

## Chapter 11

# H<sub>2</sub>O Recycling During Continental Collision: Phase-Equilibrium and Kinetic Considerations

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**Abstract:** During the early stages of subduction of the lithosphere, anhydrous rocks become partially hydrated, and volatiles evolve from hydrous lithologies. Where present, aqueous fluid markedly enhances reaction rates. Phase-equilibrium studies demonstrate that, under typical subduction-zone P–T trajectories, clinoamphibole constitutes a major phase in deep-seated metamorphic rocks of MORB composition; other hydrous minerals are either absent or of relatively minor abundance. Clinoamphiboles dehydrate at pressures <2 GPa, so blueschists and amphibolites expel H<sub>2</sub>O at great depth, and commonly achieve the stable eclogitic assemblage of garnet + omphacite + rutile ± phengite. Partly serpentinized mantle beneath the oceanic crust devolatilizes at comparable pressures. In contrast, for reasonable subduction-zone P–T gradients, white micas ± biotites remain stable to pressures substantially exceeding 3.5–4.0 GPa. Accordingly, when the micaceous lithologies that dominate the continental crust (granitic, pelitic, and quartzofeldspathic gneisses) are subducted to depths of ≥100 km, they fail to evolve significant H<sub>2</sub>O, and may transform incompletely to the stable eclogitic assemblage of coesite + jadeite + K-spar + garnet + rutile + phengite. Thus, although all “juicy” rock types expel volatiles during compaction and shallow burial, the especially deep underflow of partly hydrated oceanic crust-capped lithosphere probably generates most of the ultrahigh-pressure volatile flux along and above a subduction zone prior to

continental collision; as large volumes of sialic crust enter the convergent plate junction, volatile flux at deep levels severely diminishes.

Although rate-enhancing volatiles evolved during prograde metamorphism diffuse into the overlying, hanging-wall lithosphere (mantle wedge), aqueous fluids also migrate back up the subduction channel, with proportions depending on the relative permeabilities of the lithologic units involved. Tectonic slices of a collisional sialic massif may move back to shallow depths along the subduction zone, propelled chiefly by buoyancy. Rehydration attending exhumation and retrogression characteristically is incomplete; its extent reflects the coarse grain size and relative impermeability of the units undergoing exhumation, as well as declining temperature and general lack of aqueous fluid. Hence, in addition to phase-equilibrium constraints, retrograde and prograde reactions are sensitive functions of kinetics, reflecting the presence or absence of H<sub>2</sub>O.

## 1. INTRODUCTION

During ultrahigh-pressure (UHP) metamorphism, continental crust is carried beneath the nonsubducted plate to depths exceeding 100 km (Schreyer *et al.*, 1987; Coleman and Wang, 1995). In the course of this descent, pressure within the slab rises, while temperature only gradually increases; volatiles—principally H<sub>2</sub>O (and some CO<sub>2</sub>)—may be added to relatively dry portions of the downgoing plate, and driven off from the more volatile-rich parts. Early, pre-eclogitic stages of these reactions are illustrated diagrammatically in Fig. 1.

Eventually, some of the subducted material, metamorphosed under high-pressure (HP) or UHP conditions (Harley and Carswell, 1995; Schreyer, 1995; Maruyama *et al.*, 1996) decouples from the descending slab and, driven largely by buoyancy, returns to more normal continental crustal levels (Ernst, 1970; England and Holland, 1979; Cloos, 1993; Chemenda *et al.*, 1995; 1996). During more-or-less adiabatic exhumation, temperature tends to remain relatively elevated, whereas if material ascends along an active subduction channel, it cools by thermal conduction across both upper and lower bounding surfaces (Hacker and Peacock, 1994; Hacker *et al.*, 1995; Ernst *et al.*, 1997). In either case, pressure declines with ascent. Volatiles gain access to the rising sialic mass, or diffuse away from it, depending on the composition, grain size, permeability, and deformation of the various constituent units. Some evolved fluids rise into and through the overlying mantle wedge, whereas the rest migrates back up the conduit provided by the subduction channel. The presence or absence of a separate aqueous phase during recrystallization is extremely important because this fluid has the capacity to catalyze reactions enormously (Rubie, 1986).

