scenario be made compatible with the theory for pressure solution, which has been repeatedly tested? It can't.
- Confusion arises over the role of grain boundary films, fuelled by sometimes unhelpful nomenclature. Rocks may have pores with fluid, but the solid-solid boundaries will in general support normal stresses higher than fluid pressure. Despite this there is abundant evidence that H₂O rich films can exist along grain boundaries, without being squeezed out. Therefore they support stress, and should *not* be referred to as “fluid films”. In the pressure solution literature this idea has been widely accepted for decades e.g. “the diffusion of matter in an aqueous intergranular film which can support shear stress is an essential part of the process” (Rutter, 1983); “grain boundaries are considered to contain fluid in some interconnected form which cannot be squeezed out” (Spiers, *et al.*, 1990). There is a huge body of work on how stress relates to boundary aqueous film thickness (Israelachvili, 2011). In contrast, the phrase “fluid film” has led to a mistaken vision that, when there is a fluid in pores, and grain boundaries contain aqueous films, those films are at a pressure equal to the fluid pressure P_f . Were this to be the case, a rock where every grain was surrounded by a film at pressure P_f , no differential stress could be supported by the rock as a whole. This is a purely mechanical assertion but it shows the limitations of such a vision – we can't set up a mechanical description of stressed rocks, let alone a chemical one.
- Force of crystallisation can be explained using a model of stressed grain boundary films, just as pressure solution is and with the same mathematics, for example (Wolterbeek, *et al.*, 2018).
- We do not in fact even need grain boundary film for diffusion creep. We just need grain boundaries. In the original papers predicting such a process, the normal stress at the interface is recognised as controlling the chemical potential there (Herring, 1950).

Differences in chemical potential create gradients *inside* the lattice which lead to Nabarro-Herring creep. The boundaries are just sources and sinks for vacancies. For grain boundary diffusion, if an effective boundary width is proposed then a flow law is deduced (Coble, 1963) which works just as well today as it did 50 years ago. The deduction does not need a particularly detailed knowledge of the grain boundary structure, but is founded on the fundamental effect of normal stress. Not mean stress. Normal stress.

In summary, the way forward to understand chemical effects in stressed systems is to create and test models based on *rates* of processes, underpinned by *local* thermodynamic equilibria, whilst accepting that no global equilibrium can exist. There is a vast spectrum of interesting behaviour to explore, starting here.

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Interplay between deformation and chemical diffusion: An example from mechanically-controlled microstructures

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Recent microstructural observations show that the heterogeneity of material given by different material properties can lead to the development of heterogeneous stress and pressure distributions at all scales as well as to unexpected chemical gradients. Such heterogeneous microstructures are called mechanically-controlled (e.g. Zhong et al., 2017). In fact, mechanically-controlled microstructures, e.g. inclusion–host environment, preserve information on pressure and stress behaviour at geological time scale. The pressure variation can be determined from maintained chemical zoning in such microstructures by specialized equilibrium thermodynamic approach (Tajčmanová et al., 2014; 2015).

In the classical view of metamorphic zoning, fast viscous relaxation (and therefore constant pressure) across the microstructure is assumed, with chemical diffusion being the limiting factor in equilibration. We have focused on the other possible scenario – fast diffusion and slow viscous relaxation – which brings an alternative interpretation of chemical zoning found in high-grade rocks. Here, we provide insight into the role of mechanically maintained pressure variations on multi-component chemical zoning in minerals.

In this contribution, the appropriate modification of a macroscopic flux for a system with a pressure variation is derived and a consequence of using mass or molar units in diffusional fluxes is discussed. The use of appropriate units in the equations for fluxes for a system under pressure variation is essential because the sign of the molar volume and the density difference can be opposite, and this can significantly influence the trend of chemical zoning.

Furthermore, we show that mechanically-controlled petrographic observations serve as witnesses of the stress state of the Earth's interior and can be thus used to infer rheological properties to improve the extrapolation of experimental data. We document that metamorphic rocks produced in orogenic belts as an outcome from natural processes over geological time scales may be a source of unique rheological constraints and a calibration for the extrapolation of laboratory measurements. The new calibration offers a unique opportunity for considering the rheological behaviour of minerals that experienced long-term deformation at natural conditions.

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Feedbacks between fluids and deformation in the upper mantle

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Experiments and theoretical considerations predict strong feedbacks between deformation and melts, namely strain localization controlled by the presence of melts or fluids and fluids/melt focusing controlled by deformation. Yet, peridotite massifs and mantle xenoliths, which record deformation and melt/fluids transport through the shallow mantle (lithosphere and lithosphere-asthenosphere boundary), feature a wide variety of relations between melts and deformation. I will present some of these observations, which range from strong feedbacks between deformation and fluids/melt distribution to weak relations between the two processes, focusing on recent petrostructural studies of the pargasite and phlogopite-bearing Finero peridotite massif (Italian Western Alps) and in mantle shear zones of Zabargad, which record the last stages of rifting in the Red Sea. The former observations (Tommasi et al., 2017) indicate that the presence of hydrous melts in a deforming peridotite allows for accommodation of large amounts of deformation by stress-controlled dissolution–precipitation and advective transport of matter by the melts and in fast grain boundary migration in olivine. It produces therefore significant rheological weakening in the upper mantle. However, this weakening is transient. Total crystallization or extraction of the melts is accompanied by a marked change in dominant deformation processes and strengthening of the peridotites, leading to onset of strain localization. The latter is not correlated to the local abundance in pargasite or phlogopite, implying that crystallization of amphiboles or phlogopite, even at concentrations of 25 vol.%, does not produce rheological weakening in the upper mantle. Petrostructural observations in the Zabargad peridotites point to progressive strain localization associated with decreasing temperature conditions and correlated with a change in the composition of the percolating fluids, from melts to mantle derived fluids to sea-water contaminated aqueous fluids. In mantle shear zones in Zabargad (Red Sea) and in the Ronda peridotite (S Spain, Hidas et al. 2016), the presence of fluids allowed for activation of dissolution-precipitation, but at a lesser extent than hydrous melts in Finero and the associated weakening is probably much smaller. Similar conclusions may be derived from the analysis of the shallow mantle in the Oman ophiolite and in the Lanzo peridotite, where there is microstructural and geochemical evidence for shear-controlled segregation of the melt, but poor support for melt-controlled strain localization (Higgie & Tommasi 2012, 2014). Altogether, these observations point to a strong control of the deformation on the fluids percolation. They also suggest that the effect of the presence of fluids or melts on the mantle rheology is more complex, being strongly dependent not only on the fluid fraction, but also on its composition.

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Neoproterozoic $^{40}\text{Ar}/^{39}\text{Ar}$ mica ages mark the termination of a billion years of intraplate reworking in the Capricorn Orogen, Western Australia

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The tectonic history of the Proterozoic Capricorn Orogen, Western Australia, records complex intraplate reworking lasting nearly one billion years. Although the Paleo–Mesoproterozoic reworking history is well defined in the crystalline basement of the Gascoyne Province, at the western end of the orogen, the younger reactivation history remains unclear. Four reworking events affected the orogen at 1820–1770 Ma, 1680–1620 Ma, 1320–1170 Ma, and 1030–900 Ma. These events were succeeded by a breakout in predominantly dextral strike-slip reactivation of major shear zones across the Gascoyne Province. Currently, the age of this reactivation is constrained by only one date of c. 570 Ma from a single shear zone, but field relationships imply that some of the shear zones must be older than a suite of c. 755 Ma dolerite dykes. In order to constrain the age of fault and shear zone reactivation we obtained new $^{40}\text{Ar}/^{39}\text{Ar}$ dates for mica and *in situ* SHRIMP U–Pb dates for xenotime within shear zones. Our results when combined with previously published data, show that reactivation occurred between 920 and 830 Ma. These dates overlap with the youngest reworking event, the 1030–900 Ma Edmundian Orogeny. Furthermore, Neoproterozoic U–Pb phosphate ages are known from the bounding cratons and faulting within the adjacent Mesoproterozoic sedimentary basins suggest this event is of regional significance. In contrast to previous suggestions that this Neoproterozoic reactivation was the result of a collision from the west, we propose that it reflects north-south compression that caused dextral strike-slip fault reactivation in the north and exhumation of the southern part of the orogen.

Unravelling the structural and metamorphic evolution from MT–MP to LP–HT: a journey through the crust in the Georgetown Inlier (NE Australia)

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Globally pervasive 2.1 to 1.8 Ga orogenesis has previously been suggested to represent the amalgamation of the Nuna supercontinent. However, more recent evidence suggested ongoing orogenesis until ~1.6 Ga (Nordsvan et al., 2018; Pourteau et al., under review).

In NE Australia, the Proterozoic Georgetown Inlier has been identified as an allochthonous terrane, possibly sourced from Laurentia, sutured to the North Australian Craton during the final phases of the Nuna amalgamation. To test this record and unravel the tectono-metamorphic evolution of the Georgetown Inlier we combine a multi-scale structural analysis with petrological observations, thermodynamic modelling, and geochronology.

The Georgetown Inlier is characterised by metasedimentary rocks intruded by ca. 1580–1550 Ma granites that are overlain by flat-lying non-metamorphosed ca. 1552 Ma felsic volcanic rocks. At the inlier scale, the metamorphic grade increases eastward from the lower greenschist facies to the lower granulite facies (Withnall 1988; Boger and Hansen, 2004). Field and microstructural observations indicate that the dominant foliations striking NW–SE (S3) and E–W (S4) are defined by a retrograde greenschist facies mineral assemblage replacing earlier MP–MT and HT–LP assemblages. In D3 and D4 low strain domains, earlier foliations are preserved. These fabrics were re-oriented, transposed and overprinted during D4. The S2 fabric has a N–S enveloping surface; however, in places, S2 was re-oriented into a composite S2–S4 E–W striking differentiated crenulation cleavage. In the Robertson River area, the S2–S4 foliation is defined by SPO (shape preferred orientation) of Bt and LPO (lattice preferred orientation) of Qz–Ilm, where Grt porphyroblast is pre- to early-S2 and locally preserves an earlier fabric (S1), while St is early- to syn-S2 (Bell & Rubenach, 1983; Passchier and Trouw, 2005). Garnet Lu–Hf geochronology and pressure–temperature estimation indicate prograde medium–P/T metamorphism at 1598 ± 6 Ma (Pourteau et al., under review), likely associated to the S1 or early-S2 history. Staurolite was replaced by andalusite growing late-S2, while in the vicinity to the granites sillimanite replaced andalusite. The sillimanite assemblage (Sil–Bt–Grt–Pl–Kfs–Qz) has a wide stability field (570–650 °C, 0.5–0.65 GPa). Locally, it is associated with partial melting of metasedimentary rocks related to the regional thermal anomaly caused by the emplacement of granites between ca. 1580–1550 Ma. The S-type granites in the central and eastern Inlier record S3 and S4 foliations. This evidence suggest that the granites were emplaced late- to post-S2. On the other hand, in the eastern migmatitic complex partial melting of paragneiss occurred early-, syn-, to post-S2 (Hills, 2004). S2 in the migmatitic paragneiss is defined by a Sil–Bt–Grt–Pl–Kfs–Qz–Ilm HT assemblage, stable between 700 to 820 °C and 4 to 8 kbar.

The ca. 1.6 to 1.5 Ga evolution of the Georgetown Inlier indicates that orogenesis occurred on hot immature crust, not suitable to record higher pressure mineral assemblages.

However, the unique continuous lithostratigraphic crustal section from the lower greenschist facies (upper crust) to the granulite facies in the east (lower crust) reflects how the most evolved fabric and its defining assemblage define different dominant metamorphic overprints in the same crustal volume (Spalla et al., 2005) in different times and different thermal conditions. The petro-structural observations and the P – T estimates clearly show differences from a modern style continental collision which are characterised by substantial crustal thickening. Furthermore, concurrent orogenesis in other Australia Proterozoic terranes show similar evidence for hot orogenic events and minor crustal thickening (McLaren et al., 2005; Cutts et al., 2013), suggesting that these ca. 1.6 Ga events might have implications for the evolution of the Nuna supercontinent.

