

Metamorphic Fluids, Mass Transport, and Metasomatism

Questions to be Considered in this Chapter:

1. What is the nature of fluids that accompany metamorphism?
2. What volumes of fluid pass through crustal rocks during metamorphism?
3. What occurs when various elements become mobilized during metasomatism?

Fluids play an influential role in many igneous and metamorphic processes, where they may partake in various types of reactions or act as a transporting medium for the movement of soluble material. We have often encountered processes influenced by fluids and material transport. We noted the effects of introduced fluids on the melting of rocks and the effects of released fluids from crystallizing igneous bodies. We have seen the role of fluids in seafloor and hydrothermal metamorphism, in the development of fenites associated with carbonatites, and in metasomatism of the mantle, in the amphibolite facies-granulite facies transition, and in infiltration processes. Fluids are essential components in pegmatite and ore genesis as well. Fluids can change the transport properties of a rock by dissolution or precipitation of material, or by creating fractures due to fluid pressure (“hydrofracturing”). Fluids can also affect the mechanical properties of rocks, and therefore the nature and extent of deformation in areas under stress. In this chapter, I summarize what we know about crustal fluids and then provide a brief introduction to mass transport and metasomatic processes.

1 METAMORPHIC FLUIDS

Fluids are believed to be nearly ubiquitous during metamorphism (at least at low and medium grades), but there is little direct remaining evidence concerning their nature in the rocks that we now collect at the Earth’s surface. Virtually all of the intergranular high-temperature/high-pressure fluids that were in equilibrium with the metamorphic mineral assemblage during peak metamorphic conditions escaped as pressure was released upon uplift and erosion. The only direct evidence for metamorphic fluids that remains is found in the small high-density fluid inclusions trapped in many metamorphic rocks (see the summaries by Hollister and Crawford, 1981; Roedder, 1984; and Crawford and Hollister, 1986). The existence of fluids trapped in a rock, however, is not an indicator of the *quantity* of fluid that existed during metamorphism. Nor is there any guarantee that the fluids coexisted with the peak equilibrium mineral assemblage and were not trapped during a later event following uplift. Studies of freezing and CO₂-H₂O homogenization temperatures for complex fluid inclusions using a heating-freezing microscope stage, however, suggest that many (but not all) inclusions were trapped under metamorphic conditions. The nature of the fluid inclusions commonly correlates with the metamorphic mineral assemblage as well, further strengthening the argument that some fluid exists as a discrete phase during metamorphism. The heating-freezing technique has even been used as a geothermobarometer to estimate the conditions of metamorphism (e.g., Touret, 1981). Recovery of fluids from geothermal

wells provides further direct evidence for the participation of fluids in metamorphism (e.g., White et al., 1963; Muffler and White, 1969; Bird et al., 1984; Schiffman et al., 1984; Yardley et al., 1993).

Other evidence for metamorphic fluids is less direct but also compelling. The existence of hydrous and carbonate minerals under peak metamorphic conditions all but requires that a fluid exists to maintain sufficient volatile pressure to stabilize the volatiles in the minerals. Experiments on mineral-fluid equilibria and thermodynamic treatment support this contention and commonly permit us to characterize the type of fluid present. For example, we are able to constrain the temperature of metamorphism and X_{CO_2} of CO_2 - H_2O fluid mixtures on the basis of calcareous or ultramafic mineral assemblages and the location of reaction equilibria on T - X_{CO_2} diagrams. We could even speculate as to whether the fluids were infiltrating or internally buffered. In addition, numerous stable isotopic studies indicate that the characteristics of many metamorphic rocks can be explained only if the original isotopic composition (usually $\delta^{18}\text{O}$) of the rocks interacted and exchanged with fluids with which they were initially out of isotopic equilibrium (e.g., Garlick and Epstein, 1967; Rye et al., 1976; Rumble et al., 1982; Nabelek et al., 1984; Bowman et al., 1994; Lewis et al., 1998).