The present synthesis briefly summarizes experimental phase-equilibrium constraints on H<sub>2</sub>O-bearing minerals stable in the lithosphere (e.g., Massonne, 1995), and qualitatively traces the complex recycling of H<sub>2</sub>O attending

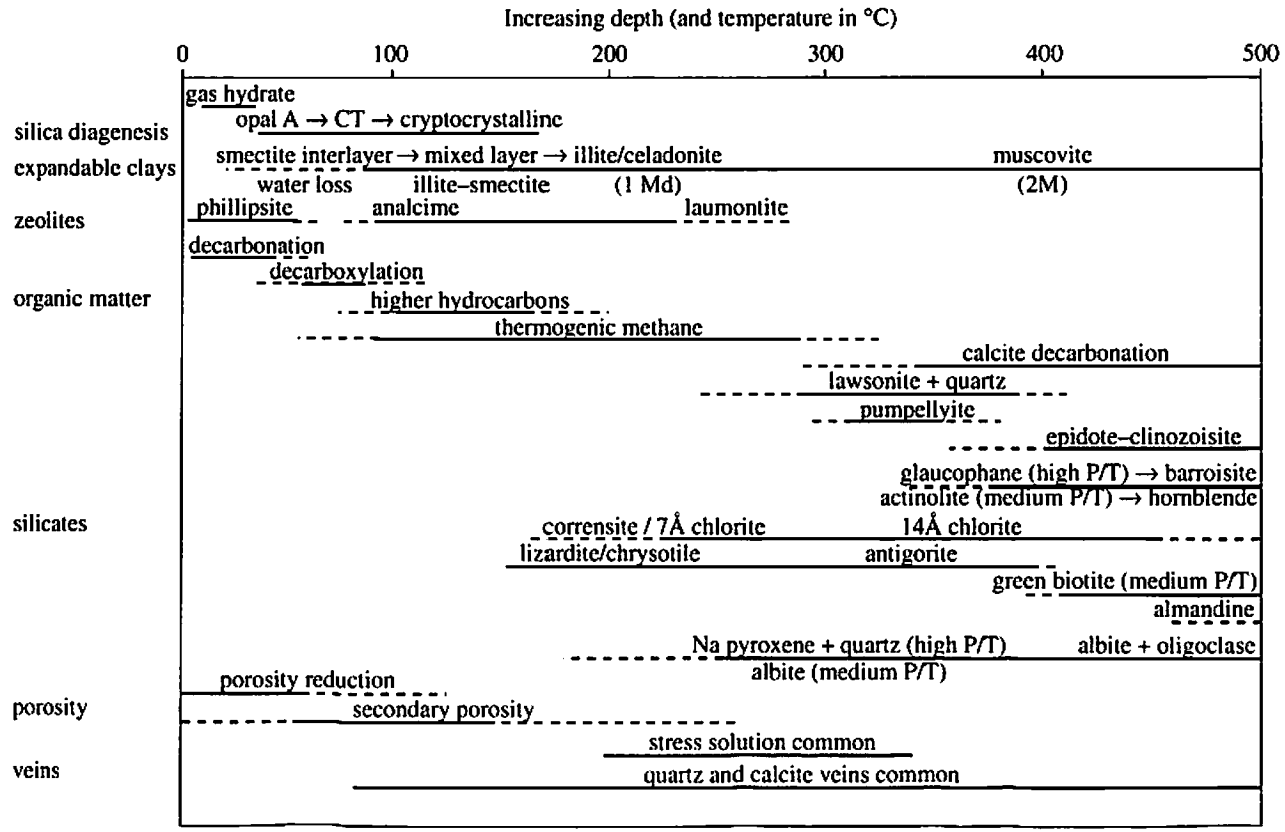


Figure 1. Schematic representation of hydration and fluid expulsion history of crustal rocks in early stages of the subduction of a lithospheric plate, generalized after Frey (1987) and Ernst (1990).

continental collision. Although carbon dioxide is important in certain subduction-zone histories, we do not consider the fate of CO<sub>2</sub> sequestered in carbonate strata, nor accessory carbonate minerals present in silicate-rich lithologies.