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Diffusion Creep in Eclogites: Relationships between Mineral Reactions and Deformation

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Eclogites are the most important pieces of evidence for subduction of oceanic crust. Different lines of argument suggest low stresses and episodic seismic deformation for the deformation of eclogites (e.g. Stöckhert 2002). Many eclogite bodies are weakly deformed but usually are characterized by strong crystallographic preferred orientation (CPO). The CPO is often used to infer crystal plastic deformation (dislocation creep) with a dominant Burgers vector [001] for omphacite. However, extrapolation of experimental data (Moghadam et al. 2010) indicates high stresses for dislocation creep of jadeite and omphacite dominated lithologies.

We are presenting new data for naturally deformed eclogite samples from the Bohemian Massif and from the Tauern window. In both sample sets the CPO of omphacite is strong and consistent with previously observed patterns. However, chemical data of omphacite and garnet indicate well developed mineral zoning for individual grains that are inconsistent with dynamic recrystallization. Instead, the zonation patterns indicate preferential growth of omphacite and garnet in the elongation direction during deformation and that deformation took place over a large part of the prograde (pressure increasing) P,T-path. Garnet grains do not show any CPO. Aspect ratios of omphacite grains are higher than those of garnet indicating faster growth rates of omphacite in the elongation direction. These observations suggest deformation by diffusion creep rather dislocation creep. The results are consistent with low stresses during deformation. The CPO of omphacite appears to form from a preferential growth of grains which have their [001] direction parallel to the extension direction during deformation (preferential growth of certain orientations). Garnet appears to grow preferentially in the extension direction regardless of the crystal orientation. Neighbourhood relationships of omphacite and garnet indicate a random distribution and are consistent with homogeneous (random) nucleation of the phases. Only quartz grains are clustered with garnet at the strain shadow sides of grains. The clustering of quartz is explained by strain compatibility during growth of omphacite and garnet: the faster growing omphacite causes dilatancy by grain boundary sliding (Lifshitz sliding) at the ends of garnet grains, leading to the precipitation of quartz.

The zonation patterns are not truncated at grain boundaries normal to the shortening direction but growth rims are only thinner at these sites indicating that diffusion creep did not operate by dissolution – precipitation. Only preferential growth accommodated the shape changes. The growth can only occur while there is a reservoir of reacting minerals available, consistent with the prograde reaction path. Given the aspect ratios of grains and the pressure changes involved in the reactions, strain rates for the eclogite deformation can be estimated to be on the order of 10^{-13}s^{-1} .

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Episodic deformation and mineral growth – the record of mylonites from the DAV, Eastern Alps

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During deformation and metamorphism of rocks, nucleation and growth of minerals takes place driven by the reduction in strain energy and by chemical disequilibrium. During strain-induced grain boundary migration (SIGBM) crystalline volume with high stored strain energy is replaced by strain-free crystal volume. Grain boundary migration can also be driven by the reduction in interfacial free energy (grain growth), and/or driven by chemical disequilibrium. Given the relative high contribution of stored strain energy introduced by dislocations, compared to interfacial free energies and chemical driving forces, SIGBM is usually dominating during crystal-plastic deformation (e.g., Stünitz, 1998). In dislocation-free crystalline volumes and/or at high chemical disequilibrium, the other driving forces for grain boundary migration are effective. Grain boundary migration might also involve rotation of grains or subgrains by coupled dislocation glide, so called coupled grain boundary migration (e.g., Hobbs and Ord, 2015). “Nucleation” in the sense of grain size reduction might be involved, e.g. by subgrain rotation at sites of high strain or by heterogeneous nucleation of a new phase in case of high chemical driving forces. The relative contributions of these processes are dependent for example on pressure, temperature, stress, strain-rate and material, including fluid availability. Here, we present microfabrics in quartz-rich mylonites from the Deferreggen-Antholz-Vals (DAV) shear zone in the Eastern Alps that underwent deformation and metamorphism during Early Alpine (Eoalpine, $450\pm 50^\circ\text{C}$) and Late Alpine ($300\pm 50^\circ\text{C}$, main activity of the DAV) times (e.g., Stöckhert 1984; Mancktelow et al., 2001; Schulz et al., 2008). We discuss how deformation, nucleation and growth during the microfabric development of the mylonites are related.

The mylonites comprise about 80% quartz with minor amounts of albite, mica, garnet, tourmaline and monazite surrounded by apatite, allanite and epidote forming a corona microstructure. Elongate quartz grains with long axes of several hundreds of μm and width of a few tens of μm define the main foliation and represent a first stage of deformation. The elongate quartz grains show c-axes aligned preferentially in a plane perpendicular to the long axes of grains. Grains oriented with the c-axes parallel to the y-axis of the finite strain ellipsoid show the highest aspect ratio, indicating prism $\langle a \rangle$ glide. Dislocation glide probably coupled with grain boundary migration is the dominating deformation mechanism. The elongate shape of the corona microstructure aligned in the foliation and deflecting it, indicates coeval metamorphic breakdown reactions of monazite. A shear band cleavage (C' -type) with one dominating set of cleavage planes at an angle of $30\text{--}45^\circ$ to the main foliation represents a second deformation stage. Biotite and fine-grained quartz are present within the shear bands. Garnet and tourmaline commonly show an elongate bookshelf structure within the first foliation. The sense of shear indicated by the bookshelf structure is consistent to that indicated by the shear band cleavage. All rock-forming minerals, including quartz indicate fracturing during shear band formation. Biotite, quartz and albite can occur within the interspace between the fragments. Small isometric quartz grains with diameters $< 10\ \mu\text{m}$ within the cleavage planes are commonly strain free and characterized by a high grain boundary porosity, suggesting a stage of nucleation with the involvement of precipitation from the pore fluid. The preferred orientation of new grains with the c-axis perpendicular to the shear bands on the other hand indicates the contribution of dislocation glide coupled to grain boundary migration during growth. Larger grains with internal misorientation and sutured grain boundaries indicate strain-induced grain boundary migration. In contrast, the new strain-free quartz grains show a foam

structure with small convex grains and coarser concave grains with the angle between boundaries at triple junctions is 120°. This foam structure indicates that grain boundary migration was eventually driven by the reduction in interfacial free energy after deformation.

The microfabric reflects the difference in rheological behaviour of the rock during different stages. The elongate quartz grains indicate deformation by dislocation glide as dominant mechanism during an initial stage. Dislocation glide-controlled deformation requires high differential stresses on the order of a few hundred of MPa and high strain rates on the order of 10^{-10}s^{-1} at the relevant temperature conditions of $450\pm 50^\circ\text{C}$. At this stage, the pore fluid pressure must have been low in order to allow for such high differential stresses. At a later stage of greenschist facies conditions at which biotite was still stable, the shear bands formed associated with fracturing of the rock-forming minerals. Distributed fracturing at these conditions indicates high differential stresses and strain rates. Pore fluid pressure increased transiently, probably related to increased connectivity of the pore space due to fracturing, where mainly quartz and minor biotite precipitated from the pore fluid along the shear band cleavages and in the interspace between fragments. The preferred crystallographic orientation of quartz grains within the shear band indicates that growth was coupled with dislocation glide during ongoing deformation. Yet, deformation after sealing of the fractured rock eventually ceased and grain boundary migration of small new grains was driven by the reduction in interfacial free energy at low differential stresses. The quartz mylonite from the DAV records episodic deformation and mineral growth, with transiently high and then relaxing stresses as well as episodic fluid availability.

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The Role of Dissolution and Precipitation in the Development and Evolution of Phyllonites, or Mind your Ps and Qs

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Geochemical modelling of grain boundary fluid compositions in the context of microstructural observations and microchemical data shows that both the initial development of phyllonites and the subsequent metamorphic differentiation of those phyllonites can be explained by a pressure solution-precipitation mechanism. The phyllonites under examination occur in the East Derby Shear Zone (EDSZ), south-central Connecticut, USA, and contain multiple generations of lower greenschist facies Alleghanian cleavages overprinting a staurolite/kyanite-grade Acadian schistosity in the Wepawaug Schist. As the ~500m wide EDSZ is approached from the east, the schist displays progressively greater degrees of replacement of staurolite, garnet, biotite, and eventually Na-rich muscovite ($X_{Pg} = 0.2-0.3$) by Na-poor muscovite ($X_{Pg} \sim 0.05$) \pm chlorite. Na-rich muscovite cores rimmed by Na-poor (Alleghanian) rims are identified by WDS element mapping and electron microprobe analysis confirms the high-grade and low-grade crystallization of cores and overgrowths, respectively. Muscovite grains in overprinting, Alleghanian cleavages are themselves zoned (Growdon et al. 2013; this study; see also McWilliams et al. 2013;), and truncate Acadian micas preserved in microlithons. These features establish a dissolution-precipitation mechanism for the development of these overprinting cleavages, and are inconsistent with dislocation creep. .

One common characteristic of these Alleghanian slaty cleavages is the concentration of phyllosilicates into “P-domains,” and the concentration of framework silicates into quartz- and feldspar-rich “Q-domains.” Early generations of Alleghanian phyllonitic cleavages in these P domains (identified by ⁴⁰Ar/³⁹Ar dating) are defined by coexisting Na-poor muscovite + chlorite, whereas later crosscutting cleavages contain exclusively Na-poor muscovite. The differentiation of muscovite from chlorite (and from quartz and albite) can be explained by an examination of the compositions of the grain boundary fluid attending this differentiation. Indeed, the solubilities of chlorite, quartz and albite as calculated by SUPCRTBL (Zimmer et al, 2016) increase relative to muscovite at high pressure. High pressures occur at sites of high normal stress perpendicular to the developing cleavage, where $P_{fluid} \sim \square_1$ (e.g. Spiers 2004). At these sites the aqueous stability field of muscovite increases at the expense of chlorite and albite. Here, muscovite precipitates as chlorite and albite dissolve, leaving an increasingly pure muscovite P-domain. Conversely, at extensional sites of relatively low normal stress where $P_{fluid} \sim \square_3$, the solubilities of chlorite and albite decrease and thus precipitate. As a result extension in Q-domains leads to the precipitation of and the increasing concentration of new quartz and albite \pm chlorite. In fact some extensional sites are filled exclusively by chlorite. In fact, these chlorite veins can be progressively transposed into the dominant fabric to produce bands of pure chlorite (e.g. Wintsch and Yea, 2013).

The significance of this work is the conclusion that the development of these phyllonites occurred entirely by a dissolution-precipitation mechanism. This conclusion suggests that the use of experimentally derived dislocation creep flow laws for phyllosilicates (e.g Shea and Kronenberg, 1993) in similar rocks does not apply to these phyllonites. Clearly, deformation accommodated by dislocations migrating through a crystal lattice cannot explain the zoning of individual muscovite grains, the truncation of Na-rich muscovite grains by Na-poor muscovite grains, and especially not the metamorphic differentiation of the P-domains. The direct and important implication is that pressure solution creep is activated at even lower shear stresses than is dislocation creep at least under greenschist facies conditions.

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Localised deformation and carbonate alteration during gold mineralisation

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Massive fluid-flux and alteration halos many metres wide are typical features of orogenic gold deposits characterised by broad potassic and sodic alteration halos, sulphidation of oxide phases, silicification and carbonate alteration of the host rocks. At Jundee Gold Mine, Western Australia, gold occurs in super high grade zones (>1000 g/t) with an associated quartz-carbonate-sulphide alteration assemblage, which appears no different to most other orogenic gold deposits. However, the alteration zones that surround the super high gold grades are unusually narrow, typically only a few centimetres wide.