When mud or shaly sediment is first deposited, it may have an initial porosity in excess of 50%, the pore space being occupied by meteoric water or seawater brines. Compaction, cementation, and recrystallization usually reduces the initial porosity to vanishingly small values at depths of burial corresponding to the beginning of regional metamorphism. Rice and Ferry (1982) estimated that high-grade rocks probably have less than 0.1% porosity. Initial pore fluids, therefore, are probably driven out early and contribute little to the fluid phase attending subsequent metamorphism. Volatile components bound in hydrous or carbonate minerals, however, are typically released during metamorphism. Average slates contain about 4.5 wt. % bound H_2O and 2.3 wt. % bound CO_2 (Shaw, 1956), whereas high-grade schists contain about 2.4 wt. % H_2O and 0.2 wt. % CO_2 (and granulites contain hardly any volatile components at all). Release of these bound volatiles (by devolatilization reactions) between the slate and schist stages amounts to approximately 1.5 moles of fluid (mostly H_2O and CO_2) per kilogram of rock. Walther and Orville (1980) calculated that, if this fluid were released at once at 500°C and 0.5 GPa, it would occupy about 12% of the rock volume.

Fluids may also be introduced into rocks during metamorphism. Metamorphism of a basalt to a greenschist typically involves the addition of 5 to 10 wt. % H_2O from the surroundings. Fluids added during metamorphism may be meteoric, magmatic, or metamorphic (released by devolatilization reactions at greater depth). Stable isotopic data suggest that meteoric and magmatic waters have interacted with the rocks in numerous metamorphic terranes, particularly those with plentiful shallow-level plutonism and hydrothermal circulation (hydrothermal and "regional contact" metamorphism). A. B. Thompson (1983), however, warned us that, although fluid generation via devolatilization is a

consequence of most forms of metamorphism, fluids may not be present at all times and in all places during any metamorphic event.

1.1 The Nature of Metamorphic Fluids

At the high temperatures and pressures of regional metamorphism, a free "vapor" phase is usually a **supercritical fluid** because the conditions are above that of the critical point of CO_2 - H_2O mixtures. There is no distinction between a gas and liquid, and the density of supercritical fluids at high pressure and temperature is close to that of water at 25°C and 1 atm (Ferry and Burt, 1982).

1.1.1 VOLATILE SPECIES For the moment, let's consider just the volatile species in supercritical metamorphic fluids (see Ferry and Burt, 1982; Labotka, 1991; and Huizenga, 2001, for reviews). These are composed predominantly of O, H, and C, with lesser amounts of S, N, etc. Figure 1 illustrates the volatile species that coexist in C-O-H-S fluids at 1100°C and 0.5 GPa. Because a single C-O-H-S fluid phase contains four components, the phase rule tells us that $F = 4 - 1 + 2 = 5$ (or three at fixed P and T). There is thus considerable variance possible in such fluids unless some species are buffered by the solids. In Figure 1, sulfur fugacity is controlled by pyrrhotite, and the resulting fluid species are projected from sulfur to the C-O-H face of the compositional space. The resulting fluids in equilibrium with such buffered f_{S_2} are thus only divariant.

Figure 1 is divided into regions of bulk fluid composition labeled with the predominant species in each region (other species are always present but occur in very low concentrations). Fluids between the H_2O - CO_2 join and the O corner are relatively oxidized and consist of mixtures of CO_2 , H_2O , and O_2 . Remember that free oxygen is generally buffered to very low concentrations, and thus fluids in the CO_2 - H_2O - O_2 triangle (light shaded) probably do not occur during metamorphism. Fluids in the H_2O - CH_4 -H triangle are more reduced and are dominantly $\text{H}_2\text{O} + \text{CH}_4 + \text{H}_2\text{S}$. In all cases, of course, the proportions vary with the bulk composition (X_{bulk}) of the fluid mixtures. Increasing carbon concentration eventually stabilizes graphite, which then buffers the carbon content of the fluids and prevents fluids

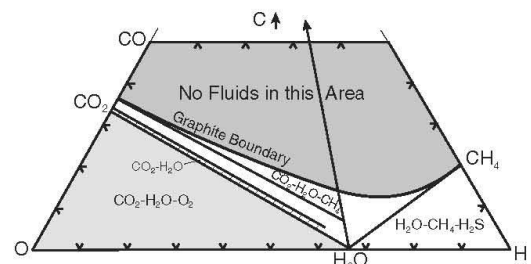


FIGURE 1 Fluid speciation in the C-O-H-S system at 1100°C and 0.5 GPa projected from S to the C-O-H triangle (mole proportions). f_{S_2} is determined by pyrrhotite with the composition $\text{Fe}_{0.905}\text{S}$. After Holloway (1981).

from developing more C than the buffered assemblage. Fluids in the dark shaded C-rich portion of Figure 1 thus cannot ordinarily occur.

