Disequilibrium Metamorphism of the Earth's Lithosphere and some Geodynamic Implications

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Abstract

Most changes in mineralogy, density, and rheology of the Earth's lithosphere take place by *metamorphism,* whereby rocks evolve through interactions between minerals and fluids. These changes are coupled with a large range of geodynamic processes and they have first order effects on the global geochemical cycles of a large number of elements.

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

Keywords: Metamorphism, fluid-consuming reactions, disequilibrium, porosity generation, strain localization

1. Introduction

Most of the Earth's lithosphere evolves under conditions where metamorphic processes are the dominant transformation mechanism, and metamorphism provides strong feedbacks on a large range of geodynamic processes. Metamorphism has first order effects on lithospheric responses to the buoyancy forces arising from variations in lithospheric thickness (Zoback, 1992), including the subsidence of sedimentary basins (Kaus et al., 2005), the stability of deep mountain roots (Jackson et al., 2004), and the extension of high topography regions (Andersen and Jamtveit, 1990). Generation of mechanically weak metamorphic rocks may contribute to strain localization and even the formation of intracontinental orogens (Raimondo et al., 2014).

Many of the most important physical feedbacks between metamorphism and lithosphere-scale geodynamics are related to changes in the density and rheology of the lower crust and upper mantle. These changes are often driven by localized infiltration of aqueous or carbon-bearing fluids along tectonically produced shear- or fracture zones (Newton, 1989). The associated metamorphic reactions are usually fluid consuming (often referred to as *retrograde* metamorphism) and produce mechanically weaker rocks comprising sheet silicates and/or carbonates. Near the Earth's surface, fluid-consuming weathering reactions involving magmatic and metamorphic rocks are low-temperature analogs to retrograde metamorphism (Fletcher et al., 2006; Røyne et al., 2008).

Fluid-consuming reactions furthermore play a key role in the global geochemical cycles of a large range of elements transported by fluids, including carbon and sulfur, and engineered acceleration of retrograde carbon-consuming reactions involving CO_2-rich fluids and metastable mafic and ultramafic rocks has repeatedly been proposed as a means of in situ carbon sequestration by mineral precipitation (Oelkers et al., 2008; Kelemen et al., 2011).

Despite of the geochemical and geodynamic significance of fluid consuming metamorphism, most quantitative studies of metamorphism have focused on *prograde,* fluid-producing metamorphism driven by the heating of sedimentary or metamorphic rocks during subduction processes or locally around magmatic intrusions into colder lithosphere. This is at least partly because the dominant paradigm in metamorphic petrology is rooted in the chemographic and thermodynamics-based conceptual framework developed by Goldschmidt (1911), Thompson (1957), Greenwood (1962), Perchuk (1970) and others. Since mineral reactions *in the presence of fluids* are usually considered to be fast compared to the expected rates of temperature and pressure variations caused by tectonic processes (Wood and Walther, 1983), the equilibrium paradigm adequately describes many aspects of prograde metamorphism. This is indeed attested by numerous powerful applications of equilibrium-based phase petrological software such as *THERMOCALC* (Holland and Powell, 1998) and *Perplex* (Connolly, 1990; 2005) in attempts to understand petrogenetic processes. However, it provides a far less satisfactory basis for understanding retrograde or fluid-driven metamorphism and associated mass transfer (metasomatism) in general. The main reason for this is that retrograde metamorphism generally takes place far from equilibrium and its rate and progress is intimately linked to the availability of fluids, rather than variations in temperature and pressure (Jamtveit and Austrheim, 2010).

An effective and quantitative characterization of far-from-equilibrium transformation processes in the lithosphere requires a conceptual framework that transcends that provided by classical thermodynamics-based phase petrology. It needs to account for the coupling between chemical, mechanical and transport processes operating simultaneously over many different time and spatial scales.

In this review paper, we argue that *disequilibrium metamorphism* is far more common and far more significant in a large-scale geodynamic context than hitherto recognized. There is an urgent need to deal with the complexity of disequilibrium metamorphism in a quantitative way, to make the study of metamorphism an integral part of geodynamics and *Earth Systems Science* in general.

2. The metastable crust

The continental crust-mantle boundary (MOHO-) temperature varies significantly with tectonic setting, crustal heat production, etc. However the most

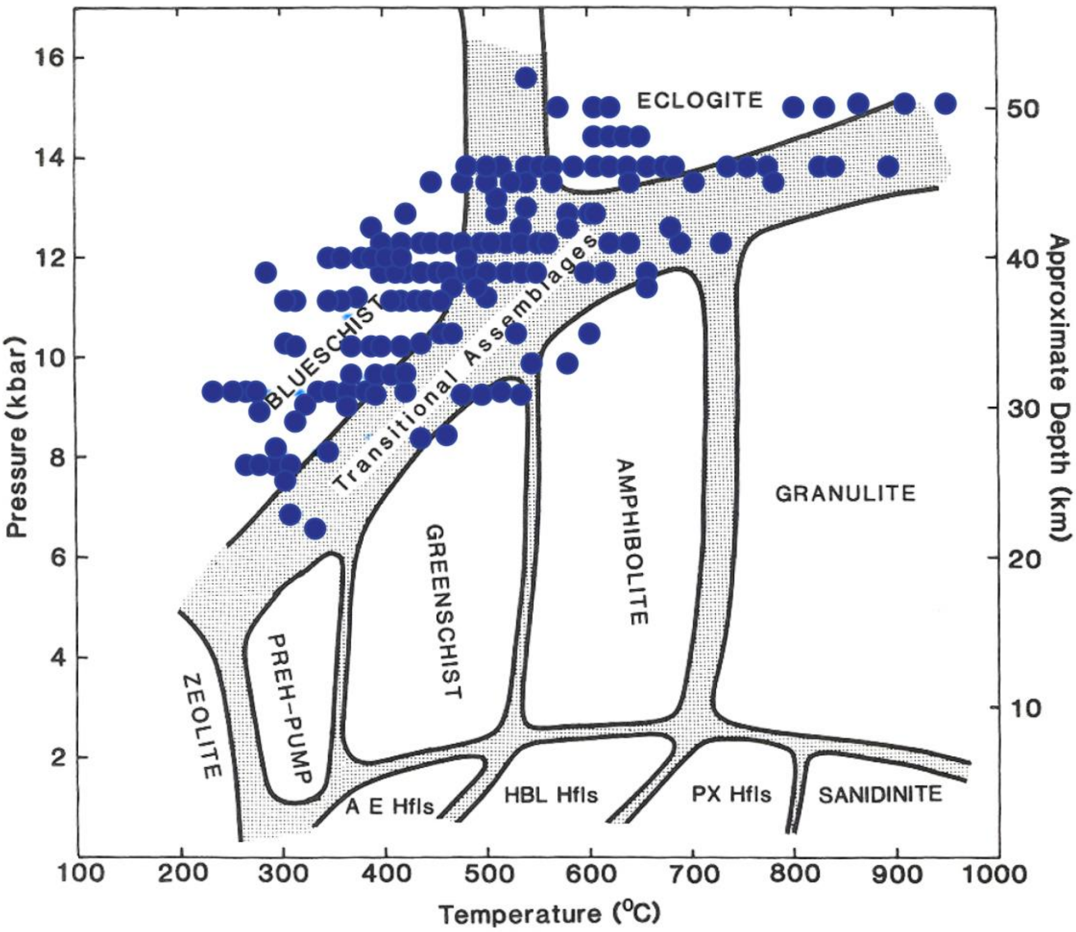

Figure 1. Pressure-temperature diagram showing the fields of the various metamorphic facies (from Yardley, 1989). Blue dots denote calculated MOHO temperatures as a function of crustal thicknesses for continental regions with surface heat flux less than 100 mW m^{-2} (from Mareschal and Jaupart, 2013). It is clear from this diagram that granulite- and amphibolite-facies rocks are largely metastable at MOHO conditions.