We have examined a number of mineralised intervals from a single lode at Jundee to identify the key microstructural features of the super high grade mineralisation and understand how this unusual deposit formed. Drill-cores are examined with continuous line-scan X-ray fluorescence (Minalyze) and hyperspectral logging (Hylogger) to quantify mineralogy and any subtle changes in geochemistry not visible in the core. Sub-samples of 30-50 cm were taken and mapped using the new Maia Mapper μ XRF mapping system to show microscale variations in trace element chemistry. Finally, thin-sections and polished blocks were examined by scanning electron microscopy and electron backscatter diffraction to establish key relationships in the mineral paragenesis and focus on the processes that accompanied gold mineralisation.

The continuous XRF logging shows that many of the mineralised zones occur at interfaces either between intrusives of apparently similar mineralogy but subtly different chemistry, or completely different rock types. In a number of cases where these contact appear faulted the alteration is asymmetric with respect to the lithological boundary showing a strong link between deformation and alteration. At the scale of the drill core, the alteration halos are zones with respect to their chemistry with broad potassic halos, surrounding carbonate haloes, which themselves surround intense silicification. At the larger, lode scale, the carbonate and silica alteration intensity decreases upwards, as does the gold grade, but the rocks still show added potassium, sulphur and arsenic.

A combination of micro-XRF and phase mapping shows the distribution of veins and more pervasive carbonate and silica alteration in key high-grade samples. The key observations from these datasets are as follows:

- Metamorphic albite is replaced by K-feldspar and muscovite in sulphide-bearing rocks,
- Several chemically distinguishable carbonate vein sets,
- Carbonate and quartz veins are mutually cross cutting,
- Super high gold grades are associated with the margins of intense carbonate alteration in an otherwise silicified rock,
- The most altered samples consist of chlorite, calcite and quartz, and
- Gold occurs in a range of microstructural settings including fractures in pyrite, distributed through the matrix, and at vein margins.

Electron backscatter diffraction (EBSD) datasets show that in pervasively carbonate altered wall-rock zones that are rich in gold, the calcite is strongly deformed and undergoing dynamic recrystallisation. These wall-rock zones have been cut by later calcite veins and these are also deformed by dislocation creep. Recrystallisation has occurred by a combination of subgrain rotation and grain-boundary migration. In the gold-rich zones, the calcite is fully recrystallized

with very little internal deformation remaining. We interpret these microstructures to show that fluid flow is occurring during ongoing deformation with repeated cycles of veining and dislocation creep and that the gold has been introduced relatively late. The fluid flow associated with gold deposition has driven rapid recrystallization of the surrounding, deformed rocks.

Thermodynamic, flow-through models show that the range of observed mineral assemblages can be achieved by progressive fluid flow of a single fluid that adds sulphur and dissolved calcite to the rocks. A CO₂-bearing fluid alone is not sufficient to produce the amount of calcite observed throughout the highly altered zones. The fluid flow up fault zones and alters the wall-rocks asymmetrically with alteration preferentially located in the hanging-wall side of the faults. Rheological contrasts produced by different units are sufficient to localise intense brittle deformation even when the units are of a similar rock-type. Following the initial alteration, producing calcite rock rocks, further deformation continues by dislocation creep of calcite with intermittent fracturing to cause new veins. Models show that the reactions that produce the chlorite-calcite assemblage also produce a large volume of quartz which explain the mutually cross-cutting quartz-calcite veins and removing the need for a separate silica bearing fluid. Gold is introduced late in the sequence of events because it is often surrounded by undeformed, recrystallised calcite. This study highlights the complex interplay between fluids, reaction weakening and switches in deformation mechanisms caused by transient fluid flow during gold mineralisation in Archean rocks.

Modelling the formation of Bonanza-grade ore deposits

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The formation of large ore deposits remains a challenging scientific problem, involving many complex aspects that have been previously organised as a series of five main questions (Walshe et al., 2005). Taking this mineral system approach, we focus in particular on the (fourth) question regarding the identification of fluid pathways and underlying driving forces, to try and understand how deep mineralising fluids can pass through the low permeability crust and form deposits close to the surface. While the nature of those fluids and the transport method for gold remain open, whether the processes involve interaction of immiscible fluids (Fuchs et al., 2017) or vapour phase (Mei et al., 2018), most scenarios involve large gradients of temperature and pore-pressure for the ore to precipitate. Such gradients can be obtained from the rapid cooling and depressurisation of deep fluids propagating along faults that reactivate temporarily (Cox, 2016), and the episodic nature of such phenomena is also well accepted (Cox, 2016).

A model was proposed (Alevizos et al., 2014) that can explain mathematically how the in-situ generation of fluids under specific conditions can lead to the episodic slip of faults, marked by a simultaneous increase in permeability by orders of magnitudes, as observed in nature (see Fig.1). The behaviour of this chemo-mechanical oscillator is due to the endothermic nature of the chemical reactions considered, thermally activated and producing over-pressurised fluid when triggered. This oscillator can either lead to slow steady creep, fast creep initiated by one or more slip events, or episodic instabilities, depending on the parameters of the system. In the case of episodic stick-slip events, this system describes well the sharp localisation patterns observed, both in space and time. Cascading length-scales from the millimetre-scale principal slip zone, to the meter-scale fault core and kilometre-scale displacements (Poulet et al., 2014a) can be linked to episodic tremor and slip events (Poulet et al., 2014b) as they all represent different aspects of the same phenomenon.

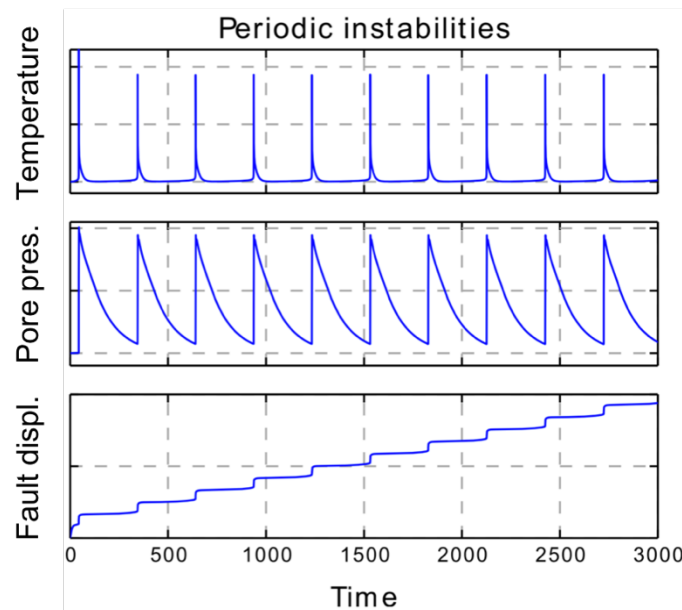


Figure 1 Evolution of temperature, pore pressure and fault displacement, for a chemical shear zone in the regime of episodic instabilities. Note that all properties are dimensionless.

This model remains a simplified representation of an extremely complex process, and has only been applied so far to closed systems as a starting point. Such oscillators have indeed to be incorporated in larger systems to investigate open chemical reactors as pointed by Hobbs & Ord (2018). In this contribution, we present an analysis of the parameter space to determine which sets of parameters can lead to the episodic stick-slip behaviour, as well as a multi-scale numerical framework based on the Redback simulator (Poulet et al., 2017) to solve the problem numerically. We incorporate the chemo-mechanical oscillator at the meter-scale as an interface into a kilometre-scale Finite Element model and investigate the impact of those episodic fault reactivation events on the propagation of deep fluids along the fault.

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Hydration of periclase breaks peridotite under serpentinization conditions

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Serpentinization of the oceanic crust along low-velocity spreading ridges or at subduction zones is a major hydration reaction on Earth, with important geodynamic consequences for the rheology and the cycle of water in the oceanic and continental crusts. This reaction produces a large volume increase of the rock, between 20 and 40% and occurs through reaction-driven fracturing controlled by stresses generated by the volume increase.

Here, we have performed laboratory experiments where we demonstrate that a peridotite specimen can be fractured during the hydration of periclase (MgO) into brucite (Mg(OH)₂), the reaction occurring with a volume increase of 110%. Two specimen of peridotite, 5 mm diameter and 1 cm height, were cored with a central hole 2 mm diameter in which a cylinder of microporous periclase was inserted. Then, confining pressure and a temperature of 200 degrees C were applied before water was injected into the periclase. The specimens were installed into the X-ray transparent triaxial apparatus HADES installed at the beamline ID19 at the European Radiation Synchrotron Facility. The process of periclase hydration was followed through dynamic X-ray microtomography imaging at a voxel resolution of 6.5 micrometers.

Under our experimental conditions, the periclase transformed into brucite through reaction-induced fracturing process. The stress generated by this reaction fractured the peridotite surrounding the periclase cylinder. The dynamics of fracturing (volume, spacing of fractures) was quantified, as well as the kinetics of periclase transformation. Using 3D digital volume correlation technique it was also possible to identify how the strain evolved into the peridotite before and during fracturing. Even if the periclase induced mainly tensile stress and the peridotite failed through the opening of tensile fractures, numerous shear strain events could be identified, showing that stress redistribution during reaction-induced fracturing could induce shear slip. Our observations provide an explanation for the existence of microseismicity measured at slow-velocity spreading ridges and attributed to active serpentinization of the oceanic crust.

Experimental Evidence for Porosity Generation and Maintenance During Olivine Carbonation

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The rate of retrograde metamorphism, the change of minerals in response to decreasing pressure and temperature, is often limited by fluid supply. Commonly observed retrograde metamorphic reactions include the hydration and carbonation of olivine. Olivine carbonation is recognized as a safe and permanent method of CO₂ sequestration (e.g., Kelemen and Matter, 2008). The use of ultramafic rocks to sequester carbon dioxide hinges upon whether porosity and fluid paths can be maintained while CO₂ is chemically incorporated in silicate rocks to form carbonate minerals. On the one hand, the transformation of olivine to magnesium carbonate may fill existing pore space and passivate reactive surfaces, preventing further carbonation reactions (e.g., Hovelmann et al., 2012). On the other hand, the increase of solid volume may generate enough stress to fracture the host rock, creating new fluid pathways and exposing unreacted surface to maintain reaction (e.g., Zheng et al., 2018). We conducted in-situ dynamic microtomography and nanotomography experiments to quantify the porosity generation during olivine carbonation. We designed a sample setup that included a thick-walled fine-grained olivine cup filled with coarse-grained olivine sands (Zhu et al., 2016). The whole sample assembly was reacted with a NaHCO₃ aqueous solution at 200°C, under a constant confining pressure of 13 MPa and a pore pressure of 10 MPa. Using synchrotron-based X-ray microtomography, the 3-dimensional (3-D) pore structure evolution of the olivine cup was documented during a continuous carbonation reaction for up to 146 hours. The dynamic microtomography data show a volume reduction in olivine at the beginning of the reaction, indicating a vigorous dissolution process consistent with the disequilibrium reaction kinetics. As the reaction proceeds, idiomorphic magnesite crystals on the surface of the olivine grains become measurable. Precipitation of the reaction products is non-uniform, resulting considerably larger volume expansion of the interior than that along the edges of the olivine cup. Stretching due to the volume mismatch causes cracking of the cup wall surface, which subsequently coalescence to form the large fractures and eventually disintegrate the porous olivine aggregate. Nanotomography images of the reacted olivine cup reveal pervasive etch-pits and worm-holes in the olivine grains. These nano- to micron-scale dissolution channels provide additional fluid pathways for reactions to proceed (Xing et al., 2018). The growth of magnesites corroborates that these olivine carbonation reactions are self-sustaining. Based on the experimental data, we propose a porosity maintenance mechanism of coupled dissolution channels and expansion cracks via non-uniform precipitation. In nature, heterogeneity in the porosity and permeability of a rock formation is common, which may cause non-uniform concentration of reaction and distribution of precipitation. The resulting volume mismatch could lead to expansion fractures. The fractures provide new fluid pathways and expose fresh reactive surfaces to sustain the carbonation. In a long-term, fluid pathways may be provided by “worm-hole” etch pitting. Dissolution channels could deteriorate rock strength over longer time scales, facilitating fracture growth.