The presence of graphite in many metamorphosed pelites and carbonates substantially limits the compositional variation of metamorphic fluids. (They must occur along the graphite boundary in Figure 1.) If f_{S_2} and f_{O_2} are buffered and graphite is present, the variance of C-O-H-S fluids is reduced to 2. We can then calculate the exact speciation at any given P and T , using the equilibrium constants for the reactions that interrelate them ($H_2 + \frac{1}{2}O_2 = H_2O$, $C + O_2 = CO_2$, etc.). Figure 2 is a plot of the relative concentrations of the major species in C-O-H-S fluids in equilibrium with graphite at 0.2 GPa, if f_{S_2} is buffered as in Figure 1 and f_{O_2} is buffered by quartz-fayalite-magnetite. Note in Figure 2 that the common assumption that metamorphic fluids are predominantly CO_2 - H_2O mixtures is true for graphite-bearing assemblages at very high temperature, but CH_4 is dominant below $700^\circ C$. When graphite is absent, however, fluids may be more oxidized, and methane less common. H_2O , CO_2 , and CH_4 are the major species in metamorphic C-O-H-S fluids. H_2S is less abundant in most metamorphic fluids than indicated by Figure 2 because the amount of sulfur is usually much more limited than the pyrrhotite buffer.

We can use several calcareous and ultramafic mineral assemblages to estimate the composition of H_2O - CO_2 fluids, buffered either along univariant T - X_{CO_2} reactions or at invariant points. Ferry and Burt (1982) presented tables of calculated fluid species from carbonates, pelitic schists and granulite facies gneisses.

1.1.2 NONVOLATILE SOLUTES Although we commonly treat metamorphic mineral equilibria as solid-solid or solid-volatile species reactions, when a fluid species is present,

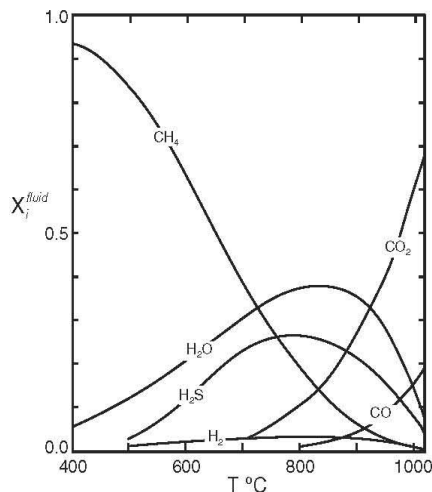
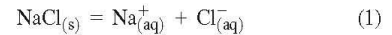


FIGURE 2 Speciation in C-O-H-S fluids coexisting with graphite at 0.2 GPa, with f_{O_2} buffered by quartz-fayalite-magnetite and f_{S_2} controlled as in Figure 1. X_i^{fluid} is the mole fraction of each species in the fluid. From Holloway (1981).

each solid phase will also progress toward equilibrium with that fluid. Just as in mineral-melt equilibria, chemical components will be distributed (partitioned) between every mineral and the fluid in some equilibrium proportionality. We are familiar with this concept for very soluble phases, such as salt in water. Salt will dissolve and Na^+ and Cl^- will be distributed between water and halite for saturated solutions in equilibrium. Consider the reaction:



where the subscript (s) indicates a solid and (aq) indicates an aqueous species. The distribution can be expressed as a constant, K_{SP} , the **solubility product** constant:

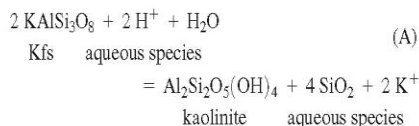
$$K_{SP} = a_{Na^+} \cdot a_{Cl^-} \quad (2)$$

where a indicates solute activities. The activity of solid NaCl at the pressure and temperature of interest is always 1.0, and is therefore dropped from the denominator of the expression on the right side of Equation (2) under saturated conditions.

