Metamorphism: The Role of Fluids

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The evolving lithosphere is affected in a major way by metamorphic processes. Metamorphism affects the lithosphere’s chemical and mineralogical composition, as well as its physical properties on scales ranging from a nanometer to the size of tectonic plates. Studies of metamorphism during the last couple of decades have revealed that fluids are as important in a changing lithosphere as water is in the biosphere. History-dependent characteristics of metamorphic rocks, such as their microstructure, compositional variation, and deformation features, reflect the dynamics of fluid–rock interactions. Migration of the fluids produced during prograde metamorphic processes or consumed during retrogression links metamorphism at depth to the evolution of the hydrosphere, the atmosphere, and the biosphere.

Keywords: metamorphic fluids, rate of metamorphism, mechanical effects, fracture patterns

The Evolving Lithosphere

Most of the Earth’s lithosphere evolves under conditions where metamorphic processes are the dominant transformation mechanism. From the early 1980s until quite recently, the metamorphic evolution of the Earth’s crust was to a large extent regarded as a more or less passive recorder of its pressure and temperature history, as dictated by plate tectonics (cf. England and Thompson 1984). Today, however, metamorphism is recognized to be almost as dependent on the presence of fluids as biological systems are on the presence of water (Yardley 2009). Fluid–rock interactions during metamorphism can control large-scale geodynamic processes by defining mechanical strength, and thus they can influence the support of mountain belts (Jackson et al. 2004). Fluid–rock interactions can also govern lithosphere density and thus the subsidence of sedimentary basins (Kaus et al. 2005), and they can affect the volatile content of the mantle wedge during subduction, thereby affecting arc magmatism (Kerrick and Connolly 2001a). Metamorphic volatilization processes may furthermore affect the elastic properties of rocks (Boudier et al. 2010) and thus impact our ability to interpret seismic data.

The release and consumption of fluids during metamorphism are two fundamentally different processes. When igneous and metamorphic rocks formed at elevated temperature are exposed to water or other fluids at lower temperature, they usually react, forming minerals with a higher proportion of volatile components. Retrograde metamorphism therefore depends critically on the nature and abundance of externally derived fluids (Jamtveit et al. 2000, 2008). More than any other factor, including pressure and temperature changes, the timing of retrograde metamorphism is controlled by external fluid supply. Near or at the Earth’s surface, similar rock-fluid reactions play an important role in weathering (Røyne et al. 2008), which also involves natural sequestration of CO₂ by carbonate mineral formation (Kelemen and Matter 2008).

A fundamentally different situation arises when volatile-rich sedimentary or metamorphic rocks experience prograde metamorphism. A key process in this case is the expulsion of fluid from the sites where it is generated (Connolly 2010 this issue). Migration of fluids to and from the sites of retrograde and prograde metamorphism plays a key role in the global water and carbon cycles and ultimately in the coupling of metamorphism with the near-surface hydrosphere, atmosphere, and biosphere (e.g. Kerrick and Connolly 2001b; Svensen et al. 2004; Rüpke et al. 2004; Kelemen and Matter 2008).

Metamorphic Rate Controls

Interpretation of metamorphic mineral assemblages and microstructures, within the conceptual framework of equilibrium thermodynamics, has provided valuable insight into the conditions of formation of metamorphic rocks (e.g. Spear 1995). The equilibrium assumption is based on the idea that metamorphic reactions are fast compared to the rate of change of externally controlled variables, such as temperature and pressure. Although the equilibrium approach may be a good approximation in some situations, it ignores all history-dependent features of the rocks, thereby excluding the most important sources of direct information about the underlying processes that generated the rock (Fig. 1). The central role of kinetics in controlling both microstructures and mineral assemblages has been illustrated by numerous experimental, theoretical, and petrographic studies over the last two decades (for example, Rubie 1998; Lüttge et al. 2004). Several of these studies identify slow nucleation as a key limiting factor. Moreover, since most phase transformations take place by dissolution–reprecipitation reactions (Putnis 2009), it is clear that fluids are a central ingredient in metamorphism, even when their role is merely catalytic. Limited or transient availability of intergranular fluids has been proposed as the most plausible explanation for slow reaction rates during regional metamorphism (Baxter 2003).
A generic rate law for metamorphic reactions may be expressed by the equation:

$$R \approx k(T) \Delta G^n A_s$$

where $R$ represents the rate of reaction (for example, in mol m$^{-3}$ s$^{-1}$), $k(T)$ is a temperature-dependent kinetic rate constant, $\Delta G$ represents the overstepping of the equilibrium condition (or chemical affinity), $n$ is a constant, and $A_s$ is the specific surface area. In most models of metamorphic kinetics, the rate of reaction, $R$, falls with time because the reactions push the system towards equilibrium, causing a decrease in the reaction affinity. Also, as the reaction progresses, the reactive mineral surface area decreases, the amount of reactants diminishes, and the reactant grain may be shielded from the fluid by product phases (e.g. Martin and Fyfe 1970). Such models, however, largely ignore the complexity of reactive fluid–mineral interfaces.

Recent studies have demonstrated that the processes taking place at the interface across which fluids and minerals interact is far more complex than previously thought. The interface itself can evolve in a highly dynamic way, leading to complex pore structures and fracture patterns (e.g. Putnis 2009; Renard et al. 2009). Most importantly, these surface processes generate reactive surface areas that are much larger than those predicted by existing reactive-transport models, and they continue generating new surface area by enhancing fracturing and porosity as the reactions proceed. This is absolutely essential for maintaining reasonable rates of volatilization in the Earth's crust. Mechanical effects such as reaction-driven fracturing can increase reactive surface area, so for a while, the reaction rate accelerates with time rather than continuously decreasing from the onset of reaction (Røyne et al. 2008; Jamtveit et al. 2009).

For small systems, such as inside mineral inclusions, mechanical effects can have the opposite effect, slowing or even halting reaction progress by preventing the system from expanding, a phenomenon known as mechanical closure (Schmid et al. 2009).

**FLUID PRODUCTION**

Prograde metamorphism in most cases produces fluids through devolatilization. These released fluids tend to move upward because of the difference between their density and the density of the surrounding rock. It has long been recognized that rocks undergoing prograde metamorphism have a discrete fluid phase only during the time that devolatilization reactions are actually taking place (Walther and Orville 1982). If the rate of fluid production is high relative to the rate at which fluid can escape through preexisting permeability, fluid escape will be associated with local hydrofracturing (Flekkøy et al. 2002). Evidence is seen in abundant veining during regional metamorphism of volatile-rich rocks (e.g. Fisher and Brantley 1992; Widmer and Thompson 2001).

The intimate coupling between devolatilization and fluid migration is evident from numerical modeling (Connolly and Podlachikov 1998). Simulations suggest that fluid loss, even on a crustal scale, generates porosity waves as focused
pulses of fluid. The existence of such waves is supported by observations of pipe-like, fluid-release structures associated with the intrusion of sills into sedimentary basins, where heat from the sills has driven fluid production, causing an increase in fluid pressure (Fig. 2; Jamtveit et al. 2004). Recent studies have provided strong evidence that the release of greenhouse gases by metamorphic fluids produced in carbon-rich sedimentary rocks has triggered some of the largest climate changes in the history of the Earth (Svensen et al. 2004).

**FLUID CONSUMPTION**

When metamorphic rocks cool, they often do not back-react with fluids to form a lower-temperature mineral assemblage. The main reason is that fluids produced during prograde metamorphism escape and are no longer available. Supply of external fluids is therefore essential for retrograde metamorphism to proceed. Furthermore, if such external fluids are supplied, they are likely to be strongly out of equilibrium with the rock that they infiltrate. Consequently, retrograde volatilization is often fast and can produce a variety of complex features typical of far-from-equilibrium systems, including dendritic mineral growth and oscillatory variations in the composition of mineral grains.

In a system that is essentially closed to all major components, except the externally supplied volatile components (usually $\text{H}_2\text{O}$ or $\text{CO}_2$), volatilization normally results in a significant increase in total solid volume. Under far-from-equilibrium conditions, this can produce local overpressures far beyond what is required to fracture the rock (e.g. Ostapenko 1976; Wheeler 1987). Because the fracturing generates new surface area where volatilization begins, the overall rate of volatilization increases, allowing pervasive fluid–rock interaction at considerably larger scales than would otherwise be possible.