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Earthquake induced metamorphism

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Prior to orogeny, the lower continental crust is dry, strong, and often under considerable tectonic stress. This also applies to unserpentinised oceanic lithosphere. Transformation to rheologically weaker rocks that subsequently undergoes more or less localized ductile deformation occurs through fluid-induced metamorphism. Earthquakes may play a key role during the incipient stages of this transformation process both in continental and oceanic settings, by connecting initially dry rock volumes to external fluid reservoirs. Deep crustal earthquakes often evolve through an initial stage of dynamic rupture, that creates asymmetric damage of the wall rocks at very high stress levels. Heating during the subsequent seismic slip, may cause melting and melt injection into fragmented wallrocks. When fluids follow in the wake of the rupture, fluid-rock interactions within the permeable wallrocks lead to mechanical weakening by the production of fine grained and hydrated products. This may induce shear deformation of the wallrocks subsequent to the initial fragmentation. Reduced ability to hold differential stress, causes significant pressure perturbations within volumes of mechanically weaker product rocks and may cause local high pressure metamorphism in the absence of tectonic burial. Earthquakes occurring below the normal seismogenic regime may be triggered by local fluid production in systems experiencing a rise in temperature, otherwise stress pulses related to shallower earthquakes is a generic mechanism that will provide transient loading of the lower crust and associated aftershocks in any orogenic setting.

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Coronitic eclogites formed by seismic shock: An example from Yangkou in the Chinese Su-Lu high-pressure metamorphic belt

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The relationship between high-pressure metamorphism and deformation can be seen by field and petrologic study of the outcrop of a variably eclogitized gabbro at Yangkou in the Chinese Su-Lu high-P metamorphic belt. A block of former quartz-bearing gabbro transformed into coesite- and quartz-bearing coronitic eclogites, and a metagabbro preserving all the igneous minerals except plagioclase. The igneous plagioclase is replaced by the assemblage of fine grained Na-plagioclase + epidote + phengite + kyanite. These high-P rocks gradate continuously forming a P-T gradient of ~1.3 GPa and ~500 °C – ~3.3 GPa and ~670 °C within 20 m. The preservation of the igneous fabric (pseudomorphs after the igneous minerals and the garnet coronas) in the eclogites shows that the high-P metamorphism was associated with negligible shear deformation but with compression, which caused a bulk volume reduction of 10–15 %. Foliated eclogites at Yangkou locally preserve the igneous fabric. This implies that shear deformation postdates the eclogitization. Therefore, conventional structural analysis of foliation and folding retrieves no information about the main form of deformation – bulk volume reduction, and would likely reach a conclusion that the role of tectonic pressure is subsidiary. Compression during eclogitization is currently considered to take place during subduction to mantle depths. However, the pressure difference recorded by the variably eclogitized gabbro corresponds to a depth difference of 60 km, and is thus not explained by subduction of a 20-m gabbro. In addition, the variable transformation of the gabbro to the eclogites cannot be explained by the availability of fluid, as has been proposed earlier both for Yangkou and for many other localities. The reasons for this include: (1) H₂O contents in the different types of eclogitized gabbro at Yangkou are approximately the same, as shown by both chemical analysis and pseudosection modelling; (2) the amount of fluid may affect the amount of reactions in a given rock volume but not the magnitudes of the intensive variables (P, T, chemical potentials) in it; (3) at the eclogite-facies P-T conditions H₂O cannot be restricted to within narrow zones but would diffuse rapidly outwards, facilitating eclogitization of the wallrocks, especially in the subduction process taking place for millions of years. The fact that the wallrocks to the eclogites in fracture zones remain untransformed at many localities means that the eclogitization was a transient process. On the other hand, mineral growth textures and deformation microstructures are similar to features typical of seismogenic rocks. Stellate growth of high-pressure microlites (dendritic, skeletal, and micropoikilitic garnet, spherulitic omphacite + quartz intergrowth) on relict igneous minerals and randomly oriented crystallites replacing plagioclase are common features in the coronitic eclogites (fine equant grains of omphacite, phengite and kyanite) and the metagabbro (fine acicular kyanite and epidote). Broken igneous biotite and augite overgrown by skeletal garnet are not annealed. Intergranular coesite in the eclogite breccia thrust over the coesite-bearing coronitic eclogite is preserved, the timescale for the partial transition of coe ↔ qz is estimated to be ~28 hr. All these observations are consistent with shock compression and subsequent quenching of a gabbro in the crust, coeval with the earthquake recorded by the eclogite breccia. Therefore, it is considered likely that the eclogites at Yangkou formed in response to a shock caused by the passage of a seismic wave through a gabbro intruded in the crust.

Asymmetric damage and metamorphism across a lower crustal fault from the Bergen Arcs, western Norway

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In the lower crust, seismic faults circulate fluids to dry rocks and trigger metamorphic reactions necessary for large-scale crustal weakening. Pseudotachylytes are direct field evidence for the propagation of seismic ruptures, however, the precursors to their formation remain poorly understood. We describe a 1.7 m displacement fault from the Bergen Arcs in order to elucidate the rupture evolution and sequential metamorphism of a pseudotachylyte-bearing fault in the lower crust. Cutting through granulite, the fault is characterized by an asymmetrical damage zone, ultracataclasites and zoned pseudotachylyte with an associated amphibolite facies mineral assemblage ($P < 1$ GPa, $T = 600-700^{\circ}\text{C}$). The damage zone extends up to 6 cm from one side of the fault and is defined by host rock fragmentation that lacks a major shear component. This type of asymmetrical off-fault damage is diagnostic of dynamic ruptures; cracks that propagate near the Rayleigh wave speed (Ngo et al., 2012). The damage can shed light on the propagation direction and velocity of the lower crustal fault. The millimeter-thick ultracataclasites are present on either side of the fault and display signs of shearing and growth along the outer rims of garnet and diopside clasts. Image analysis of the garnet clasts from the ultracataclasites and damage zone give fractal grain size distributions ($D = 1.6-1.8$) indicative of brittle deformation. The presence of injection veins within the damage zone, and ultracataclasite and wall rock clasts within the pseudotachylyte is evidence that brittle fragmentation and cataclasis were precursors to melting. The fault presents an interesting case of the codependence between deformation and metamorphism, and how they both take part in the transformation of the lower crust during an earthquake. Additionally, the observation of asymmetrical damage across the fault suggests that dynamic ruptures propagate within the lower crust, providing constraints on the mechanisms for faulting at high confining pressures.

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Evidence of high-pressure shock deformation in granular zircon

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Granular zircon is a term broadly applied to grains viewed in scanning electron microscopy (SEM) images that appear to have a polycrystalline texture. Such grains have been reported from a wide range of geological environments, including high-strain shear zones [1], shocked rocks from meteorite impact craters [2], impact melts [3], detrital grains [4], Apollo breccia samples [5], and meteorites [6]. It thus appears that grains with an external granular texture that have a similar appearance can be produced in diverse environments. However, in polished section it is apparent that the granular aspect of some grains results from recrystallization of the near surface environment, and is not penetrative [4]. Here the term granular zircon refers to grains that consist of recrystallized neoblasts. This work focuses on using quantitative orientation analysis by electron backscatter diffraction to distinguish granular textured zircons that are uniquely produced during meteorite impact events. Specifically, the studied examples involve grains created through polymorphic phase transformations in rocks that experience near total fusion of all silicate phases. Through application of this method, granular textured zircon produced in impact environments can be readily distinguished from those produced in non-impact settings.

Non-granular zircon grains from most geological settings (igneous, metamorphic, sedimentary rocks) consist of one near-uniform crystallographic orientation, with minor variations if crystal-plastic deformation or brittle fracturing has occurred. Granular grains produced from endogenic processes typically show similarly limited variation in crystallographic orientation, often with $<10^\circ$ of angular misorientation [4]. Notable exceptions include granular zircon from amphibolite-facies shear zones [1], which show a wider range of angular dispersion. In contrast, granular zircon grains from various impact melts show non-uniform orientations that are highly systematic. Typical grains consists of $\sim 1\ \mu\text{m}$ sized low-strain neoblasts that occur in three principle orientations, each oriented $\sim 90^\circ$ from the other. Neoblasts of each orientation can occur in clusters [7] or be interspersed at the neoblast scale [8-10]. The systematic orientation relations among neoblasts define a misorientation relationship of $90^\circ/\langle 110 \rangle$, which results in coincidence of clusters for poles to (001) and $\{110\}$ when data are plotted on stereonet. The systematic orientations result from the polymorphic transformation of zircon to reidite, a high-pressure polymorph of zircon stable at 30 GPa [11-12], and the reversion of reidite back to zircon along the same crystallographic pathways [8,13]. The transformation to reidite occurs over ms to s timescales during shock compression; reversion back to zircon is likely to also occur over s timescales, as reidite is not stable above 1200°C [11], and typical impact melt reaches temperatures $>2000^\circ\text{C}$ [e.g., 14]. Formation of neoblasts that comprise granular zircon occurs in the zircon stability field at high temperature conditions, as evidenced by the presence of ZrO_2 (baddeleyite) produced during dissociation of zircon above 1673°C [8]. Identification of the systematic orientation relations among zircon neoblasts can thus serve to uniquely identify granular produced during meteorite impact from those produced by endogenic processes that did not involve high-pressure phase transformations in the process.

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Earthquakes, metamorphism and rheological weakening in dry and strong granulites

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The rheology and the conditions for viscous flow of the dry granulite facies lower crust are still poorly understood. Furthermore, anhydrous granulites can survive metastably during Wilson cycles, unless they are infiltrated by fluids that trigger metamorphic reactions [Austrheim, 2013]. A picture is emerging in which a seismically active lower crust provides an environment for enhanced metamorphic and rheological transitions, due to fluid-rock interaction and associated reaction weakening in the fractured domains [Austrheim, 2013; Jamtveit *et al.*, 2016]. The observation that viscous shearing in a dry and strong lower crust often localizes in pseudotachylyte veins [e.g. White, 1996; Austrheim, 2013] is consistent with this picture. However, the deformation mechanisms responsible for the associated weakening and viscous shear localization in pseudotachylyte veins are yet to be fully explored.

We investigated examples of pristine and mylonitized pseudotachylytes in anorthosites from Nusfjord (Lofoten, Norway) [Menegon *et al.*, 2017]. Mutual overprinting relationships indicate that pristine and mylonitized pseudotachylytes are coeval and resulted from the cyclical interplay between brittle and viscous deformation. The stable mineral assemblage in the mylonitized pseudotachylytes consists of plagioclase, amphibole, clinopyroxene, quartz and biotite, with limited amounts of garnet and K-feldspar. Amphibole-plagioclase geothermobarometry and thermodynamic modeling indicate that pristine and mylonitized pseudotachylytes formed at 650–750°C and 0.7–0.8 GPa. Thermodynamic modeling indicates that the host anorthosite was effectively dry (devoid of grain boundary aqueous fluid) and that limited amount of H₂O infiltration (0.20–0.40 wt. %) was necessary to stabilize the mineral assemblage in the mylonitized pseudotachylytes.