recent compilations of heat flow data (Mareschal and Jaupart, 2013) suggests that most MOHO temperatures fall in the range 300-700°C for crustal thicknesses in the range 30 to 50 km. The implication of this is that almost all granulite facies rocks, and a large fraction of the amphibolite facies rocks comprising the Earth’s crust are metastable (Fig. 1) and will be highly reactive in the presence of fluids of almost any plausible composition. Granulites and amphibolites make up the major part of the lower and middle crust (Rudnick and Fountain, 1995) and many of these feldspar-rich rocks are metastable even in the absence of fluids, but survive due to the sluggishness of solid-state processes. The same applies to the peridotites making up a significant fraction of the subcontinental mantle. In the presence of a hydrous fluid these would convert to serpentine-bearing assemblages below 500-600°C, depending on pressure (cf. Schmid and Poli, 1998) and fluid composition (Johannes, 1969). Likewise, the oceanic lithosphere, being mostly made up of igneous rocks, is obviously metastable in the presence of fluids at normal crustal temperature conditions. Although a significant fraction of the oceanic lithosphere gets serpentinized during interactions with seawater, serpentinization only extends to a maximum of 3 to 4 km into the footwall of axial detachment faults even at slow spreading ridges (Cannat et al., 2010). Thus most of the oceanic lithosphere remains largely unaltered (cf. Iyer et al., 2010).

Most of the rocks constituting the Earth's crust, continental or oceanic, have thus formed at higher temperatures than the temperature they experience when the geothermal gradient has settled back towards a steady state situation. The reason why they maintain their high temperature mineralogy is simply that the lower crust and upper mantle are dry (Yardley, 1995; Yardley and Valley, 1997); *dry* in the sense that the chemical potential of volatile components such as H_2O or CO_2 are too low to produce hydrous phases or carbonates. This is incompatible with the presence of a separate fluid phase. In addition, many mineralogical transformations occur via dissolution in (or reaction with) a fluid phase and precipitation of product minerals. Without the "catalytic" effect of the fluid, these transformations do not occur on geologically relevant time scales.

Recent experimental work (Yardley et al., 2014) indicates that a fracture-filling fluid introduced to lower crustal granulites would be consumed by fluid-consuming reactions within a time scale of less than 100 years. The implication of this is that during an orogeny or any other event that triggers fluid movements in the lithosphere, *most of the crust will act as an effective sink for fluids*. Only a small fraction of the continental lithosphere, and in particular the shallow part, will produce fluids through prograde metamorphism of sedimentary rocks (which compose <<10% of the Earth crust) or low-grade metamorphic rocks. Most of the middle and lower crust will be retrogressed, *if* exposed to fluids. Geochemical evidence from such volatilization processes can be seen in extremely fractionated fluid inclusions formed during eclogitization of lower crustal granulites, where fluids are depleted in water to the extent that they even precipitate daughter crystals of Br, Cl-salts (Svensen et al, 1999).

This implies that fluid migration in the lower crust and much of the oceanic lithosphere *is associated with porosity generation* by tectonic or other forces. Without porosity and permeability generation, the lower crust is non-porous and impermeable to fluid migration.

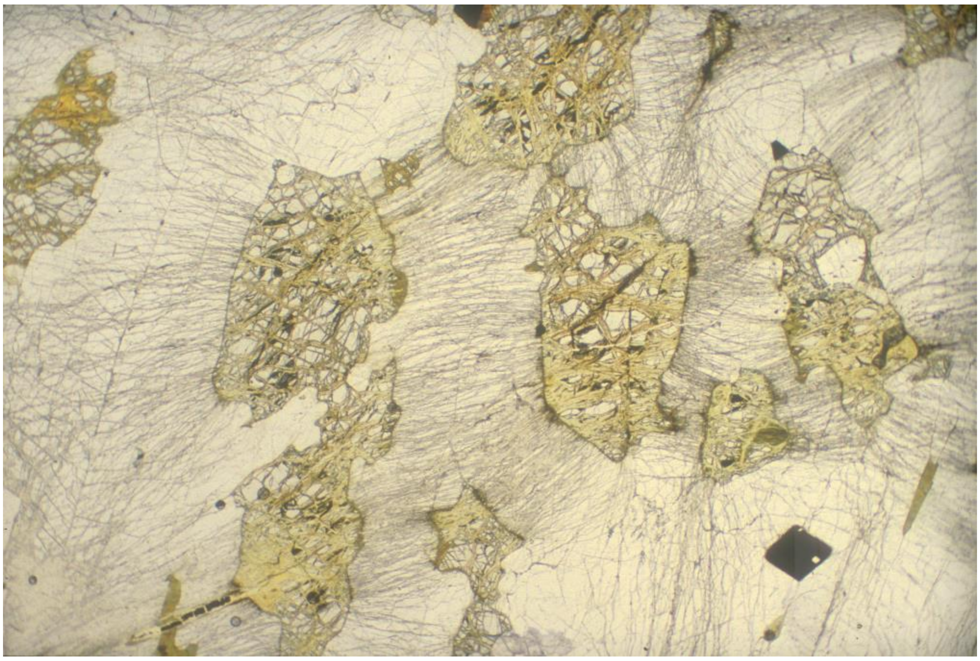

Figure 2. Microphotograph of reaction-driven fracturing around partly serpentinized olivine crystals in a plagioclase matrix from a troctolite from the Duluth Igneous Complex. A dense network of microfractures connects individual olivine crystals and provides pathways for fluid migration.

3. Disequilibrium fluid-consuming metamorphism

Fluid-consuming metamorphic reactions are typically characterized by a substantial increase in solid volume, which in extreme cases may reach 30-40% such as during serpenitnization, as well as an entropy change on the order of 60-80 $Jmol^{-1}K^{-1}$ (Fyfe et al., 1958). When such reactions take place far from thermodynamic equilibrium, the associated dissipation of energy by heat and deformation processes may cause significant perturbations of the temperature and stress fields of the lithosphere. More than 50 years ago, Schuiling (1964) proposed that anomalously high heat-flow values near oceanic ridges could be caused by serpentinization reactions. This was supported more recently by Delescluse and Chamot-Rooke (2008) based on heat flow data from the Indian Ocean. Schuiling (1964) assumed that the rate of serpentinization was given by the rate of sea-floor spreading. Recently, Iyer et al. (2010) calculated the rate of serpentinization at ocean spreading centers based on the kinetic experiments of Martin and Fyfe (1970). Their results are consistent with the geophysical data of Carlson (2001) who estimated that the amount of water present in serpentinites in an average crustal column of the Atlantic lithosphere should be on the order $\approx 10^5$ kg/m^2. Taking this as a representative

global average, combining it with an annual global sea-floor production rate of ca. 2.5 km^2/year (Conrad and Lithgow-Bertelloni, 2007) and making the conservative assumption that the serpentinization reaction takes place on average 100K below the equilibrium temperature (Iyer et al., 2010) indicates that sea-floor serpentinization alone dissipates energy at a rate in excess of 5 GW. This is comparable to the average global energy dissipation rate by earthquakes, and underscores the potential significance of disequilibrium metamorphism for a range of geodynamic processes.

It is important to note that the total energy dissipated during metamorphism also has a contribution from irreversible deformation processes driven by reaction induced differential stress. As predicted by Wheeler (1987) based on thermodynamic considerations and later confirmed by Jamtveit et al. (2000, 2008, 2009), Jamtveit and Hammer (2012), and Kelemen and Hirth (2012) based on microstructures, volatilization reactions may produce local stress perturbations beyond the breaking threshold of rocks (a few hundred MPa, depending on confining pressure) (Fig.2).