Study of natural UHP assemblages has documented the metastable persistence of low-pressure assemblages at surprisingly great depths, evidently due to the absence of an aqueous fluid phase (Austrheim, 1990; Jamtveit *et al.*, 1990; Hirajima *et al.*, 1993; Austrheim *et al.*, 1997; Zhang and Liou, 1997; Austrheim, *this volume*) as well as the metastable persistence of HP and UHP assemblages and mineral inclusions during exhumation (Chopin, 1984; Smith, 1984; Sobolev *et al.*, 1990; Liou and Zhang, 1996). Quantification of the relevant reaction rates is essential to an overall understanding of volatile recycling accompanying continental collision. It is clear from experimental studies that reaction rates are strongly influenced by the presence or absence of volatile constituents, especially H<sub>2</sub>O (Rubie, 1990; Hacker, 1996). Volatile-rich rocks expel aqueous fluids during compaction and shallow-level underflow (Fig. 1), such that during the deep subduction of crustal lithologies, retained volatiles are sequestered exclusively in relatively refractory silicate phases (Poli and Schmidt, 1997). Under UHP conditions, aqueous fluid is probably not common as a separate phase (Rumble, *this volume*), and free H<sub>2</sub>O becomes available only to the extent that such minerals undergo dehydration reactions.

In this chapter, we emphasize the special role played by pressure-limited clinoamphibole and antigorite in catalyzing the rate of attainment of equilibrium in deeply subducted mafic rocks. For quartzose felsic lithologies, H<sub>2</sub>O is sequestered in micas that remain stable at UHP; accordingly, such rocks may not significantly devolatilize at depths of about 100 km, and therefore may fail to recrystallize to the stable UHP phase assemblage.

## 2. PHASE-EQUILIBRIUM CONSTRAINTS

In aggregate, four principal rock types constitute most of the noncarbonate, volatile-bearing subducted and recrystallized sialic crust: metabasalts and metagabbros; variably serpentized mantle materials; pelitic schists, metagraywackes, and high-grade gneissic equivalents; and metagranitoids. Because the partial fusion of granitic rock types is treated in detail by Patiño Douce and McCarthy (*this volume*), our discussion concentrates on mafic, ultramafic, and felsic lithologies.

### 2.1 Metabasalts

Glaucophane–crossite, barroisite, and hornblende are important constituents in pre-eclogite mineral assemblages. Although common as low-temperature, low-

pressure prograde and retrograde minerals, most other hydrous phases such as actinolites, micas, epidotes, chlorites, and chloritoid are uncommon, minor phases in UHP metabasalts of normal compositional ranges. The consistency of occurrence of this extremely limited subset of hydrous phases has been documented through a generation of petrologic studies world-wide (e.g., Banno, 1964; Ernst *et al.*, 1970; Cortesogno *et al.*, 1977; Dal Piaz and Ernst, 1978; Sobolev and Sobolev, 1980; Hirajima *et al.*, 1993; Beane *et al.*, 1995; Chopin and Sobolev, 1995; Dobretsov *et al.*, 1995; Krogh and Carswell, 1995; Liou *et al.*, 1996; Zhang *et al.*, 1997).

Various experimental studies have been performed on metabasaltic bulk compositions, encompassing the temperature and pressure range 300–1050°C and 0–3.5 GPa (Essene *et al.*, 1970; Helz, 1973; Liou *et al.*, 1974; Helz, 1979; Spear, 1981; Gilbert *et al.*, 1982; Apter and Liou, 1983; Moody *et al.*, 1983; Poli, 1993; Liu *et al.*, 1996; Poli and Schmidt, 1997). As documented by long-term experiments and reaction reversals for unaltered, chemically pristine mid-ocean ridge basalt (MORB), barroisitic to pargasitic amphibole is the major hydrous phase at temperatures >650°C. The Ca-amphibole stability field contracts drastically at high pressures, and disappears at ≤1.6–2.4 GPa, depending on temperature. The phase relations for unaltered MORB illustrated in Fig. 2 (Liu *et al.*, 1996) are generally applicable to unmetasomatized oceanic basalts and gabbros. Substantial amounts of lawsonite and sodic amphibole characterise metabasaltic rocks at moderate pressures and at temperatures <500–600°C (Maresch, 1977), but the glaucophane stability field is limited at elevated pressure, analogous to the P–T behavior of Ca-amphiboles (Koons, 1982; Carmen and Gilbert, 1983; Welch and Graham, 1992). Lawsonite remains stable in rocks of MORB composition as an important mineral under UHP conditions (Okamoto and Maruyama, 1997; Ono, 1997), but only at low temperatures characterized by unnaturally low thermal gradients of ~2–5°C/km, as shown in Fig. 3.