Of course, most silicates are far less soluble than halite, even at high temperatures, but we can still explore the solubility of minerals in equilibrium with C-O-H fluids experimentally, and we can use the results to model the composition of metamorphic fluids in equilibrium with various mineral assemblages at elevated temperatures and pressures. Helgeson and colleagues have pioneered the quantitative thermodynamic modeling of metamorphic fluids and aqueous species at elevated temperatures and pressures (see Helgeson et al., 1978, 1981). From a combination of thermodynamics and experimental data on mineral solubilities, we can in many cases estimate the composition of metamorphic fluids from the associated mineral assemblages. I will provide some examples of how we can use the relationship between the mineral assemblage and the fluid species activities to model metasomatism shortly. For now, I shall briefly review what we presently know (or think we know) about the dominant solute species in metamorphic fluids.

The minerals in which igneous and metamorphic petrologists are most interested are silicates, and the predominant anion is oxygen. Because of this, and because very little oxygen dissolves in the fluid as O^{2-} , we concern ourselves mostly with the exchange and transport of *cations* with the fluid. Unfortunately, this does not necessarily simplify our job because electrical neutrality requires that an equivalent number of *anions* (or anionic complexes, such as SO_4^{2-}) must also be present in the fluid solution. Petrologists agree that the dominant anion is chloride, but it is generally not possible to estimate the total dissolved chloride in metamorphic fluids (which are now mostly gone). As a result, even if we know the solubility of a mineral in chloride brines, the amount of a cation in solution may be considerably less if little Cl^- or other anionic ligands are available. One way to partially circumvent this problem is to calculate the *ratios* of dissolved cations, rather than the

absolute concentration of each (Helgeson, 1967; Eugster, 1986). Many mineral reactions involve the exchange of several species with the fluid, so that the equilibrium conditions for the reaction also depend on *ratios* of the species. For example, the equilibrium constant for Reaction (A) is given below:

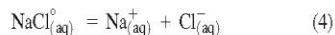


$$K_{\text{SP}} = \frac{(a_{\text{SiO}_2(\text{aq})})^4 \cdot a_{\text{K}^+}^2}{a_{\text{H}^+}^2} \quad (3)$$

To define the K-feldspar/kaolinite equilibrium, we thus need know only the ratios of the activities of the aqueous species, and not the activity of each individual one. Regardless of the convenience of solute ratios, it would be nice at this point to know what silicate mineral constituents are most soluble in high-*T-P* aqueous solutions and to what extent.

Although we are used to considering dissolved solutes in aqueous solutions as ionic species, the dissolved constituents are much more associated in most metamorphic fluids (Helgeson et al., 1981; Eugster, 1986; Labotka, 1991). The **dielectric constant** (ϵ) of water expresses its ability to shield charged dissolved ligands by *solvation* (surrounding them with a layer of charged bipolar H₂O molecules). ϵ decreases with increasing temperature and decreasing pressure. When ϵ is large, as in near-surface waters, solutes are readily shielded and tend to occur as charged ionic species. When ϵ is small, charged species are suppressed.

We may consider the dissociation of an electrolyte as a reaction of the sort:



where $\text{NaCl}_{(\text{aq})}^{\circ}$ is the concentration of associated NaCl molecules in solution [not solid NaCl, as in Reaction (1)]. From Reaction (4) we can define the **dissociation constant** for NaCl° as:

$$K_{\text{NaCl}^{\circ}} = \frac{a_{\text{Na}^+} \cdot a_{\text{Cl}^-}}{a_{\text{NaCl}^{\circ}}} \quad (5)$$

Figure 3 shows how the dissociation of NaCl in aqueous solutions varies with temperature and pressure. We can see that NaCl is highly dissociated ($K_{\text{NaCl}^{\circ}} > 10$) in saturated surface waters, but the dissociation constant decreases significantly with increasing temperature and decreasing pressure. Under conditions of contact metamorphism $K_{\text{NaCl}^{\circ}}$ may be 10^{-2} or less, so that the associated NaCl° molecules outnumber the dissociated Na^+ and Cl^- ions in the fluid by over two orders of magnitude. Under regional metamorphic conditions the associated species are still 5 to 10 times as prevalent as dissociated. Chlorides (NaCl , KCl , CaCl_2 , MgCl_2) are the most common associated species in natural metamorphic fluids, but hydroxides [$\text{Al}(\text{OH})_3$, $\text{KAl}(\text{OH})_4$], acids (H_4SiO_4), sulfates, carbonates, fluorides, etc. may also be present.