Diffusion creep and viscous grain boundary sliding are identified as the main deformation mechanisms in the mylonitized pseudotachylytes based on the lack of crystallographic preferred orientation in plagioclase, the high degree of phase mixing, and the synkinematic nucleation of amphiboles in dilatant sites. Creep cavitation during grain size sensitive creep maintained a dynamic porosity that facilitated fluid distribution and phase nucleation in the shear zone. Extrapolation of flow laws to natural conditions indicates that mylonitized pseudotachylytes deforming by grain size sensitive creep are up to 3 orders of magnitude weaker than anorthosites deforming by dislocation creep, thus highlighting the fundamental role of lower crustal earthquakes as agents of fluid infiltration and rheological weakening in dry and strong granulites.

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Dynamic earthquake rupture preserved in a creeping serpentinite shear zone

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The mechanisms that allow stable creeping shear zones to become transiently unstable and destructive are poorly understood, yet critical for an improved understanding of fault mechanics and seismic hazard. Recent laboratory experiments on serpentinite suggest that extreme dynamic weakening at earthquake slip rates is accompanied by mineral amorphization, dehydration and possible melting, processes that may allow for efficient rupture propagation in creeping serpentinite shear zones. However, hypotheses arising from laboratory experiments and numerical modelling remain untested in nature because ancient earthquake ruptures have not previously been recognized in serpentinite shear zones. Here, we document the preservation of high-temperature reaction products that formed by coseismic amorphization and dehydration in a plate boundary-scale serpentinite shear zone. Widespread fibrous serpentine growth, pervasively developed foliation, and dissolution textures, indicate that distributed deformation occurred in the shear zone by slow pressure solution-mediated creep. The main shear zone fabrics are cut by polished magnetite-coated fault surfaces <300 μm thick containing small inclusions of serpentinite. Within the inclusions, Transmission Electron Microscope (TEM) observations show the progressive formation of amorphous material and high-temperature dehydration products. The highest-temperature products at distances of <50 μm from the polished fault surfaces are aggregates of nanocrystalline olivine and enstatite, indicating peak coseismic temperatures of $c. 925 \pm 60^\circ\text{C}$. Finite element modelling suggests that frictional heating during earthquakes of magnitude M_w 2.7–4 can satisfy the petrological constraints on the coseismic temperature profile. Our results suggest that earthquake ruptures can propagate through creeping serpentinite shear zones, and that the signatures of transient frictional heating in serpentinite can be preserved in the fault rock record.

Deformation twins yield tectonic ages in monazite

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The chronology of deformation episodes is an invaluable record to investigate Earth's tectonic history and the timing of extra-terrestrial impact events. Despite its importance, the dating of deformation episodes is renowned to be challenging due to the equivocal textural relationship of phases suitable for geochronology growing during deformation and subsequent polymetamorphic overprints (Jourdan et al., 2012). Another recent approach for deformation chronology is to investigate the capability of accessory phases to record such events (Erickson et al., 2015; Moser et al., 2009). The closure temperature of accessory phases such as monazite is considered high (800°C) and can therefore withstand subsequent metamorphism and erosion. Several studies have documented the partial resetting of the U-Th-Pb chronometers during crystal plastic deformation (Moser et al., 2009; Piazzolo et al., 2012); however, the spatial resolution of conventional analytical methods is insufficient to directly target sub-micron deformation microstructures.

Twinning, a symptomatic microstructural feature in tectonically deformed and shocked monazites (Erickson et al., 2015; Hay and Marshall, 2003), has significant potential and may hold the key to unlock the timing of deformation. Twins generated by deformation are usually very narrow (<1 micron) and therefore cannot be dated by conventional microanalytical techniques. In this contribution, we used a combination of Electron Backscattered Diffraction (EBSD) and atom probe microscopy (APM) to investigate the interaction of crystal-plastic deformation and the resetting of isotopic chronometers. We have analysed the composition of a twin from a ~1,700 Ma monazite grain deformed at ~1,000 Ma. Our results indicate that the monazite host is composed of relatively high Ca content (~1.1 at.%) with abundant Ca-Pb-Si clusters that we interpret to represent apatite nano-inclusions. Conversely, the twinned domain has a homogeneous Ca distribution and a lower Ca content (~0.8 at.%). The standard-corrected ²⁰⁸Pb/²³²Th age from the twin indicates that the chronometer was entirely reset during twinning. We propose a mechanism for Pb and trace element mobility during shearing of the crystal lattice.

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Dynamic recrystallisation and its effect on ice deformation: the future depends on understanding this!

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The flow rate of polar ice sheet ice, from the land to the sea, will be the most important control on global sea level change over the coming decades and centuries. Ice flow rates will increase in response to rising global temperatures and will also increase locally in response to more dramatic changes in ice sheet configuration, that alter the driving stresses for flow; most particularly the collapse of floating ice shelves. Ice flow comprises a component of ice deformation and a component of sliding at the base of the ice sheet. It is likely that both components will increase in a warming world.

This presentation will focus on our understanding of ice deformation and its application to ice sheets. Terrestrial ice sheet temperatures are all above $0.8T_m$ (T_m = melt temperature) and the majority of ice sheet ice is above $0.9T_m$ (-30°C is $0.89T_m$). Overburden pressures suppress fracture (crevassing) within the top 40 to 70m so that the bulk of the ice sheet (from hundreds of metres up to 4km thick) acts as a high homologous temperature metamorphic rock. Deformation occurs by “high temperature” creep mechanisms that can occur without significant dilatation. Mechanical behaviour is described by a power-law creep equation (strain rate is proportional to stress raised to a power n : the stress exponent) with Arrhenius temperature dependence. All natural glacial ice samples and all ice samples deformed in the laboratory have a crystallographic preferred orientation (CPO) and have microstructures indicative of the operation of recrystallisation processes. Experiments show us that ice rheology evolves with strain and empirically we link this to the changes in CPO and grain size that occur as ice deforms; changes that are intimately linked to dynamic recrystallisation.

Ice strength (the flow law), CPO and microstructure are controlled by a rate balance of different deformation and recrystallisation mechanisms. Experimental data show us that the CPO and microstructure, as well as strength, vary as a function of temperature, strain rate and strain (Qi et al., 2017). Furthermore CPO and strength evolve differently for different deformation kinematics; axial shortening versus shear for example (Budd et al., 2013; Treverrow et al., 2012). Our interpretation is that the CPO and microstructural changes depend on the balance of the rate of lattice rotation and strain induced grain boundary migration (Qi et al., 2017). Rotation becomes more significant at lower temperatures, higher strain rates and higher strain. Changes in strength relates to the CPO evolution, as individual ice crystals are very anisotropic, and changes in microstructure, as finer grains will increase the strain rate contribution of grain size sensitive deformation mechanisms.

The convention in ice sheet modelling is to use an ice flow law that is based on the mechanical data (stress and strain rate) at very low strain ($\sim 1\%$), sometimes with a linear adjustment (an enhancement factor) for the weakening that occurs between 1% and 10 - 20% strain. Because the microstructural and mechanical changes that occur as a function of strain are also controlled by strain rate (or stress) this approach presents problems. Experimental data sets where mechanical behaviour at 1% strain and at higher strains can be compared all show an increase in the stress exponent n from the 1% strain data to the higher strain data (Bons et al., 2018; Qi et al., 2017; Treverrow et al., 2012). Typical 1% n values are around 3, whereas those at higher strain are around 4, and this alone makes a huge difference to large scale model outputs (Bons et al., 2018). It is clear that natural ice has been deformed to high strain: generally

much higher than has been achieved in the laboratory. The challenge now is to develop robust high-strain flow laws that can be applied robustly to ice sheet models.

One aspect of ice deformation behaviour that is poorly captured in the experimental literature is the effect of chemical impurities. Ice sheets contain very small (up to ~10 ppm) proportions of particulate and/or solute impurities that come from atmospheric dust and aerosols. Although impurity levels are low, the limited data we have shows that the additional chemistry has a significant effect on mechanical behaviour (Hammonds and Baker, 2016, 2018) and on microstructural evolution (Craw, 2018; Weikusat et al., 2017). The effect is probably related to the impurity effect on grain boundary mobility (Eichler et al., 2017; Weikusat et al., 2017) and the impact this then has on recrystallisation processes. The vast majority of laboratory ice deformation experiments use pure water ice. Probably the most important change we need to make to experimental programmes to understand ice mechanics is to use the “impure” ice chemistries characteristic of the Earth’s ice sheets. Implementing this will not be easy.

Deformation of ice to significant strain in the laboratory is restricted to strain rates at least two orders of magnitude faster than the fastest rates that occur in nature. CPO and microstructure can be quantified in experimentally and naturally deformed ice and similarity of experimental and natural CPOs provides some confidence that processes in the laboratory and nature are equivalent and the extrapolation of laboratory derived flow laws to natural systems is reasonable. However, whatever we do in the laboratory, validating the up-scaling, from small samples deformed quickly in the laboratory to large ice masses deforming slowly, is one of the most crucial activities in developing our ability to predict future ice flow contributions to sea level change. I will report on new attempts to use ice sheet scenarios to provide data for comparison with the extrapolations of laboratory mechanical data.

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POSTER Presentations

Alphabetical

Metasomatic reactions in bornite: insights from hydrothermal experiments and microscopic and mineralogical characterization

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Bornite (Cu_5FeS_4) is a widespread copper iron sulfide in many types of ore deposits, such as sediment-hosted Cu, porphyry Cu, volcanogenic massive sulfide (VMS), and iron oxide-copper-gold (IOCG) deposits (Cook et al., 2011). It forms complex intergrowths with chalcopyrite (CuFeS_2), chalcocite (Cu_2S), covellite (CuS), and digenite ($\text{Cu}_{1.8}\text{S}$) (Ciobanu et al., 2017), which are produced due to exsolution and/or metasomatic reactions (Grguric and Putnis, 1999; Zhao et al., 2014; Zhao et al., 2017). The phase relation in the Cu-Fe-S system comprises of extensive solid solutions, with or without miscibility gaps, (e.g., bornite-digenite) and high- and low-temperature phases. Hence the mechanisms and conditions of metasomatic reactions involving bornite are still poorly understood.

To address this problem, in this work, we studied the bornite metasomatic reactions under well-controlled experimental conditions (pH 1-6, with or without oxygen), at 160-200 °C, and under autogenous vapor pressures. Microscopic and mineralogical studies were carried out using FE-SEM, EPMA, PXRD, and synchrotron-based *in situ* PXRD. It was found that secondary phases formed under all conditions. During the initial stages of the metasomatic reaction, basket-weave like exsolution texture consisting of chalcopyrite lamellae, enclosed by digenite as a second decomposition product, was found within bornite grains. This solid-state exsolution depends on temperature and is driven by the composition of the hydrothermal solution (with or without the addition of copper and sodium salts). In parallel to exsolution, interface coupled dissolution-precipitation (ICDP) mineral replacement reactions started from the surface of the bornite and progressed towards the interior of the chalcopyrite lamellae/digenite assemblage revealing textural features such as porosity in the product phases and a sharp reaction front. Two contemporaneous replacement reactions were observed: (i) the relatively faster replacement of chalcopyrite lamellae by digenite around the core of the mineral grains, and (ii) the relatively slower replacement of digenite by covellite around the surface of the mineral grain.

This study provides new insights into the stability of bornite during the formation of hydrothermal copper ore deposits. The textures observed in this study mimic what has been observed in natural samples. The results suggest that complex texture in copper iron sulfides, which are commonly observed in natural specimens, is derived from simultaneous process of solid-state exsolution and dissolution-precipitation processes, therefore, the relation between these two processes requires further investigations.