Synthesis experiments involving mafic igneous rocks of more aluminous composition have been interpreted to suggest that epidote and chlorite possess broad stability ranges at temperatures <600–650°C (Pawley and Holloway, 1993; Schmidt and Poli, 1994; Poli and Schmidt, 1997). At these temperatures epidote and chlorite should coexist with actinolitic amphibole at low pressures, and with glaucophane–crossite at intermediate pressures. In contrast, in the senior author's experience with—and interpretation of—natural parageneses in rocks of MORB composition, the volume fractions of chlorite, actinolite, sodic amphibole, epidote, and in many cases, white mica, progressively decrease to zero as UHP conditions are approached. The lack of reaction reversal—hence demonstrated chemical equilibrium—in these earlier laboratory studies is the likely explanation for this discrepancy. In metabasalts more potassic than MORB, white mica is

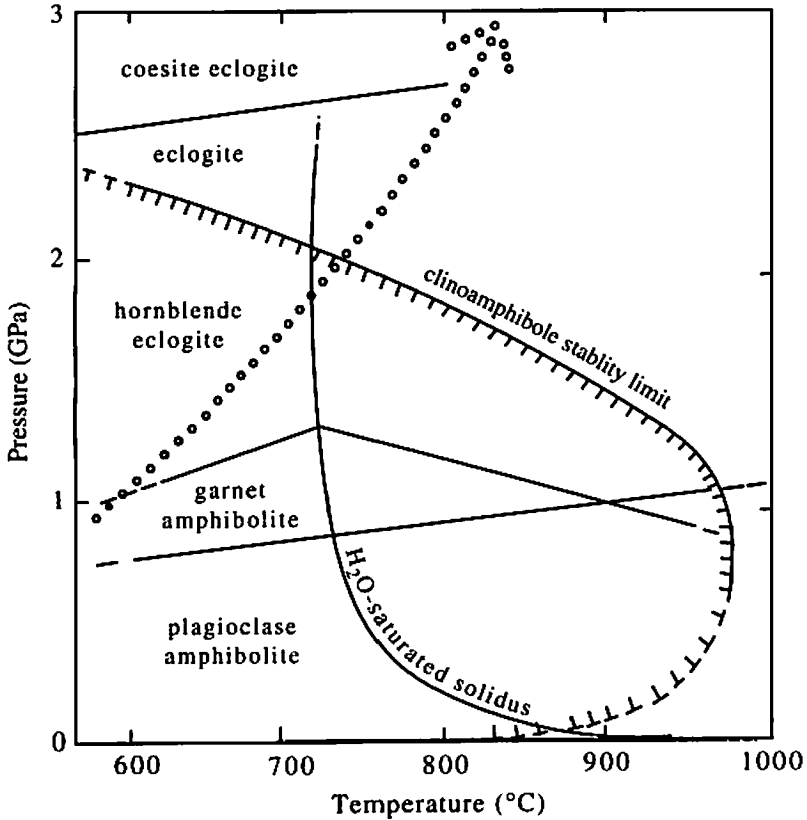


Figure 2. Petrogenetic grid for the amphibolite → eclogite transformation in the basalt–H<sub>2</sub>O system with oxygen fugacity defined by the FeSiO<sub>4</sub>–Fe<sub>3</sub>O<sub>4</sub>–magnetite–SiO<sub>2</sub> buffer, experimentally determined by Liu *et al.* (1996). Run lengths were up to 1630 hours at low temperatures; several reversals demonstrate a close approximation to chemical equilibrium. The illustrated P–T trajectory for a prograde subduction-zone thermal gradient (open dots) is ~10°C/km.

stabilized to relatively elevated pressures, and may be an associate of garnet, omphacite, and rutile in the HP/UHP paragenesis of altered mafic rocks. Although chloritoid has been reported in some synthesis experiments (Pawley and Holloway, 1993; Poli and Schmidt, 1997), there is little likelihood that this mineral represents an important phase in subducted MORBs because of its unusual Al<sub>2</sub>O<sub>3</sub> + FeO-rich composition and restricted thermal stability.