Several experimental studies have confirmed that reaction-driven fracturing may represent an effective mechanism that generates fresh reactive surface area during volatilization processes (Ostapenko, 1976; Jamtveit et al., 2009; Okamoto et al., 2011; Malvoisin et al., 2012, Dunkel and Putnis, 2014). Some of these are illustrated in figure 3.

Disequilibrium metamorphism is therefore, in general, characterized by a strong coupling between chemical and mechanical processes. This coupling has been proposed as a key factor in controlling the rate of a variety of volatilization processes, including spheroidal weathering (Fletcher et al., 2006; Røyne et al., 2008), serpentinization (Iyer et al., 2008; Plümper et al., 2012), as well as the rate of subsurface carbonation of ultramafic rocks by ground waters (Kelemen et al., 2011). Recent modeling studies by Rudge et al (2010) and Ulven et al. (2014) analyze how the overall rates of such volatilization processes are controlled by reaction kinetics, transport properties and thus porosity, as well as geometrical constraints for 1D and 2D scenarios respectively. These models do account for reaction produced fracturing but do not, however, account for possible clogging of fracture space by mineral precipitation. By ignoring possible clogging effects induced by growth in the pore

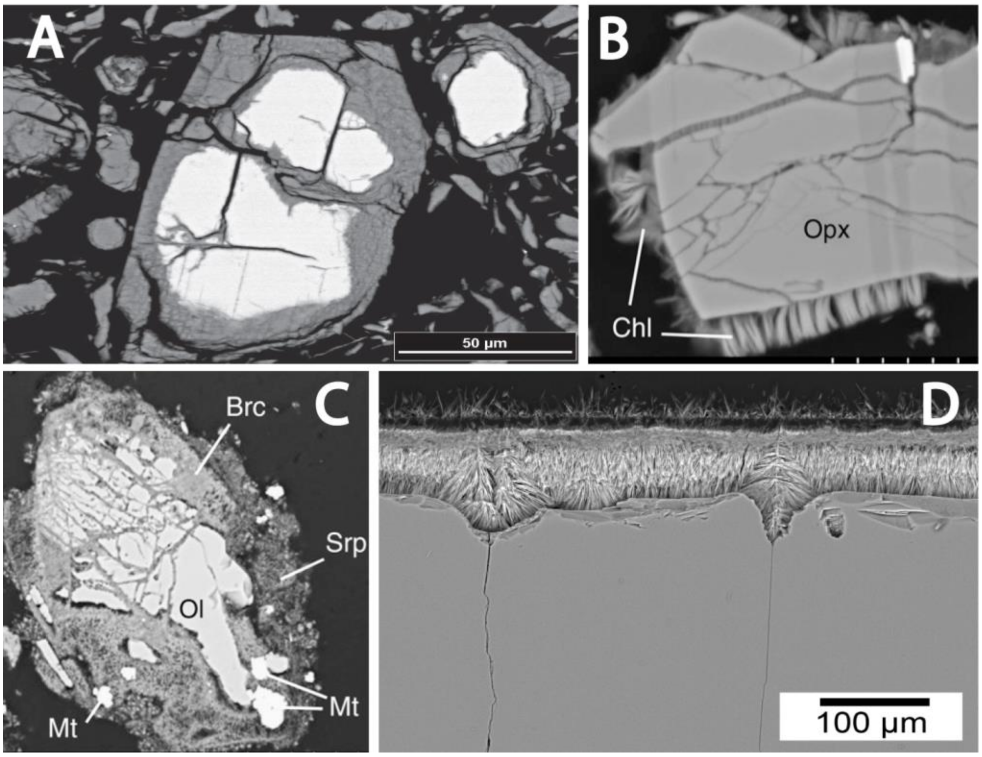

Figure 3. Reaction-driven fracturing during experimentally produced volatilization reactions. A) Leucite partly replaced by analcime (from Jamtveit et al., 2009). B) Orthopyroxene partly replaced by chlorite (from Okamoto et al., 2011). C) Olivine partly replaced by serpentine, brucite and magnetite (from Okamoto et al., 2011). D) Scolecite replaced by tobermorite (Dunkel and Putnis, 2014). All experiments were carried out under hydrothermal conditions at temperatures in the range 150 to 250°C.

space, they thus tend to overemphasize the positive feedback between reaction progress and transport rates. It has been experimentally demonstrated that fluid consuming reactions in porous peridotites lead to clogging of the pore space and a retardation of reaction rates (Hövelmann et al., 2012), and a better understanding of the conditions by which growth in pores space leads to clogging effects in contrast to porosity increase by reaction driven fracturing, remains one of the key problems to be addressed in future studies of fluid consuming metamorphism in the lithosphere (cf. Røyne and Jamtveit, 2015).

Figure 4 Liesegang banding in soapstone that formed at the expense of serpentinite during a carbonation process at the Linnajavri ophiolite, Northern Norway (Beinlich et al., 2012). The banding is defined by variable amounts of magnesite and talc (dark layers are magnesite rich). Field of view ca 1 meter. Photo: Bjørn Jamtveit.

4. Dissipative structures

Within the near-equilibrium paradigm of metamorphism, where mass fluxes are linearly related to chemical potential gradients (cf. Fisher, 1973, 1978; Joesten, 1977; Foster, 1981), the formation of emergent structures such as banding or other forms of more or less regularly spaced elements is not possible. In far-from-equilibrium (dissipative-) systems however, a non-linear coupling of chemical reactions, transport processes, and/or mechanical processes may produce a variety of patterns.

Already in the 70s, observations of metamorphic segregations such as crenulation cleavages and other examples of metamorphic banding (Fig. 4) were recognized as having originated by the metamorphic processes themselves rather than by inherent heterogeneities or external templates. They were in other words recognized as 'emergent structures', the outcome of some self-organizing and thus non-linear process. Quantitative models explaining such structures were put forward by Fletcher (1977) and Robin (1979), who both invoked couplings between chemical and mechanical processes in their models. The fact that such patterns required that the rocks were substantially out of equilibrium, even at scales approaching the grain size, did not however seem to be regarded as a result with wide ranging implications, although metamorphic layering became a frequently used example of geochemical self-organization (cf. Ortoleva et al., 1982; Wiltschko and Morse, 2001, Hobbs et al., 2011).

While crenulation cleavage and Liesegang-banding have perhaps been the favorite examples of metamorphic pattern formation since the heydays of geochemical self-organization (cf. Ortoleva et al., 1987), two new and perhaps even more important patterns have recently emerged as key components in metamorphic transformation processes: *Pore structures*, and *fracture patterns*. Since most fluid-consuming reactions also lead to an increase in solid volume, and thus potentially to clogging of pore space and reduction in permeability, reaction driven porosity and fracture generation is essential in securing continued supply of fluids during the reactions and may completely control its progress (Putnis, 2002; Ulven et al., 2014).

4.1 Pore structures

The pore space of a metamorphic rock may be influenced by a range of different processes, including the pore structure of its sedimentary or magmatic protolith. At near equilibrium conditions, the fluid distribution is mainly a function of the fluid-solid and the solid-solid surface energies (Laporte and Provost, 2000). However, when a metamorphic reaction takes place at far-from-equilibrium conditions, pore structures may arise that reflect the reaction dynamics rather than minimization of surface energies. In some cases, porosity may form by mechanical processes such as fracturing, but in other situations, complex pore networks may emerge solely from coupled reaction-transport processes. An example of the latter is commonly seen during pseudomorphic replacement processes, where single crystals are replaced by a new mineral or assemblage of minerals while retaining the external shape and size of the original crystal.