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Microseismicity on an ultraslow ridge segment: implications for serpentization

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Serpentinisation is the process of peridotite hydration. As a fluid consuming reaction, it requires fluids to get access to the reactive mantle rocks. The occurrence of abundant water above a thin crust makes serpentization a typical feature of oceanic lithosphere. It preferentially occurs at ridge axes and subduction zones where tectonic activity is intense and fracturing can break through the crust and make path for water to reach deeper levels (Sibson 2000; Ranero et al. 2003). Water circulation is often accompanied by hydrothermal activity which can be associated with further fracturing and potentially seismicity due to heat exchanges, water transport and serpentization (i.e. Crawford et al. 2013; Horning et al. 2018). The amount of water in the mantle is crucial because of the changes in the mantle rheology it induces, such as a lower density and a reduction of mechanical strength (Escartin et al., 1997). These changes have big consequences on the processes occurring at plaques boundaries and more generally on lithospheric dynamics, but also on global volatiles cycles.

Ultra-slow ridges are characterized by a very low magmatic activity and a lithospheric extension largely accommodated by tectonics (as opposed to fast spreading ridges where extension is mostly accommodated by magmatic activity) (Dick et al., 2003; Tucholke et al. 2008). These properties have two major consequences: 1) entire portions of seafloor are devoid of crust, directly exposing the mantle, 2) intense fracturing of the lithosphere leading to deep seawater penetration. This makes ultra-slow ridges perfect places to study the interplay between serpentization and tectonics in the simplest setting.

This study focuses on an ultra-slow ridge segment of the South-West Indian Ridge (SWIR) where an up to 20 km deep aseismic zone has been observed on top of particularly deep seismic activity (up to 30-35 km deep) (Schlindwein and Schmid 2016; Schmid and Schlindwein 2016). The limit between the seismic and aseismic zone is thermally controlled. It follows a 400-500°C isotherm which corresponds to the limit of serpentine stability. The aseismic zone is thus interpreted as a serpentized section where the rock has been sufficiently weakened to prevent seismic activity and fracturing has been efficient enough not to limit the depth of serpentization. We estimated the intensity of the deep seismic activity by the mean of the Gutenberg-Richter law's a and b values. From these values we extracted the damaged volume created by such activity (Jamtveit et al. 2018) which represents the possible reactive volume for serpentization as it will be brought into the serpentine stability field either by tectonic exhumation or by seafloor extension.

Our results highlight the primary role of seismic deformation in the creation of a network of cracks through which water can reach large depths and react with the surrounding mantle as soon as the serpentine stability field is reached. We suggest this is not only valid for ultra-slow ridges but also for all ridge sections where seismic activity extends into mantle rocks. Indeed, these fractured rocks are most likely to enter the serpentine stability field during lithospheric cooling away from ridge axis.

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Reaction pathways and timescales of fluid-rock interaction

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Fluid-rock interaction has important consequences for planetary scale mass transport and the physicochemical state of the Earth's crust. However, little is known about characteristic alteration timescales despite its importance for quantifying the temporal evolution of the Earth's crust, the duration of ore deposit formation and rates of geological carbon cycling. Alteration studies of ultramafic rocks are particularly well suited to address this important topic due to their reactivity with fluids and relatively simple chemical composition. Here we present two case studies of hydrothermally altered ophiolite sequences that display distinct alteration micro-textures despite their seemingly similar alteration setting and conditions. In both cases alteration was driven by influx of carbon-bearing alteration fluid causing extensive formation of secondary carbonate-bearing alteration assemblages.

Peridotite alteration of the Oman ophiolite resulted in the formation of secondary ophicarbonates (serpentine + carbonate) and listvenite (carbonate + quartz). In both cases secondary phases record alteration controlled changes of the fluid composition and display distinctive spherulitic growth textures indicating far-from-equilibrium alteration conditions and potentially fast reaction rates. Macroscopic textures imply that fluid influx was aided by concomitant brittle deformation and repeated opening of fluid infiltration pathways.

In contrast, serpentinite carbonation from the Linnajavri ophiolite, Norway, has resulted in texturally equilibrated secondary soapstone (talc + carbonate) and listvenite that formed within zones of structural permeability. The alteration assemblages are separated by sharp reaction fronts that are oriented parallel to fluid flow paths indicative of advection dominated fluid transport.

For the texturally equilibrated alteration assemblages, bulk rock major and trace-element concentrations and their isotope ratios allow for estimates of reaction front propagation velocity and thus fluid advection rate in a mid-crustal hydrothermal system. We infer that fluid-rock interaction producing disequilibrium textures proceeds faster than that producing texturally equilibrated assemblages, which provides constraints on the reaction durations of other carbonated ophiolite occurrences and in analogy amphibolite, albitite, charnokite, etc. Furthermore, the deduced timescale of hydrothermal rock alteration bridges the gap between typical timescales of relatively long lasting and short-lived geological processes such as regional scale Barrovian metamorphism and seismic events.

Phase transitions under differential stress: Deviatoric stresses or pressure?

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We performed deformation experiments for the Calcite-Aragonite system in a (Griggs-Type) solid medium deformation apparatus, using different sample geometries. The confining pressure (σ_3) was maintained below the Calcite-Aragonite transition while the first principal stress (σ_1) exceeded the transition pressure, changing with sample strength. Thus, the bulk sample pressure, $P_{3D} = (\sigma_1 + 2\sigma_3)/3$ was closely varying around the transition pressure. Light microscopy, Raman spectroscopy and electron backscatter diffraction (EBSD) show systematic, strongly heterogeneous patterns in the distribution of the phases, grain-sizes and deformation. These result from stress, strain and pressure variations within the sample. To better understand different mechanisms contributing to the phase transition and grain size reduction, the local distribution of first order parameters as pressure, stress and strain must be known.

We performed numerical modelling in order to quantify the stress, pressure and strain distribution within the deforming sample. The numerical results are compared to the stress distribution, as inferred from grain size, and finite strain. These show a good fit with modelling results using a viscous power law rheology. As the distribution of stress and strain in the numerical model matches the experiments, the modelled pressure is expected to depict the experimental conditions as well.

Finally, patterns of modelled pressure, stresses and strain are compared to experimentally produced phase-transition patterns. From this comparison the confining stress (σ_3) can be excluded as being a driving force for the phase transition. However, the discrimination between local σ_1 and local pressure (defined like P_{3D}) still needs better quantification regarding experimental measurements.

Modeling the Effects of Inhomogeneous Pressure Distribution in the Evolution of Metamorphic Rocks

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Recent studies of metamorphic petrology provide the evidence of pressure deviations from the lithostatic values as well as spatially inhomogeneous distributions. Such discrepancies arise from the complex chemo-mechanical interactions between the minerals which take place deep in the Earth. Conventionally, we assume the pressure takes the value given by Archimedes's formula which is directly proportional to the depth. Nevertheless, when considering deforming rocks together with mineral reactions, stresses emerge from both volume changes due to reactions and the overburden which lead to inhomogeneous pressure distributions. Thus, in general, the Archimedes's formula is not applicable. Previous studies of metamorphic rocks separated the chemical and the mechanical actions on the mineral assemblages. This separation results in inappropriate models since the volume changes, caused by the chemical interactions between the minerals, strongly influence the inhomogeneous pressure distribution, and thus, its description requires a comprehensive treatment of the coupled chemo-mechanical interactions. Herein, we address the mechanical effects acting upon a chemically active metamorphic rock which results in inhomogeneous pressure distributions. We present a fully coupled thermodynamically-consistent model for chemo-mechanical interactions in multicomponent solids. We describe the Helmholtz free energy of a multicomponent elastic solid undergoing both diffusion and chemical reaction. Our formulation of the constitutive equations, which describe the evolution of the system towards equilibrium, satisfies the second law of thermodynamics. Furthermore, we present simulation results which give an insight into the phenomenon and verify the interleaving between the chemical and mechanical responses.

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A Locally Conservative Stabilized Continuous Galerkin Finite Element Method for Two-Phase Flow in Poroelastic Subsurfaces

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We study the application of a stabilized continuous Galerkin finite element method (CGFEM) in the simulation of multiphase flow in poroelastic subsurfaces. The system involves a nonlinear coupling between the fluid pressure, subsurface's deformation, and the fluid phase saturation, and as such, we represent this coupling through an iterative procedure. Spatial discretization of the poroelastic system employs the standard linear finite element in combination with a numerical diffusion term to maintain stability of the algebraic system. Furthermore, direct calculation of the normal velocities from pressure and deformation does not entail a locally conservative field. To alleviate this drawback, we propose an element based post-processing technique through which local conservation can be established. The performance of the method is validated through several examples illustrating the convergence of the method, the effectivity of the stabilization term, and the ability to achieve locally conservative normal velocities. Finally, the efficacy of the method is demonstrated through simulations of realistic multiphase flow in poroelastic subsurfaces.

Formation and effects of silica-rich veins in the Lindås Nappe, Bergen Arcs, Norway

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Fluids are critical for retrograde metamorphism to proceed. Without fluids, metamorphic rocks persist metastably at low temperature and pressure conditions (e.g., Jamtveit & Austrheim, 2010). One of the main processes inducing retrograde metamorphism is therefore brittle failure, since fractures and faults facilitate fluid transport into otherwise dry rocks.

Within the Lindås nappe in the Bergen Arcs, granulitic anorthosites, gabbros and mangerites are partially hydrated to eclogites and amphibolites. In some cases this hydration is related to fluid entry along seismic faults, preserved as pseudotachylites (Austrheim et al., 1996), while others occur associated with silica-rich veins or pegmatites (hereon referred to as veins). Substantial work has been done on the role of seismicity in the Lindås nappe but the formation and effects of the silica-rich veins is commonly overlooked.

The silica-rich veins show strong variability: they have different mineralogies, with various amounts of quartz, feldspar, mica, sulfide minerals, and others. Some of the veins are parallel to their host rock foliation and appear sheared, while some are macroscopically undeformed. All of the veins are surrounded by either eclogite or amphibolite.

We discuss several questions related to their formation and their effects on their surroundings:

- Are they true magmatic pegmatites or more dominated by hydrothermal fluids? What is their source?
- Are they purely intrusive or have they replaced their hosts?
- Are there several stages of vein formation or only one?
- Did they trigger retrograde metamorphism to eclogite and amphibolite, or did they form within the already transformed, weaker rocks?
- What is the influence of the veins on the further rheological behaviour of their host?
- How are the veins related to the pseudotachylites?

The silica-rich veins appear to play an additional role in the fluid-induced metamorphism from granulite to eclogite and amphibolite in the Bergen Arcs.

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Grain- versus grain boundary-based quantification of shape preferred orientations in natural rock salt before and after experimental deformation

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Among the advantages of studying rock salt is that deformation mechanisms common in many metamorphic rocks are accessible at laboratory conditions. Natural rock salt commonly consists to $\geq 95\%$ out of halite and only requires low temperatures and pressures to flow viscously. Ductile deformation of salt produces foliations defined by a shape preferred orientation (SPO) of halite grains, which should play a significant role not only on deformation behaviour and microstructural development but also on seismic velocity anisotropy. The influences of SPO has not been sufficiently studied. To assess the influence of petrofabric characteristics such as grain size, ellipticity, alignment of grain boundaries, grain boundary shape and grain orientation it is necessary to be able to reliably quantify those characteristics and ultimately quantify the strength and geometry of the shape preferred orientation.

Analysing grain fabrics directly from images can be problematic for automated software. The commonly used way is to manually trace grain boundaries with a vector graphics software, combining reflected microscopy, SEM and EBSD data to identify and treat grain boundaries and cracks/fractures separately. The vector graphic maps are analysed with specialized software such as ImageJ and FracPaQ. The established method to quantify SPO is to define grains from which parameters such as the grain areas, equivalent circular diameter, and lengths, orientations, and ratios of long and short axes can be derived.