**Serpentinization**

Serpentinization is probably the most important metamorphic hydration process. The reaction of olivine-rich, mantle-derived peridotite to form serpentine is associated with a reduction in rock density from ~3.3 g/cm³ to less than 2.7 g/cm³. Hydration of end-member forsterite ($\text{Mg-olivine}$) can be described by the reaction:

$$2\text{Mg}_2\text{SiO}_4 + 3\text{H}_2\text{O} \rightleftharpoons \text{Mg}_5\text{Si}_3\text{O}_{10}(\text{OH})_4 + \text{Mg(OH)}_2 \quad (2)$$

forsterite + water $\rightleftharpoons$ serpentine + brucite

In a natural system, the Fe component of the original olivine is at least partly absorbed by a corresponding Fe component in the brucite. Iron often subsequently contributes to the very important redox reaction that oxidizes ferrous Fe to ferric Fe to form magnetite ($\text{Fe}_3\text{O}_4$), while hydrogen from the water is reduced to H₂ (Peretti et al. 1992; Bach et al. 2006). The hydrogen generated can sustain microbial communities (Takai et al. 2004). In the presence of carbon, serpentinization can produce CH₄, which has been observed seeping from mid-ocean ridges (Charlou et al. 1998). Such an environment, with possible production of abiotic methane and other hydrocarbons, is regarded as the most likely location for the origin of life (Konn et al. 2009).

Complete serpentinization results in a solid volume increase of nearly 50% and causes a pronounced change in rheology, magnetic properties, and porosity. Reaction (2) also produces considerable heat (~290 kJ/kg forsterite consumed); serpentinization has therefore been suggested as an explanation for observed heat-flow anomalies in ocean basins (Delescluse and Chamot-Rooke 2008).

The serpentinization rate is highest at temperatures close to 300°C (Martin and Fyfe 1970). At lower temperatures, the kinetic constant, $k(T)$, limits the overall rate, whereas at higher temperatures, the approach to equilibrium decreases the affinity of hydration, $\Delta G$, and thus the reaction rate. The higher the reaction rate and the associated rate of rock-volume increase relative to the rate of ductile deformation, the more probable it is that serpentinization causes fracturing, because there is insufficient time for the rock to accommodate the stress of the extra volume generated. Figure 3 shows fracture patterns developed in serpentinized peridotites. The characteristic length scales of the fractures vary over more than 4 orders of magnitude, from a few meters to less than 100 micrometers.

**Natural CO₂ Sequestration**

In the presence of C-bearing fluids, carbonation of peridotite (Fig. 4) produces even more heat than hydration, and the process is expected to be even faster than hydration at temperatures greater than 200°C (Kelemen and Matter 2008). Carbonation is a natural CO₂-sequestration process, and although the maximum rate of carbonation occurs at temperatures below the metamorphic regime (150–200°C depending on pressure), the physical and chemical processes involved, and their coupling, are very similar.

![Figure 2](image_url) A satellite image from the Loriesfontein area in the western part of the Karoo Basin, South Africa. The road in the upper left of the image provides scale. The dry landscape is dominated by a relatively flat topography with numerous circular hills. These hills, seen as bright “blobs” in the image, are hydrothermal pipes filled with brecciated and metamorphosed shale. They formed as methane degassed during contact metamorphism of black, organic-rich shale, some 182.5 million years ago. The dolerite intrusions responsible for the contact metamorphism are now about 100 meters below the surface. The methane emitted at the paleosurface contributed significantly to global warming in the Jurassic (Svensen and Jamtveit 2010). The pipes are typically 100–150 meters in diameter.
Petrographic studies indicate that C-bearing fluids often infiltrate peridotite through preexisting fractures developed during seafloor serpentinization. However, carbonate mineral growth itself produces sufficient swelling pressure (e.g. MacDonald and Fyfe 1985) to generate additional fractures. There is little doubt that both serpentinization and carbonation of peridotite are to a major extent influenced by mechanical processes, in particular, generation of reactive surface area by fracturing over a wide range of scales.

Mechanical Effects

Most experimental studies on the rates of metamorphic reactions have been carried out using fine-grained rock powders; fracturing cannot be observed. This limits the relevance of the results and the kinetic models based on them. Peridotites, in particular, are often coarse grained and almost invariably undergo extensive fracturing during reaction with fluids (e.g. MacDonald and Fyfe 1985; O’Hanley 1992; Iyer et al. 2008). Some of this fracturing can occur as a response to far-field (tectonic) stresses, but there is ample evidence that the volume change associated with the serpentinization process itself generates stresses sufficient to fracture rocks and mineral grains under a range of conditions (e.g. Iyer et al. 2008; Jamtveit et al. 2008).