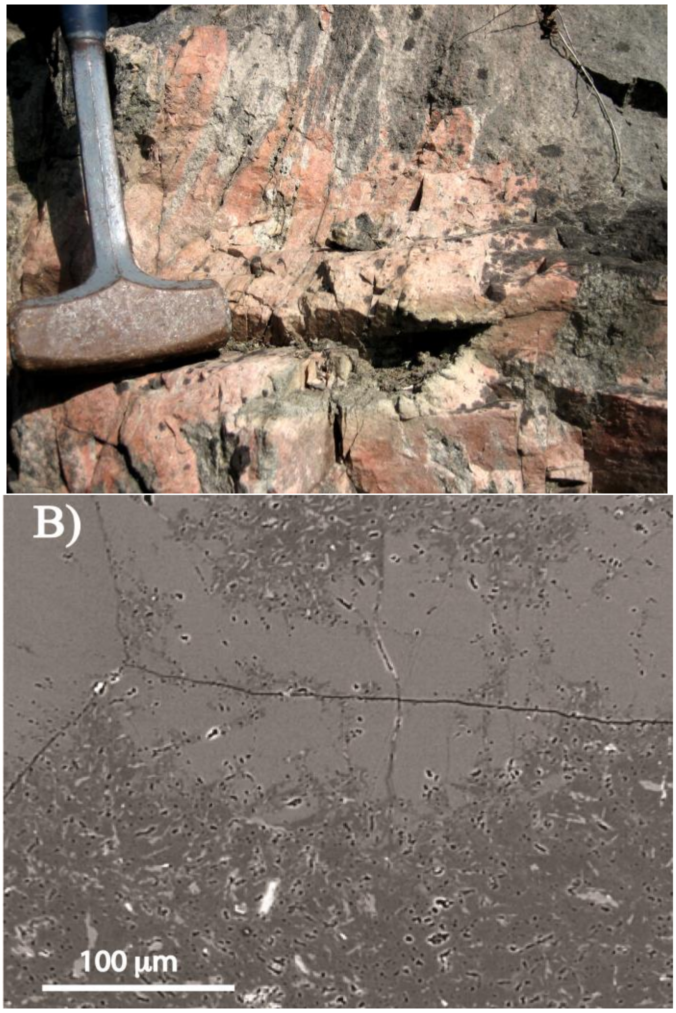

Figure 5. (a) Alteration of a mafic intrusion to red albitite. Ringsjø, Bamble, Norway. (b) Back scatter SEM image showing replacement texture during albitization of oligoclase feldspar. The smooth lighter gray is the original oligoclase, while the darker phase replacing it is pure albite with some muscovite and minor hematite.

The conservation of shape, as well as the observation that in many cases crystallographic information is transferred from parent to product was originally interpreted to imply that pseudomorphism must take place by a solid-state mechanism. However, the fact that pseudomorphism is rarely isochemical and can be readily reproduced in fluid-mineral interaction experiments (Putnis, 2009) confirmed that pseudomorphism results from the coupled dissolution of the parent phase and precipitation of the product within a thin film of solution at the reaction interface. The propagation of the reaction interface through the parent crystal depends on porosity being generated in the product phase, enabling mass transfer from an external fluid reservoir.

Figure 5 shows an example of such a reaction interface where a solid pore-free single crystal is replaced by a porous product. In this example the parent phase is a Ca-bearing feldspar (~20% $CaAl_2Si_2O_8$ – 80% $NaAlSi_3O_8$) while the product is almost pure albite $NaAlSi_3O_8$. (Engvik et al., 2008). There is only a small molar volume reduction associated with this replacement reaction. The porosity arises because in the reactive fluid the parent phase is more soluble than the product and hence some material is lost to the fluid phase during the replacement. In this example, no fluid is consumed to produce the solid products only to form fluid-filled pore space.

The amount of porosity produced by this reaction is determined by a combination of molar volume change and relative solubility in the specific fluid composition (Pollok et al., 2011). During the replacement process the porosity must be interconnected, although being a dynamic and transient feature, the porosity itself will tend to coarsen with time, eventually being annealed out altogether if contact with fluid is maintained. Thus in the example in Fig.5 the replacement reaction has stopped either because of lack of fluid, or loss of connectivity of the pores.

In the example above, the crystallographic orientation of the product phase is the same as in the parent because the precipitation is epitaxial on the dissolving mineral surface. A very well studied example of a model system in which crystallographic orientations are preserved is the pseudomorphic replacement of KBr by KCl (Putnis and Mezger, 2004; Putnis et al., 2005; Raufaste et al., 2011; Pollok et al., 2011) which shows the sharp interface between the parent and product phase.

In contrast, when the product phase has no common crystallographic or structural characteristics with the parent, the product phase will be polycrystalline and the porosity may include the spaces between individual crystals in the product as well as intracrystalline porosity. Examples of such a case are the replacement of marble ($CaCO_3$) by apatite ($Ca_5(PO_4)_3(OH,Cl)$ (Jonas et al., 2014) and ilmenite by rutile (Janssen et al., 2010).

Clearly, the complex and highly dynamic pore structures that emerge from these replacement processes provide first order controls on the overall reaction rate and mechanism, as well as the mass transfer between minerals and fluid.

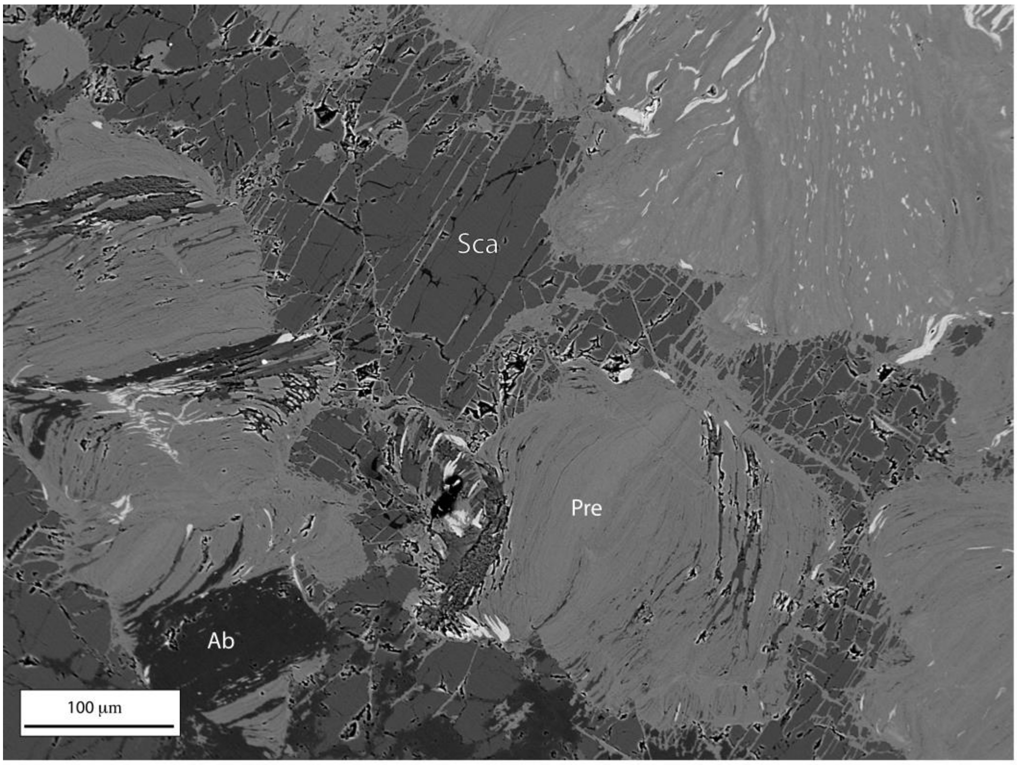

Figure 6. Reaction induced fracturing of scapolite (Sca) around bent aggregates of prehnite (Pre), albite (Ab) and titanite (bright inclusions). The fracturing and bending occur as prehnite, albite and titanite replace phlogopite (no longer present) during low grade metamorphism, causing volume expansion which generates compressive stresses. These stresses crack the brittle scapolite and bend the more ductile prehnite. The fractures allow more fluid into the system, continuing the replacement process. The sample is from the Bamble sector, SE-Norway. From Jamtveit and Austrheim, 2010.