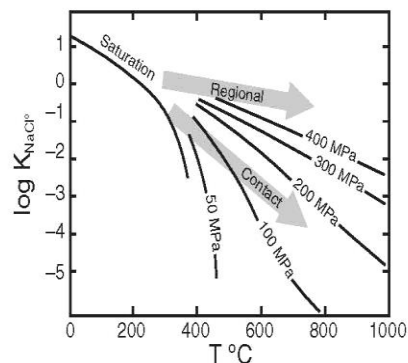


FIGURE 3 Variation in the dissociation constant of NaCl in aqueous solutions with temperature and pressure. Shaded arrows indicate regional and contact metamorphic *P-T* paths. After Sverjensky (1987). Copyright © The Mineralogical Society of America.

Natural observations and experiments addressing dissolved species show that their concentrations depend upon temperature, pressure, and the composition of the rock and fluid (including the volatile species and the concentration of other solutes). Although exceptions abound, the following broad generalizations seem justified at our current state of knowledge.

In addition to halides, alkalis, particularly Na, are usually the most soluble constituents. On the basis of fluid inclusions, Crawford (1981) concluded that most fluids are chloride brines in which NaCl dominates over KCl and CaCl_2 with only minor MgCl_2 . Other species are only slightly soluble. Crawford (1981) noted that CO_3^{2-} , HCO_3^- , SO_4^{2-} , and Br^- are also present in many inclusions.

Walther and Helgeson (1977) determined the solubility of quartz (or its polymorphs) in aqueous solutions at elevated temperatures. The solubility ranges from 2 ppm SiO_2 at 25°C to about 10,000 ppm (1 wt. %) at 600°C and 0.5 GPa. Ragnarsson and Walther (1985) found that corundum is much less soluble and that the Al content of metamorphic fluids in equilibrium with corundum cannot be much more than a few dozen parts per million.

Eugster and Baumgartner (1987), in their review of mineral solubilities and speciation in metamorphic fluids, used mineral solubility data, extrapolated to metamorphic temperatures and pressures, to estimate the concentrations of solute species. They noted that available data on fluids are limited, so that uncertainty is relatively large, but they were nonetheless able to semi-quantitatively estimate speciation, at least in some simple aqueous supercritical fluids in equilibrium with equally simple mineral assemblages. Figure 4 shows the results of Eugster and Baumgartner's calculations of aqueous-chloride fluid speciation associated with ultramafic rocks with a bulk composition in the Tr-Tlc-Atg sub-triangle of the CaO-MgO-SiO₂ system from 350 to 650°C. The abrupt breaks in slope for several species between 400 and 500°C correspond to changes in mineralogy. Note that dissociated ionic species

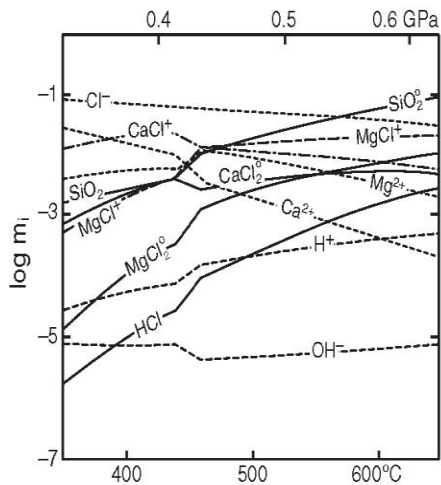


FIGURE 4 Speciation in aqueous-chloride fluids calculated for an ultramafic bulk composition, assuming a geothermal gradient of 0.1°C/bar. m_i is the molality of species i in the fluid. Solid curves represent neutral associated species. After Eugster and Baumgartner (1987). Copyright © The Mineralogical Society of America.