We present a completely new approach: SPO quantification via grain boundary property analysis from vector graphic maps. The segments that form the boundaries are analysed in terms of their length, orientation, abundance and distribution. Grain boundary-based SPOs are compared with grain-based SPOs, showing a broad equivalence. Further geometric relationships of an SPO are revealed by using line scan statistics of grain boundary intersections. This way, the directionally-dependent grain boundary density can be quantified and a maximum and minimum grain boundary density direction identified, which is important when considering the effects of grain boundaries on acoustic wave attenuation. The orientation of the minimum grain boundary density equals the orientation of the grain elongation, concluding to the direction of a shape preferred orientation. Its strength can be assessed by analysing the difference in intensity between the maximum and the minimum grain boundary density. The line scan grain boundary analysis has potential in various fields. It is not only very useful to assess the strength of shape preferred orientation but might also provide data on grain boundary shape and thus on aggregate grain shape, accommodating deformation mechanisms and possibly grain growth dynamics.

The thermodynamics of deforming metamorphic rocks.

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The Gibbs based approach to mineral phase equilibrium has clearly been very successful in guiding metamorphic petrology. However there are a few points regarding Gibbs' approach that need modification or clarification when such theories are applied to deforming systems. First, Gibbs addressed, for the most part, fluids, and very little of what Gibbs wrote is applicable directly to crystalline solids; even then he considered only solids in contact with fluids and not fluid absent conditions. This means that the constraint that the phases remain crystalline and stoichiometric is not part of Gibbs' approach; stoichiometry is important in discussing chemical potentials. Second, Gibbs was not aware of diffusion in solids (the concept had not been invented in 1878) so that he had no way for chemical components to communicate within the solid so that they had to do so by migration in an adjacent fluid. It is somewhat astounding in hindsight that his proposals that potential functions, such as what we now call the Gibbs and the Helmholtz energies, can be used to define the temperature, the chemical potential and the thermodynamic pressure. He is quite explicit that if the material is incompressible then the concept of a thermodynamic pressure is determined only by the boundary conditions and otherwise is indeterminate. Hence the thermodynamic pressure is only defined if there is a volume change associated with the deformation. Otherwise (as one would expect intuitively) it is the boundary condition that defines the thermodynamic pressure. Again the Gibbs approach carries across to deforming solids with few but significant modifications.

The important modifications for solids concern the definition of a chemical potential and the specification of the deformation gradient. Because of stoichiometry, the chemical potential of one component in a crystalline solid cannot be specified without reference to the other components. This places restrictions on the chemical potentials that are not present in fluids. The issue with the deformation gradient (which Gibbs discusses in some depth) is that in a reacting metamorphic rock, phases (and hence material particles) that are present late in the history of deformation are absent in the initial stages and hence there is no "undeformed state" to which the deformation can be referred. The way out of this is to adopt an Eulerian approach to deformation rather than the classical Lagrangian approach adopted by Gibbs. This has consequences for stress strain relations because there are now constraints put on the constitutive relations arising from the need for the deforming phases to remain crystalline. This has important implications for the development of mineral phases and for microstructure since the Helmholtz energy is no longer convex. We discuss the ramifications of these modifications to the basic Gibbs approach with respect to mineral phase equilibria in deforming systems and to the development of microstructure.

Carbonate-sulfide dissolution and precipitation - Artemis Cu-Au prospect, Queensland

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Massive polymetallic mineralization at the Artemis Cu-Au prospect within the Eastern succession of the Mount Isa Inlier, NW Queensland, discovered by Minotaur Exploration Ltd in 2014, displays a complex association of sulfides and carbonates. The mineral deposit is hosted in a vertical, few meters wide, N-S trending marble unit that is enveloped by staurolite-muscovite schist and garnet-bearing calc-silicate hornfels. The sulfide assemblage consists of pyrrhotite, sphalerite, chalcopryite, galena, arsenopyrite, cobaltite, cubanite, bismuth \pm Ag-sulfides, gold, and costibite; in decreasing order of abundance. The gangue minerals are calcite and siderite with minor garnets and accessory stilpnomelane, quartz, biotite, and alkali feldspar. Therefore, Artemis provides an excellent opportunity to study sulfidation and carbonate replacement processes. Petrographic and geochemical analyses of sulfides and gangue minerals using reflected and transmitted light microscope, micro X-ray fluorescence (XRF) analyser, scanning electron microscope (SEM) equipped with energy dispersive X-ray spectroscopy (EDS), as well as electron probe microanalyser (EPMA) were carried out.

Micro-XRF maps reveal homogeneously distributed, elevated concentrations of Fe and Mn in sphalerite; an average of 9.1 wt.% Fe and 0.5 wt.% Mn, respectively. Heterogeneous distribution of Ca, Mn and Fe in carbonates was observed (Fig. 1A). Spot EDS analyses of calcite revealed an average content of 1.4 wt.% Mn, and 0.5 wt.% Fe. Siderite contains an average of 4.0 wt.% of Ca and 2 wt.% of Mn.

Microscopic studies show that there are at least two generations of carbonates. Calcite I contains abundant rounded relicts of pyrrhotite, sphalerite, galena and chalcopryite that range in size between 2-100 μ m. Further, there are inclusions of euhedral arsenopyrite (average size of 10 μ m) and cobaltite (up to 1 mm). Calcite II does not contain rounded sulfide inclusions and is intergrown with pristine siderite. Calcite II frequently envelopes calcite I. With the exception of arsenopyrite and cobaltite, the grain boundaries between sulfides and carbonates are always lobate (Fig. 1B) demonstrating a corrosive carbonate-sulfide interface. The corrosive nature of late fluids is further evident in the rounded sulfide relicts in carbonates signifying a replacement of sulfides by carbonates. The microscale investigations of abundant sulfidation and carbonatization processes help to elucidate the role of CO₂-rich fluids in metal mobilization and subsequent sequestration in skarn and/or Mississippi Valley-type deposits.

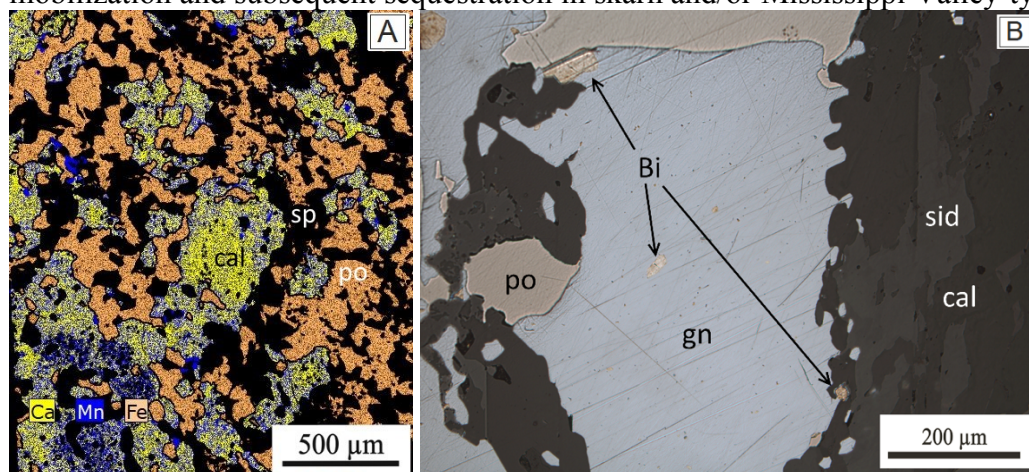


Figure 2: A: Micro-XRF map of a thin section showing Ca, Mn, and Fe distribution in carbonates along with pyrrhotite (po) and sphalerite (sp); B: Reflected, plain-polarized light image showing galena (gn) and pyrrhotite replaced by calcite (cal) and/or siderite (sid).

Stress orientation dependent reactions during metamorphism

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Grain-scale pressure variations have been recognized as important driver for the formation of distinct mineral assemblages during high and ultra-high pressure metamorphism. However, the effects of differential stress acting during hydration of granulite remain underexplored. Here we present textural evidence for the orientation-dependence of two distinct amphibolite-facies plagioclase grain boundary replacement assemblages that formed in response to large differential stress during the early stage of lower crustal hydration. The two assemblages are indicative of contemporaneous formation at local equilibrium conditions at 725 °C and 10 kbar and 14 kbar, respectively. Mineral replacement was accompanied by minor redistribution of chemical components by the alteration fluid as a consequence of the heterogeneous pressure field and local equilibria. Thus, our observations provide new insight into the driving forces behind pressure solution and indicate that differential pressure and fluid-induced mass transfer may define the evolution of metamorphic assemblages.

Phase heritage in Ti-bearing minerals

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Ore-deposits are often sites of massive fluid fluxes that significantly alter rock chemistry, mineralogy and microstructures. Deciphering the pressure-temperature-compositional history of extremely altered, or even pervasively retrogressed rocks can be challenging. As ongoing alteration or retrogression occurs new minerals form at the expense of old ones. Nucleation of these new phases often does not occur homogeneously throughout the rock, but is controlled by replacement reactions where a newly stable phase will nucleate on a chemically similar unstable phase. Nucleation itself is promoted when the interface between the new and old phase has the lowest possible energy. Consequently, many replacement reactions between chemically and structurally similar minerals (e.g. polymorphs, amphiboles-pyroxenes, feldspars) show topotaxial relationships. These relationships describe a phase heritage that has been shown to persist for more than one generation of reactions (Timms et al., 2017; this volume).

In this contribution, I have been investigating the extent of topotaxy between different phases that contain titanium. Titanium is generally considered immobile in a wide range of chemical environments including deep in the crust, in highly acidic ore systems and shallow, highly weathered regolith. Ti-bearing phases have a range of uses in geology including the following:

- Fe-Ti phases are used as oxybarometers in igneous systems
- trace elements in rutile (TiO₂) are used as an indicator mineral for gold mineralisation in heavy mineral concentrates
- rutile and titanite (CaTiSiO₅) can be dated using the U-Pb system
- akaogiite (high pressure TiO₂) has the potential to act as an indicator or meteorite impacts in the same way as reidite relates to zircon

By observing the presence or inferring the former presence of these different phases it should be possible to reconstruct a more complete geological history of most rock types.

I use electron backscatter diffraction (EBSD) mapping of grains that contain an incomplete reaction of one Ti-bearing phase to another to constrain the relationships between different pairs of minerals. Strict orientation relationships between ilmenite (FeTiO₃) and rutile, and titanomagnetite Fe²⁺(Fe³⁺,Ti)₂O₄ and rutile have been previously observed in X-ray diffraction and TEM ((Armbruster, 1981; Rečnik et al., 2015) datasets and I confirm that the following relationships are observed here:

Ilmenite → Rutile: (0001)_{ilmenite} // {100}_{rutile} and (1 $\bar{1}$ 00)_{ilmenite} // [001]_{rutile}

Magnetite → Rutile: <110>_{(titano)magnetite} // <001>_{Rutile} and {111}_{(titano)magnetite} // {100}_{Rutile}

Ilmenite transformation to titanite also shows a topotaxial relationship where:

[0001]_{ilmenite} // <100>_{titanite} and {10 $\bar{1}$ 0}_{ilmenite} // (001)_{titanite}

Rutile transformation to titanite is less strict with the rutile product forming a polycrystalline aggregate where the crystals are separated by low angle grain boundaries. This occurs because there are multiple nuclei with similar but measurably different orientations influenced by the rutile such that when the grain grow together the boundaries show the misorientation between grains. These relationships provide a basis for interpreting microstructures in altered and polymetamorphic rocks using routinely collected data and begin to illuminate processes of nucleation and growth and the relative importance of equilibrium and kinetic controls on reaction microstructure.

Deformation and retrogression initiated by hydration along pre-existing fabrics; using monazite and apatite to track and time geological events.