4.2 Fracture patterns

Examples of fracture patterns arising from volume changing reactions in systems relevant to metamorphism were shown in figures 2 and 3. While tectonic deformation, according to the Gutenberg-Richter law, riddles the crust with fractures on all scales (Molnar et al., 2007), fractures also form as a response to stress generated by reactions. In the hydrothermal experiments producing the patterns shown in figure 3, the reacting domains are not subject to non-isotropic external stress from the confining fluids. Hence, all the fractures are formed as a response to reaction driven stress. In isotropic systems, such internally driven fracturing often produces characteristic fracture patterns with a domination of four-sided domains and orthogonal fracture (T-) junctions. These internally produced fracture patterns are different from the usually conjugate sets formed by externally imposed tectonic fracturing, where fractures often intersect at angles around 60 degrees. Continued fracturing and fragmentation leads to the formation of hierarchically arranged fracture sets with characteristic scaling properties (Iyer et al., 2008; Plümper et al., 2012). Similar patterns have been described from examples of spheroidal weathering (Røyne et al., 2008; Jamtveit et al., 2011), another case of reaction-driven fracturing associated with fluid-consuming reactions.

In anisotropic systems such as minerals with pronounced cleavages or polymineralic rocks, the associated fracture patterns may be dictated by pre-existing heterogeneities or the spatial location of the volume increasing reactions. Figure 6 shows an example of reaction-driven fracturing during low-grade metamorphism of a meta-gabbro. The growth of prehnite generates stresses that both drive fracturing of the original scapolite grain, and bending of the more ductile prehnite aggregates.

Low grade metamorphism of exhumed coarse-grained sheet silicate bearing igneous or metamorphic rocks is, in fact, often characterized by a microstructural development which includes both porosity dilation and deformation of the original micas. Examples of such microstructures were described by Holness and Watt (2002) and Holness (2003) who described how the growth and K-feldspar and albite in quartzo-feldspatic rocks from a range of localities causes bending and fracturing of the original mica grains (Fig. 7a).

Figure 7b shows another example of reaction induced sheet silicate bending, in this case associated with the growth of a euhedral epidote crystal in a mafic rock from the Bamble sector in Southern Norway. The epidote crystal is oscillatory zoned with variations in Fe/Al-ratio. This may in itself be an indication of growth far from thermodynamic equilibrium (Shore and Fowler, 1997). Disequilibirum growth of the epidote crystal has generated local stresses through it's 'force of crystallization' (Weyl, 1959) to the extent that these stresses have caused fracturing and development of micro-faults within the growing epidote itself, as observed by the offsets of the planar zoning patterns (Fig. 7c). The microphotograph in Fig. 7c not only reveals a dissipative compositional pattern emerging during metamorphism (the oscillatory zoning), but also illustrates reaction driven energy dissipation by fracturing and frictional sliding (faulting).

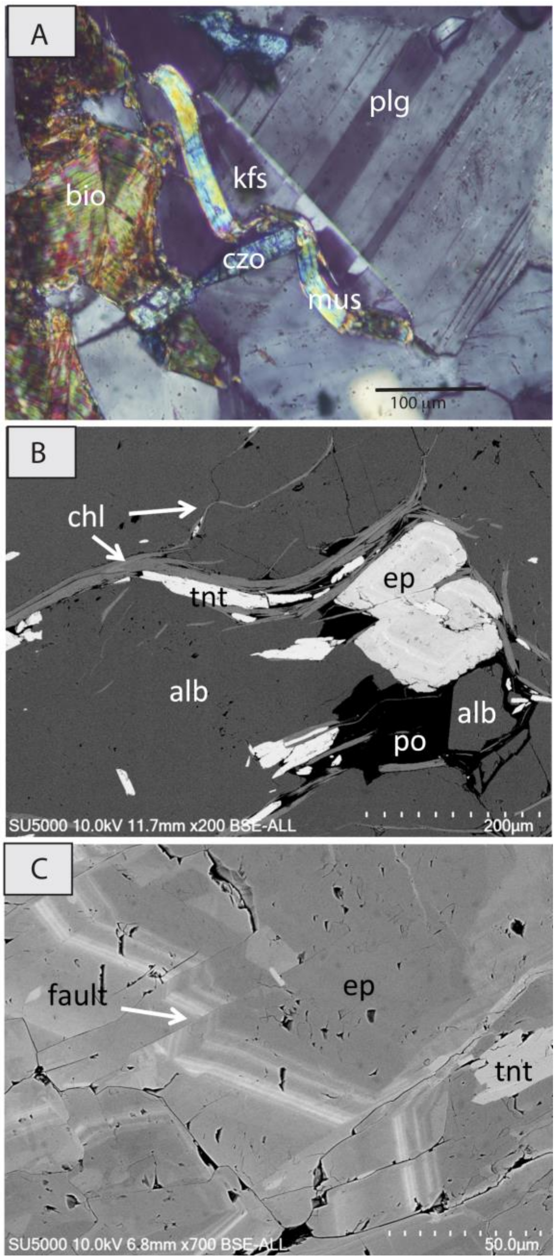

Figure 7. (a) Gneiss from Inverness-shire, Scotland. A K-feldspar (kfs) lens growing at the contact between a muscovite grain and plagioclase has forced the mica grain against a rigid grain of clinozoisite (czoo) causing it to bend and fracture. Bio=biotite (from Holness, 2003). (b) Growth of oscillatory zoned epidote (ep), albite (alb), and titanite (tnt) at the expense of chloritized biotite (chl) and plagioclase in a mafic intrusion from Varberg, Kragerø, Southern Norway. Note the bending of the chloritized biotite and the development of large pores (po) adjacent to the epidote. Euhedral albite crystals grow in these pores. (c) Details of oscillatory zoned epidote (ep) showing displacement of the zoning pattern along micro-faults (fault). The micro-faults crosscut the zoning pattern and is interpreted to form due to forces generated by the growing epidote crystal.

Both the pore structures and fracture patterns described above are features that are generated by the dissipation of energy during disequilibrium metamorphism, and both structures play a key role in securing continued fluid supply and reaction progress. However, in natural systems, fluid pathways may obviously also be affected by permeability formation caused by tectonic processes. The coupling between externally and locally generated stresses will be discussed below.

5. The stress state of the crust

The Gibbs free energy (*G*) expresses chemical potentials as a function of temperature and pressure. These have been the key independent variables in metamorphic petrology from when Eskola introduced the metamorphic facies concept almost a century ago (Eskola 1920) to Spear's already classic textbook in metamorphism (Spear 1995). The pressure-temperature-time paths that were found for metamorphic rocks by converting the pressures obtained from mineral equilibria directly to the depth of burial have been important deliverables in the application of metamorphic petrology to constrain plate tectonic processes (England and Richardson, 1977; England and Thompson, 1984).

Within the mainstream paradigm of metamorphic petrology, differential stress has not been considered an important factor in controlling neither metamorphic mineral assemblages nor metamorphic processes, except indirectly by affecting fluid migration through fracturing or other kinds of dilatant deformation (cf. Brace et al., 1970; Green 2005). The assumption has been that metamorphic rocks are too weak to sustain large differential stresses over significant periods of time. These conceptions are now being challenged by a number of observational, numerical, as well as theoretical studies, some of which will be reviewed in the following.