To our knowledge, no experimental studies so far have examined the effect of fracturing on metamorphic reaction rates. However, numerical models (e.g. Jamtveit et al. 2008; Røyne et al. 2008) have produced micro- and outcrop-scale structures very similar to those observed in natural systems (Fig. 5). A key feature of such models is that the reaction-driven fracturing accelerates the rate of reaction by increasing the reactive surface area at an early stage of the reaction. Furthermore, because the length of the fractures can easily exceed the typical diffusion distance, the overall volume of rock affected by reaction with fluid is much larger than predicted by a pure reaction–diffusion model. This argument is further strengthened by the fact that fluid-consuming reactions normally increase solid volume, and in the absence of fracturing, preexisting pores would rapidly be clogged by reaction products, blocking fluid transport and halting further reaction.
OPEN VERSUS CLOSED SYSTEMS

The issue of how to deal with thermodynamic equilibrium in open systems relevant to metamorphic rocks was the subject of heated debate in the 1950s and 1960s (Weill and Fyfe 1964 and references therein). In the context of the preceding discussions on metamorphic kinetics, the question of how to deal with open systems reappears as a central issue. The main challenge is the coupling between mass transfer and stress generation. In a reacting rock volume, where open system behavior is possible, there are two limiting scenarios. A system can change its volume and thus perturb the local stress field, or it can maintain a constant volume by exchanging mass with its environment. In practice, a combination of these two occurs, but one or the other often dominates.

The limited volume of fluids available during metamorphism often puts severe constraints on open-system behavior. The early stages of seafloor serpentinization usually lead to very modest changes in rock composition (Bach et al. 2006). This stage is invariably associated with extensive fracturing and formation of characteristic mesh textures (Fig. 5c). Later alteration under open-system conditions follows more of a volume-for-volume replacement process, which is common in other metamorphic processes characterized by high fluid fluxes, such as albitionation, rodingitization, scapolization, etc. Metamorphism accompanied by extensive alteration of chemical composition is often referred to as *metasomatism* and usually occurs in regions with high thermal gradients, such as around cooling intrusive bodies, or localized zones of deformation that act as fluid channels. Pervasive retrograde metamorphism outside such zones is almost invariably associated with reaction-driven fracturing, highlighting the general importance of mechanical processes for fluid–rock reactions in the lithosphere.

FUTURE PERSPECTIVES

Earth science is no longer a narrative about the past. Increasing the relevance of our science for resolving challenges connected with energy, the environment, water, the carbon cycle, and all natural resources demands focus on the *future* of our planet. This requires paying more attention to the processes that shape our planet than to its equilibrium state. The future of metamorphic petrology as a relevant field of research requires that we increase our focus on those features of metamorphic rocks that act as a memory of the underlying processes. Such features are not the equilibrium features. More attention is required on the complex patterns of metamorphic rocks, and in particular on the microstructures and their coupling to both chemical and physical processes. We furthermore believe that fluids are essential in controlling the evolution of the lithosphere and that they firmly connect metamorphic processes to the evolution of the hydrosphere, biosphere, and atmosphere.

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**Figure 5** Microstructures and mechanical models of fragmentation. (A) Fracturing around partly serpentinized olivine crystals in a plagioclase matrix from a troctolite (Duluth Gabbro). (B) Discrete-element model of fracturing around expanding polygons in an elastic matrix (2-phase system) (details in Jamtveit et al. 2008). Blue “grains” are unreacted and white ones are completely reacted. Rows of white hatches (broken bonds) represent fractures. Fractures connect unreacted grains to regions in contact with a fluid and thus propagate the hydration process.

(C) Mesh texture generated during serpentinization of olivine in a partly serpentinized peridotite from the Leka ophiolite complex, Norway (details in Iyer et al. 2008). (D) Discrete-element model of fragmentation of a rectangular domain (1-phase system) driven by reaction-induced swelling during reaction with a fluid that enters through domain boundaries and fracture walls (Rayne et al. 2008). Numbers 1 to 6 refer to various stages of reaction. Color code for grains as in B; numbers along the colored bar represent reaction progress; \( C_r = 1.0 \) means 100% reacted.
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