(dashed curves for Cl^- , Mg^{2+} , Ca^{2+} , etc.) tend to decrease with increasing grade (H^+ is a notable exception), whereas associated ions (MgCl^+ and CaCl^+) and uncharged species (SiO_2 , CaCl_2 and MgCl_2) all increase. Na and K, although usually quite soluble, are not considered in Figure 4 because of their low abundance in ultramafic systems. Similarly, Fe is not considered in Figure 4, although Eugster and Gunter (1981) found that Fe is generally more soluble than Mg.

Walther and Helgeson (1980) found that Ca^{2+} is a thousand times more soluble than Mg^{2+} in metamorphic CO_2 - H_2O fluids associated with calcite-bearing calcareous rocks, whereas Mg^{2+} may be more soluble in carbonated metamorphosed ultramafics (which is apparent at high temperatures in Figure 4). Helgeson et al. (1981), in their weighty monograph, summarized aqueous solutions as ranging from nearly pure H_2O - CO_2 fluids to concentrated ore-forming solutions, composed predominantly of NaCl, KCl, CaCl_2 , and MgCl_2 , with lesser concentrations of bicarbonates and sulfates-bisulfates, together with minor H_2S , SiO_2 , and chlorides of Al, Fe, Zn, Pb, Cu, Ag, etc.

Characterization of metamorphic fluids is still in the early stages of development, and the speciation obviously varies, but we are now aware that metamorphic fluids may contain a host of volatile and dissolved species. Dissolved constituents are present mostly in low concentrations, and the relative abundances are commonly Na and $\text{K} > \text{Si}$, Ca , Fe , and $\text{Mg} > \text{Al}$. In addition to Al, the high field strength (HFS) minor and trace elements such as Ti, Cr, Zr, Y, and Ni are generally insoluble in aqueous fluids, hence their use as indicators of the paleo-tectonic environment of metamorphosed igneous rocks in discrimination diagrams. The high

solubility of large-ion lithophile elements (i.e., Rb, Cs, Ba, Pb, Sr, U) explains the “decoupling” of soluble LIL and insoluble HFS elements due to the interaction of hydrous fluids with the mantle source of subduction-related magmas.

1.2 The Role of Fluids in Metamorphism

We are becoming increasingly aware that fluids are a critical participant in metamorphic and igneous processes. Aqueous fluids reduce the melting point of rocks and enhance melting. They are also released by rising and cooling magmas where they generate pegmatites and ores. Mixtures of exhaled and meteoric fluids feed hydrothermal systems above plutons and in shallow permeable areas of regional metamorphism. As discussed above, fluids released over time by devolatilization reactions may be equivalent to over 10% of the volume of a rock. Fluids can dissolve material, transport heat and solutes, precipitate minerals, exchange components as they react with minerals, and catalyze deformation processes by weakening rocks. Contact metamorphic aureoles are largest where fluids are available to transport heat and matter. Fluid buffering versus open-system behavior may control the progress of metamorphism and mineral reactions in many situations. Release and flow of fluids absorb and transfer large quantities of heat and matter. The absorption and transfer by fluids of heat alone may have profound effects upon the temperature distribution in a contact aureole or even throughout an orogenic belt, and hence upon the geologic evolution of an area (Bickle and MacKenzie, 1987). Metamorphism is thus far more complex than simple re-equilibration of minerals to increased temperature and/or pressure upon burial or proximity to an intrusion, as it is commonly perceived.

Fluid transport through rocks has a profound effect on the processes mentioned in the preceding paragraph. Although flow through a porous medium is certainly the most efficient mechanism for fluid transport, rocks are highly porous only in the shallow crust. Below 10 km, a continuous network of large open pore spaces is closed by compaction and recrystallization. Motion of a fluid along fractures or of an intergranular fluid along grain boundaries are the only ways that fluids can migrate in the deeper crust. We will return to this concept in more detail shortly.

2 METASOMATISM

Metasomatism is defined as metamorphism accompanied by changes in whole-rock composition. Because volatiles are so readily released and mobilized during metamorphism, changes in the volatile content of rocks are generally excluded, and the chemical changes that constitute metasomatism (*sensu-stricto*) are usually restricted to the redistribution of nonvolatile species. You may be familiar with the changes in mineralogy in the contact aureole at Crestmore, California, and found that the mineral assemblages were readily explained by a progressive increase in the amount of SiO_2 in the country rock marbles as the igneous contact was