For almost 30 years, since the early stages of the World Stress Map Project that was launched as part of the International Lithosphere Program (ILP) in 1986 (Zoback, 1992), it has become increasingly clear that elastic stresses generated by plate tectonics are transmitted over distances comparable to the size of the tectonic plates. Much of the intraplate continental crust is in a state of stress near the failure equilibrium (Zoback and Townend, 2001; Zoback et al., 2002). *In situ* stress measurements from several deep boreholes worldwide (including the KTB borehole) correlate extremely well with predictions made using frictional

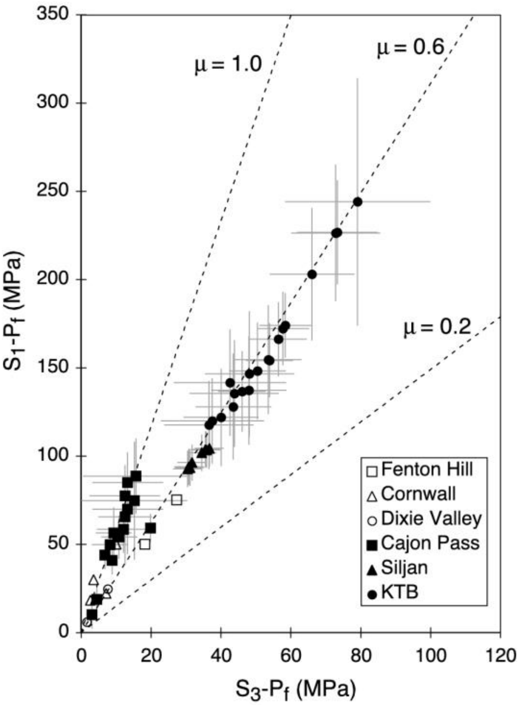

Figure 8. Stress data from six boreholes reported by Zoback and Townend (2001) illustrating that the upper crust is in a stress state consistent with that predicted by Coulomb frictional theory with a friction coefficient in the range 0.6-1. S_1 and S_3 represent the maximum and minimum stress axes respectively. P_f is the fluid pressure.

faulting theory and laboratory-derived coefficients of friction (Fig.8). High frictional strength furthermore suggests that the upper crust is too strong for fluid pressures to significantly exceed hydrostatic pressure.

Although the rheology of the lower crust and upper mantle has been subject to considerable controversy in the past, and probably varies significantly from one geological setting to another (Bürgmann and Dresen, 2008), many lines of evidence suggests that a strong lithospheric upper mantle rheology is required to account for the observed far-field stress propagation (Raimondo et al., 2014). In their classical 'jelly-sandwich' model, Chen and Molnar (1983) assume a weak lower crust. However, as pointed out by Jackson et al. (2004), a dry, metastable, and strong lower crust is essential for the survival of thick mountain roots and, hence, of high mountains. Furthermore, numerous observations of pseudotachylites and thus frictional melting in fault zones accompanied by hydration of lower crustal rocks (Fig. 9) attest to the existence of significant differential stresses in the metastable lower crust prior to re-equilibration in the presence of fluids (Austrheim, 1987; Austrheim and Boundy, 1994; Andersen et al., 2008). It is therefore reasonable to assume that metamorphic processes throughout the lithosphere often take place in systems subject to significant differential stress. This has major implications for the dynamics of metamorphism, under both near and far from equilibrium conditions.

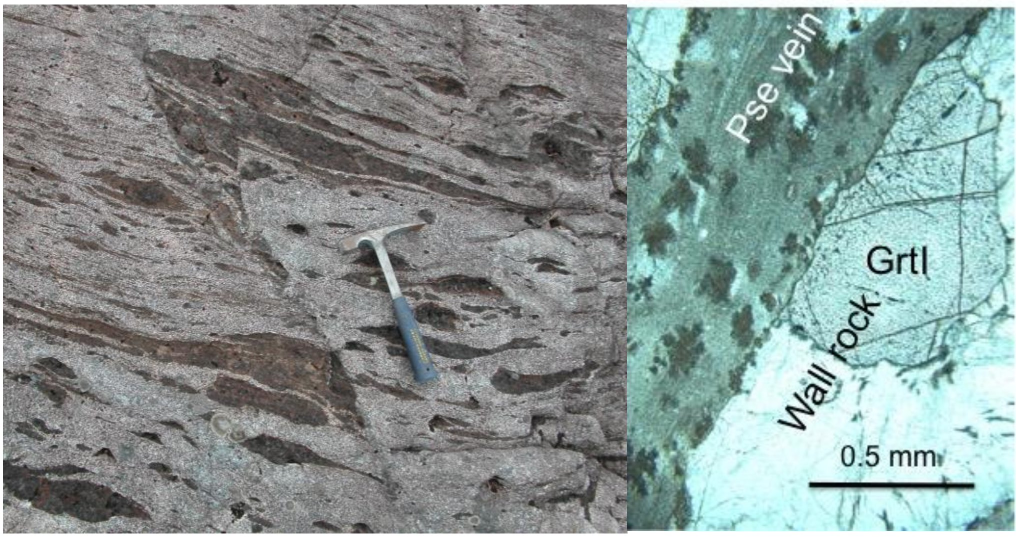

Figure 9. Fault through lower crustal granulite (left), producing a mm-thick zone of frictional melt that subsequently froze to form a pseudotachylite (Pse) vein (right) locally containing a hydrous eclogite facies mineralogy. Both the faulting, the introduction of an aqueous fluid along the faults, and the subsequent growth of dendritic garnet crystals (dark spots) in the cooling pseudotachylite must have occurred on time scales of tens of seconds (Jackson et al., 2004).

6. Reactions in stressed rocks

The common presence of significant differential stresses at all levels of the lithosphere may have a profound, and until very recently largely ignored influence on metamorphism. Fracturing and other forms of deformation may obviously affect rock transport properties and thus the kinetics of metamorphic reactions. However, even in the absence of such effects, stress may have significant effects on metamorphic reactions through its effects on reaction pathways. These two stress-effects, on the kinetics and the energetics of metamorphism, will be discussed below.

6. 1 Energetic considerations

By uniting the theories describing the thermodynamics of systems under isotropic stress with the theory of pressure solution, Wheeler (2014) concluded that "any preconceived idea that a specific mineral assemblage can be the 'most stable' in a stressed rock must be abandoned".

Following Kamb (1961), Paterson (1973) and others, Wheeler points out that the favorite pressure and temperature dependent thermodynamic variable of metamorphic petrologists, *G*, is not defined in a stressed system. In a stressed system, different surfaces of the same mineral grain will represent different chemical potentials due to variations in normal stress, and the appropriate *local* potential (μ_{local}) will be a function of the Helmholtz free energy (*F*) through the expression:

$$\mu_{local} = F + \sigma_n V$$

where σ_n is the normal stress across the relevant interface and *V* is the molar volume.

Therefore, different metamorphic reaction pathways will represent different energy thresholds that need to be overcome for reactions to proceed. Wheeler concludes that the pressure difference between metamorphic reactions taking place at a modest differential stress of 50 MPa and those occurring in a non-stressed system may be up to 500 MPa. This pressure variation corresponds to ca 18 km variation in 'apparent' depth if the effects of stress are ignored.

6.2 Kinetic considerations

A general model describing disequilibrium metamorphism in a tectonically stressed rock is a formidable task (cf. Hobbs et al., 2011; Fletcher 2015; Wheeler 2015) and currently beyond reach. The main effect of external stress is probably via its influence on rock permeability and the access of fluids, but non-hydrostatic stress is also known to affect reaction progress in the absence of a free fluid phase through its effect on the grain boundary structure (cf. Keller et al., 2010).