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The occurrence of wide shear zones, in different states of hydration and retrogression, juxtaposed to large granulite grade terranes poses questions about the relation and feedback mechanisms between deformation and metamorphism/metasomatism. At Mt Boothby, central Australia, ‘dry’ and impermeable orthogneisses have been deformed and metamorphosed into muscovite bearing mylonites. This provides an ideal natural laboratory to investigate the effects of crustal deformation processes in association with fluid flow and related transport of elements. The muscovite poor orthogneiss has developed a foliation defined by megacrystic perthite with aligned biotite, biotite that is concurrently aligned with an S plane at low angle to the foliation. U-Pb ages of monazite parallel to foliation and included in perthite indicate that this fabric has developed during the Chewings Orogeny (~1560 Ma). The orthogneiss foliation is crosscut by a mylonite in which asymmetric perthite porphyroclast float, indicating top to the south kinematics. Structural mapping results in the recognition of this shear zone being a Riedel branch of larger structures active during the Alice Springs Orogeny. In the shear zone perthite is replaced by fine-grained recrystallized K-feldspar and muscovite. Plagioclase remnants become progressively albitised and monazite is unstable. In order to time the shear zones activity apatite was dated being the stable U bearing phase in both orthogneiss and mylonite (increasing mode). Apatite U-Pb analyses result in ages of ~400 Ma and ~1500 Ma, indicating precipitation during both Alice Springs Orogeny and Chewing Orogeny. From petrography and micro-textural analyses we interpret that the shear zone was active during the Alice Springs Orogeny. Precipitation of young apatite along pre-existing fabrics in the orthogneiss also indicates the onset of metasomatic reactions in the wall-rock during the Alice Springs Orogeny. Metasomatism potentially weakening the orthogneiss resulting in failure and formation of the mylonite now exposed at Mt Boothby.

Initial Sr isotope ratios as a tracer of early crust-mantle evolution

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Determining the initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of Archean rocks is quite challenging due to the high Rb/Sr ratios of most rocks that require large corrections for in-situ produced ^{87}Sr . However, the minerals barite (sediments, hydrothermal deposits) and apatite (igneous rocks) generally have near zero Rb/Sr and thus corrections for the decay of ^{87}Rb are minimal, allowing for the direct determination of the initial $^{87}\text{Sr}/^{86}\text{Sr}$ from individual mineral grains. Barite, formed in some Archean marine settings, is less susceptible to later alteration than carbonates and thus is more reliable in reconstructing the isotope composition of Archean seawater. Due to its long residence times and redox insensitivity in the oceans, Sr isotopes can be used to link the Sr-seawater trend with crustal evolution (e.g. Satkoski et al., 2017). Stratiform barites were deposited simultaneously with chromiferous chert in the ~3.3 Ga Ghattihosahalli Schist Belt, Western Dharwar Craton, India (Jayananda et al., 2008). Strong spatial heterogeneities have been preserved in Sr isotopes and major elements despite pervasive ductile deformation and regional amphibolite facies metamorphism over long time-scales. Barite grains with Rb/Sr ratios <0.003 preserve a least radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.701338 ± 17 (2σ) that most likely records the isotope ratio at the time of formation. This low $^{87}\text{Sr}/^{86}\text{Sr}$ for seawater implies a gradual rise in $^{87}\text{Sr}/^{86}\text{Sr}$ over time rather than a steep evolution as proposed by Satkoski et al. (2016).

The initial isotopic composition of crustal igneous rocks is better preserved in the accessory mineral apatite (e.g. Tsuboi and Suzuki, 2003). In situ Sr isotope measurements of single apatite grains from granitoids and metasedimentary units deposited over a time span from 3.4-2.5 Ga in the western Dharwar Craton give clear insights into the development of Archean crust in that area. The low $^{87}\text{Sr}/^{86}\text{Sr}$ ratios exclude the presence of significantly older evolved crust in the area at 3.4 Ga. This questions the nature of the crust and high net rates of continental growth during that time (Dhuime et al., 2012, 2015).

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Preservation of oscillatory zoning in plagioclase inclusions from the Western Gneiss Region, Norway

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For many minerals, chemical diffusion is sufficiently fast on the geological time scale to homogenize chemical heterogeneities at temperatures exceeding 700 °C. Therefore, the observation of preserved chemical zoning at high temperatures is difficult to explain. This is particular problematic for oscillatory zoned minerals with sharp compositional steps experiencing high-temperature metamorphic conditions for several million years.

Here we investigate a rock specimen from the Western Gneiss Region (WGR) that experienced Caledonian ultra-high pressure (UHP) metamorphism with peak metamorphic conditions of >800°C and 3.2 GPa, and a post UHP overprint (with T >750 °C and 1.2 GPa) during exhumation. Polymineralic inclusions in garnets encompass amphibole, biotite and oscillatory zoned plagioclase of 150 x 200 µm size with thin compositional lamellae of 1-10 µm alternating from core towards the rim. The zoning of the plagioclase grain is reverse with increasing anorthite content from the inclusion core to the rim. We conducted a detailed microstructural characterisation utilizing a combination of electron microprobe analysis (EPMA), electron backscatter diffraction (EBSD) measurements and analytical transmission electron microscopy (A-TEM). The high-resolution analyses show that the compositional profile has sharp contacts between each lamella. Such sharp contacts exclude the possibility of pervasive diffusional modification.

In order to understand how such a high-temperature microstructure with sharp chemical zoning can be preserved on the million years' time scale, we apply conventional and unconventional diffusion quantification methods. It is shown that conventional (Fickian) diffusion would have equilibrated this microstructure within thousands of years. In contrast, we apply the newly developed approach where chemical diffusion is coupled to mechanical deformation (Zhong et al. 2017). We show that the preservation of such a compositional zoning in minerals can be strongly influenced by this coupling. A significant pressure gradient is developed inside the grain due to the chemical diffusion at the very early stage of the chemical re-equilibration. Due to slow viscous relaxation, this pressure gradient is then able to inhibit further concentration homogenization, explaining the preservation of the oscillatory zoning.

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Phase heritage: deciphering evidence of pre-existing phases via inherited crystallographic orientations

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Introduction: The concept of ‘phase heritage’ (e.g., Timms et al., 2017a) involves microstructural recognition of the former presence of a phase that has since transformed to another via evidence encoded in crystallographic orientations. Phase heritage relies on the phenomenon that newly grown (daughter) phases nucleate with particular crystallographic orientation relationships with the preceding (parent) phase. This phenomenon is common for displacive (i.e., shear or martensitic) transformations, well documented in the metals and ceramics literature, but is relatively uncommon in geosciences. This presentation outlines the concepts behind this approach, showcases results from software for automated analysis of EBSD data, and illustrates examples of polymorphic and dissociation phase transformations in the $\text{ZrSiO}_4\text{-ZrO}_2\text{-SiO}_2$ system, which has particularly useful applications for ‘extreme thermobarometry’ in impact environments (Timms et al., 2017a).

Theoretical considerations: The crystal symmetry of parent and daughter phases and the nature of the orientation relationship between them determine the maximum number of permissible symmetrically equivalent variants of the daughter from a single parent (Cayron et al., 2006). This means that a microstructure comprising daughter grains that have completely transformed from a parent grain define a specific pattern of crystallographic orientations. The number of variants can be predicted from the order of the parent point group divided by the order of the intersection group (i.e., the group of orientation symmetries common to parent and daughter crystals). The number of operators is given by the rotation/misorientation angle/axis relationships between the daughter and parent crystals. Therefore, if the symmetry operators for the phase transformation are known, then the phase transformations can be reverse-engineered to not only recognise the former presence of a parent phase but also to derive its unique crystallographic orientation(s). In this way, the entire microstructure of parent grains can be completely reconstructed from daughters that have inherited their crystallographic orientations. In fact, different orientation relationships can be tested using software ARPGE to find the best one for the parent reconstruction (Cayron, 2007, Cayron et al., 2010). Several generations of phase transformations via multiple, symmetrically equivalent nuclei orientations can generate complex patterns of daughter orientations. Reconstruction of parent grains from a two-stage transformation history requires knowledge of the orientation relationships for both phase transformations (e.g., Cayron, et al., 2010). Subsequent reversion from daughter to parent phases follows the reverse orientation relationships. An equal probability of the nucleation of neoblasts in symmetrically equivalent orientations can still result in a bias in the proportions of final orientations.

Thermal dissociation of zircon to ZrO_2 polymorphs: Glassy impact melt rock from the Mistastin Lake impact structure, Canada, shows that entrained zircon (ZrSiO_4) grains have dissociated to $\text{ZrO}_2 + \text{SiO}_2$ forming reaction rims of twinned vermicular baddeleyite

(monoclinic ZrO₂ stable at low-T) with interstitial silicate glass (Timms et al., 2017b). Automated analysis of EBSD map data using ARPGE successfully reconstructs parent grains of cubic polymorph of ZrO₂ from baddeleyite with complex twinning, indicating a two-stage transformation involving an intermediate tetragonal ZrO₂ stage. The former presence of cubic ZrO₂ in this sample required melt temperatures in excess of 2370°C, which represents the hottest naturally-achieved temperature recorded by any rock at the Earth's surface (Timms et al., 2017b).

High-pressure polymorphic phase transformations zircon-reidite-zircon: Granular-textured zircon from a variety of impact melt rocks preserve crystallites with approximately orthogonal crystallographic orientation clusters (Timms et al., 2017a; Cavosie et al., 2016; 2018). This distribution is readily explained by partial transformation of pre-existing zircon to the high-pressure ZrSiO₄ polymorph reidite, which occurs via up to eight symmetrically equivalent variants, arranged into two groups of four that are broadly orthogonal to one another (Erickson et al., 2017). A random selection of transformation orientations followed by random selection for the reversion to zircon statistically favours the original host zircon orientation, which is consistent with observations. This process of generating granular zircon required shock metamorphism >30 GPa to produce reidite followed by reversion to zircon via the formation of a granular texture upon release from shock pressures and waste heating (Timms et al., 2017a). Granular-texture zircon with this type of encoded microstructure has been termed FRIGN zircons (Former Reidite In Granular Neoblasts) (Cavosie et al., in review), useful for deciphering P-T history where back-transformations are complete and other evidence of pre-existing high-pressure phases have been destroyed (e.g., Cavosie et al., 2016; 2018, in press).

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Trace element mobility along deformation twins during ultra-high temperature crustal metamorphism

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Rutile (TiO₂) is routinely used in geological studies to gain a better insight into the nature and timing of metamorphic events. Rutile is used as a geochronometer (U-Pb), geothermometer (Zr) and is stable at high temperatures (up to granulite facies metamorphism). However, to correctly interpret the information provided by rutile chemistry, we need to understand the mobility of trace elements during metamorphism and deformation.

Recently, studies on the effect of ultra-high temperature (UHT) metamorphism on trace mobility within zircon from the Dallwitz Nunatak, Napier Complex (East Antarctica) has showed heterogeneous distribution of Pb, Si, Al and Ti (Kusiak et al., 2013a; Kusiak et al., 2013b). In the zircon, Pb appeared as metallic, <35 nm, inclusions, in combination with Si-rich and Al-Ti rich inclusions.

In this contribution, we have studied rutile from the Napier Complex to increase our understanding of trace element mobility during UHT metamorphism and tectonic deformation. The Napier Complex is a widely studied granulite terrane and has recorded the highest known metamorphic temperatures in the continental crust, with peak temperature estimates exceeding 1150 °C. Rutile occurs as an accessory phase mineral in a garnet-rich orthogneiss and was studied here using atom probe microscopy (APM) and correlative techniques, including electron backscatter diffraction imaging (EBSD).

EBSD revealed the presence of several deformation twins in all analyzed grains, consistent with the grains being exposed to significant tectonic stresses during metamorphism. APM analysis of the twin boundaries revealed a strong enrichment in trace elements including U, Pb, Ca, Mg, LREE and H/OH along the twin interface. The presence of Ca, Mg and the LREE along with significant hydrogen levels raises questions about the interaction between rutile and the garnet/feldspar rich matrix and the potential effect this has for U-Pb geochronology and Zr-in-rutile thermometry.

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