The presence of large regions of highly stressed lithosphere implies that local *perturbations* of the stress field caused by metamorphism may trigger a much larger response than what would be expected from metamorphic processes alone. In their recent work on serpentinization, Roumejon and Cannat (2014) attempted to connect observed fracture patterns on a broad range of scales to tectonic, thermal and reaction

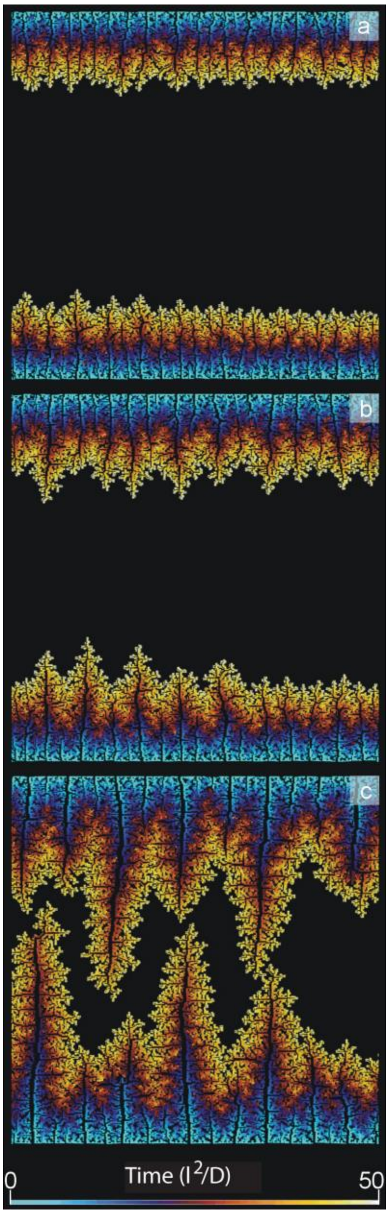

Figure 10. Simulated fracture patterns for a system subject to anisotropic external stress, with fluid invasion from the top and bottom surfaces. Initially, only the top and bottom nodes are in contact with the fluid. Nodes are coloured according to the exposure time to the fluid with a common timescale at the bottom. Time is measured in units of l^2/D, the reaction time for a single grain, where l is the critical stable crack length. The effect of increasing the anisotropy in the external stress field, that is, increasing pre-existing stress, σ_0, is shown. a) $\sigma_0 = 0$; b) $\sigma_0 = 0.005E$; c) $\sigma_0 = 0.010E$, where E is Young's modulus. The fingering instability becomes more pronounced as σ_0 is increased. Even for $\sigma_0 = 0$ the front has some roughness due to the randomness of the system, but here the roughness does not grow with time. Modified from Jamtveit et al. (2000).

driven stress. Yet, the effects of tectonic stress on the rate and progress of fluid-consuming reactions are not well understood.

A simple discrete element model (DEM) that illustrates how external stress influenced reaction progress for a fluid consuming reaction, was described by Jamtveit et al. (2000). The model was constructed to describe the progress of a reaction front whereby 'dry' granulites were converted to eclogites when infiltrated by aqueous fluids. The eclogites contain hydrous phases such as phengite and clinozoisite, yet have a higher density than the feldspar dominated protolith. Eclogitization is therefore associated with a reduction in solid volume. This may conceivably cause fracturing driven by tensile stress, provided that the rate of eclogitization is fast compared to the rate of deformation by non-brittle mechanisms. In the absence of external stress, eclogitization may progress as a stable, morphologically flat, reaction front where the supply of fluid is allowed by contraction-controlled fracturing (Malthe-Sørenssen et al., 2006). However, the presence of an externally imposed anisotropic stress field, which must have been present during formation of the eclogite shear zones, induces fingering (Fig.10, Jamtveit et al., 2000), which is also observed in the field (Fig.11). The presence of even a modestly anisotropic external stress field effectively increased the rate of pervasive fracturing and fluid infiltration into the dry rocks through its coupling with local stress perturbations caused by mineral reactions.

The effect of external stress on reactions that lead to an increase in solid volume remains another important challenge for future experimental and modeling studies. In swelling systems, such effects will be more sensitive to the local boundary conditions, and the reaction progress is probably to a large extent controlled by pore-scale and even the nanometer-scale processes that control the system's ability to keep thin layers of fluid at grain boundaries even in the presence of compressive stress (Røyne and Jamtveit, 2015).

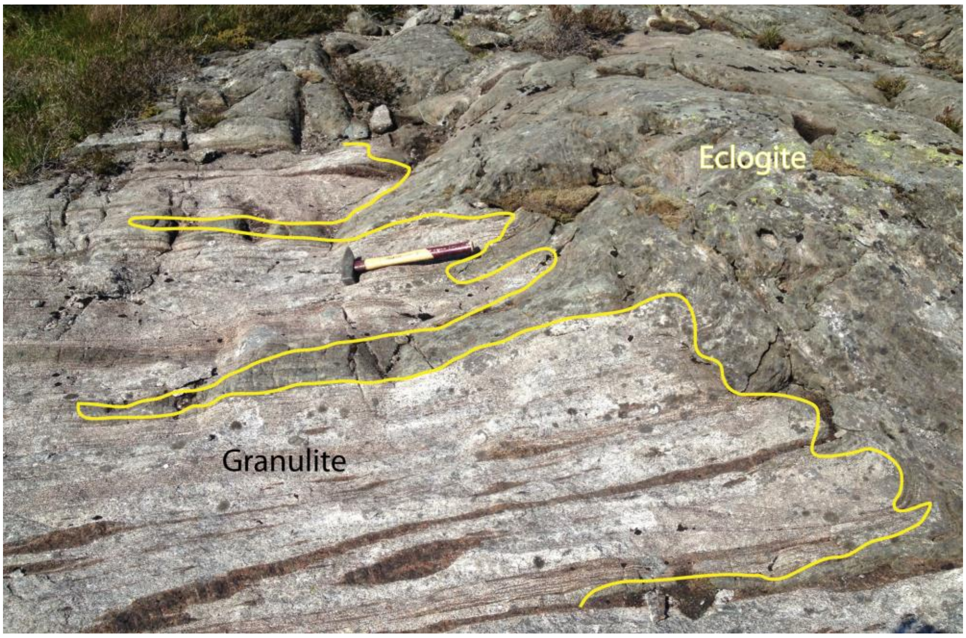

Figure 11. Eclogite fingers starting from an eclogite facies shear zone (upper right), penetrating into granulites. Note that the longest finger is crosscutting the original layering of the granulite. From Holsnøy, Bergen Arcs, Western Norway (see Jamtveit et al. 1990, for more details).

7. Geodynamic implications

The dissipation of heat by volatilization processes may generate significant heat flow anomalies, locally exceeding 20 mW/m^2 in the case of serpentinization of oceanic lithosphere (Delescluse and Chamot-Rooke, 2008), and the stress generated by volume changing reactions may cause fracturing and potentially trigger earthquakes (Pontbriand and Sohn, 2014). However, perhaps the most significant effect of fluid-consuming metamorphism in a geodynamic context is through its effects on rock rheology and its role in localizing lithospheric strain. Whereas fluid-producing, prograde, metamorphism may affect deformation by increasing fluid pressures and cause effects such as dehydration embrittlement (e.g. Green and Houston, 1995), retrograde metamorphism almost invariably leads to the formation of mechanically weaker rocks with a potential to localize strain.

Field studies reveal a strong tendency for deformation in the lower crust and to some extent also the upper mantle to be localized into discrete shear zones (see reviews by Bürgmann and Dresen, 2008 and Wassmann and Stöckhert, 2013). Within the rock mechanics community, localization is usually ascribed to strain weakening by grain size reduction and an increasing role of diffusion creep (Mehl and Hirth, 2008). Petrologic observations furthermore suggest that the development of shear zones in lower crustal rocks is almost invariably associated with the formation of hydrous phases or carbonates (Newton, 1989; Jamtveit et al., 1990; McCaig, 1997; Krabbendam et al., 2000; Austrheim, 2013), as well as other fluid-derived components such as ore minerals (Kolb et al., 2000). Microstructural observations suggest that grain size reductions and material redistribution in such zones are to a major extent controlled by fluid-mediated dissolution-precipitation creep (DPC) (Wheeler, 1992; Wassmann and Stökhert, 2013; Mukai et al., 2014).

A strong control on strain localization by fluid-consuming metamorphic reactions has been confirmed by experimental studies in reactive plagioclase aggregates (Stünitz and Tullis, 2001). In this case, very fine-grained polyphase reaction products (albitic plagioclase, zoisite, white mica and kyanite) were localized in shear bands interpreted to deform by diffusion-accommodated grain boundary sliding. Since shear stresses are generally low in zones of high strain, the negative feedback between strain and rock strength that is required to sustain localized strain in shear zones is more likely to be associated with ongoing fluid-consuming metamorphic reactions than by shear heating (cf. Wassmann and Stöckhert, 2013).

Although Bürgmann and Dresen (2008) state that “changes in rheology and weakening caused by metamorphic reactions are neither well understood nor quantified”, many lines of evidence suggest that strain localization in the ductile parts of the lithosphere is intimately linked to fluid-consuming metamorphism. The ubiquitous presence of fine-grained hydrated minerals and/or carbonates in crustal shear zones and the major role of diffusion creep mechanisms both attest to the presence of fluids during deformation. As argued in the previous sections, the dominant lithologies of the lower crust and upper mantle will be highly reactive in the presence of fluids at a large range of pressure and temperature conditions, and far-from-equilibrium metamorphism of high-grade rocks in the presence of fluids will in most cases produce a fine-grained reaction product comprised of mechanically weaker minerals than the host rock. Furthermore, fluid-consuming reactions are always exothermic, and reactions that are fast compared to the rate of heat transport will therefore cause significant local temperature increases. All of these factors will contribute to a reduction in rock strength/viscosity and to strain localization.

7.1 Fluid controls on localization

A prerequisite for reaction to occur is, however, the presence of fluids. Without the presence of fluids the progress of metamorphic reactions will be negligible and the efficiency of most diffusion-controlled creep mechanisms will be strongly reduced. As a consequence, strain localization and shear zone formation may also be suppressed. Hence, one would expect the onset of both retrograde metamorphism and localized deformation to be controlled by the presence of fluid sources. Sometimes, localization of strain during fluid consuming metamorphism can be directly related to the migration of fluids produced by prograde, fluid-producing metamorphism within the same metamorphic terrane (Barnes et al., 2004), and retrogression with shear zone development is common in the hanging walls above fluid-producing subduction zones (Peacock, 1987; Konrad-Schmolke et al., 2011). There may therefore be a direct causal link between near-equilibrium prograde fluid-producing metamorphism of lower grade rocks such as serpentinites or metasedimentary rocks, disequilibrium retrograde fluid-consuming metamorphism of high grade or magmatic rocks, and strongly localized viscous deformation of the lower crust or upper mantle.

Interestingly, a recent geochemical study of ductily deformed vein minerals and fluid inclusions from the Alpine fault, New Zealand, by Menzies at al. (2014) points to an alternative fluid source: *Downward* migration of waters through the brittle-ductile transition. Based on a variety of evidence, including stable isotope data and the presence of higher hydrocarbon inclusions in veins from exposed basement rocks, migration of meteoric waters into the deep crust has been suggested by several authors in the past (e.g. McCaig et al., 1990; Munz et al., 1995; Cartwright and Buick, 1999; Yardley et al., 2000) and Connolly and Podladchikov (2004) provided a mechanical model that demonstrates how downward fluid migration into the ductile crust may be possible in compressive tectonic settings.

Provided that localized deformation in the lower crust is controlled by the availability of fluids, downward fluid migration would present an interesting link between permeable faults in the upper crust and deeper shear-zones. A large-scale example of this may be the Alpine Fault in New Zealand, where brittle faulting in the seismogenic zone seems to be accommodated by highly localized ductile creep within narrow mylonite zones at depth (Norris and Cooper, 2003).

Sibson (2014) argues that earthquake rupturing in the upper crust will be favored by fluid overpressure in compressional/transpressional regimes. Fault-controlled downward movement of meteoric fluids from the upper crust by 'seismic pumping' (Sibson et al. 1975; Sibson 1981) or other mechanisms could then conceivably trigger reaction driven 'softening' and localized deformation below the brittle-ductile transition. This would explain the spatial correlation between localized deformation features in the upper and lower crust, as described from several strike-slip faults including the San Andreas Fault and the Dead Sea transform (Zhu, 2000; Weber et al., 2004), by a 'top-down' mechanism where the location of shear zones in the lower crust is controlled by faulting in the upper crust, rather than vice versa.

Moreover, if earthquakes in the lower crust evolve from shear zones by a self-localizing thermal runaway mechanisms (Braeck and Podladchikov, 2007; Kelemen and Hirth, 2007; John et al., 2009) rheological weakening controlled by fluid-consuming metamorphism may also be a prerequisite for seismic activity in the lower crust (cf. Montsalve et al. 2009; Priestley et al. 2008). Alternatively, deep earthquakes would have to be connected to rapid injection of fluids from the brittle crust above, or from some volume undergoing fluid-producing metamorphism below. Whatever the mechanism would be, it would have to be able to transport fluid at 'seismic rates', otherwise frictional failure would not be possible.

Whether seismic activity in the deep crust occurs after shear-zone formation or precedes it, the presence of hydrous minerals within eclogite facies pseudotachylites (quenched frictional melts) from Bergen Arcs in Western Norway and elsewhere (Austrheim, 2013) demonstrates that fluids are invariably present during seismic slip in the lower crust.

Finally, Raimondo et al. (2014), suggest that fluid-induced reaction softening might have played an important role in localizing strain to form the Petermann and Alice Springs intracontinental orogens in the middle of the Australian continent, thousands of kilometers away from any plate boundary. With all this evidence for many and varied lithosphere-scale geodynamic consequences of disequilibrium fluid-consuming metamorphism through its coupling to lithospheric stress and its effects on rheology, it is tempting to speculate about the possibility that the strain localization that eventually lead to the very formation of lithospheric plates and plate tectonics on Earth was somehow coupled to fluid processes and localized metamorphism-driven softening.

8. Concluding remarks

A significant fraction of the Earth's crust and upper mantle is unstable and highly reactive in the presence of fluids. This includes most of the lower continental crust and upper mantle, and most of the oceanic lithosphere. Metastable mineral assemblages persist under fluid-absent conditions.

When exposed to fluids, metastable rock volumes will experience rapid fluid-consuming metamorphism under far-from-equilibrium conditions. Dissipation of energy associated with disequilibrium metamorphism results in perturbations of temperature fields, changes of rock volume and associated stress generation, as well as the emergence of a variety of metamorphism-produced patterns. These are found at a wide range of scales, including nanometer to micrometer sized pore structures, and millimeter to decimeter size fracture patterns. The latter often play first order roles in controlling sustained fluid access to reactive rock volumes.

Many lines of evidence suggest that the upper crust and mantle, and locally also the lower crust may be subject to high differential stresses even far from tectonic plate boundaries. When disequilibrium metamorphism takes place in rock volumes subject to high levels of far-field (plate tectonic) stress, local reaction-driven stress may trigger fracturing and permeability increases over much larger scales than in an isotropic stress field. Thus, the rate of fluid-consuming metamorphism is expected to be enhanced is areas subject to tectonic stress.

Disequilibrium metamorphism will produce rheologically weaker rocks both through the formation of fine grained hydrous minerals and/or carbonates, and by its exothermic nature. This will contribute to strain localization below the brittle-ductile transition. Consequently, this strain localization may be controlled by the distribution of fluid sources required for fluid-consuming reactions to proceed.

Fault-controlled migration of meteoric fluids from the brittle crust, to the underlying ductile region may provide a spatial and temporal link between localized strain and seismic activity in the upper crust and shear zone controlled deformation below.

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