Because calcic and sodic amphiboles break down at near-ultrahigh pressures, metabasaltic rocks generate at least modest amounts of H<sub>2</sub>O by dehydration under conditions conducive to the production of eclogitic assemblages; accordingly, eclogitization is favored except in extremely dry, impermeable protoliths such as granulite-facies metagabbros (Austrheim, 1990; Hirajima *et al.*, 1993; Zhang and Liou, 1997).

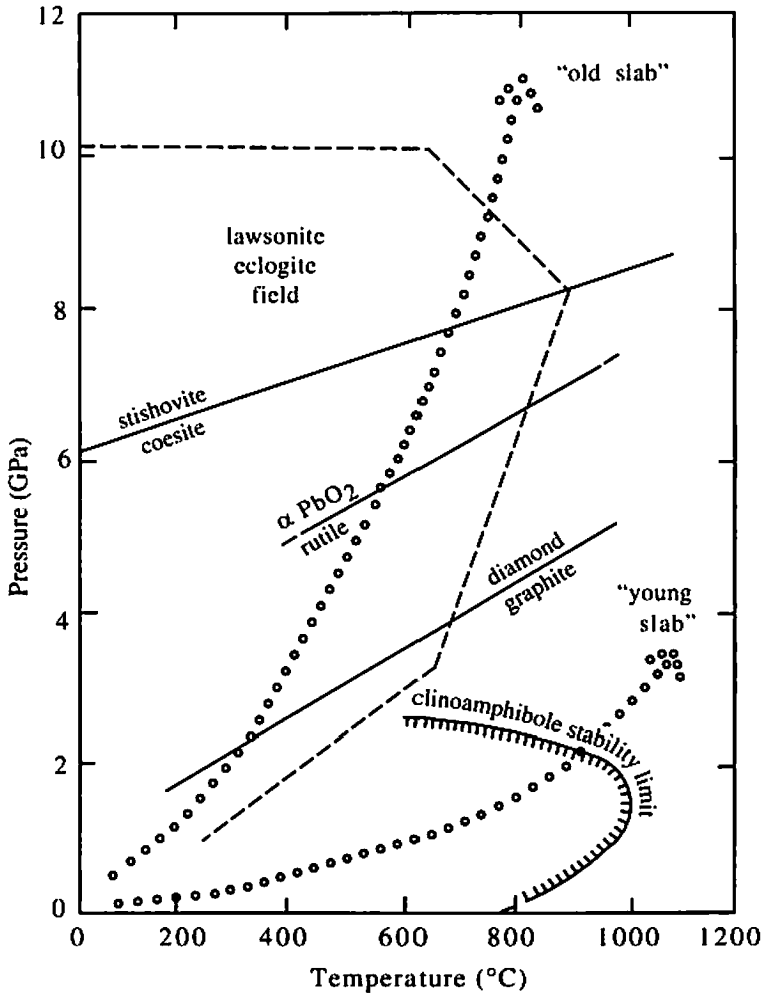


Figure 3. Synthesis fields and presumed stability relations of lawsonite in the unaltered basalt-H<sub>2</sub>O system, after Okamoto and Maruyama (1997). The rutile- $\alpha$ PbO<sub>2</sub> transition is after Akaogi *et al.* (1992). White mica joins this assemblage for K<sub>2</sub>O + Al<sub>2</sub>O<sub>3</sub>-rich bulk-rock compositions. Values illustrated for prograde subduction-zone thermal gradients (open dots) are: "old slab"  $\sim$ 2°C/km; "young slab"  $\sim$ 10°C/km.

## 2.2 Serpentinites

Antigoritic serpentinites dehydrate to orthopyroxene or talc + olivine, liberating large amounts of H<sub>2</sub>O at approximately 550–600°C and 2–3 GPa (Johannes, 1975; Evans *et al.*, 1976; Ulmer *et al.*, 1994; Wunder and Schreyer, 1997). Thus, similar to clinoamphibole, the stability of antigorite is limited by pressure

(Fig. 4). How much of the suboceanic mantle is partly serpentized is unknown, however, inasmuch as most sampling thus far has involved oceanic fracture zones, transform faults, and ophiolites—all sections characterized by unusually intense deformation and fluid circulation (e.g., Bonatti, 1976). Fully serpentized mantle has a density of  $<2.5 \text{ g/cm}^3$ , and should be virtually unsubductable. Even mantle lithosphere with  $>10\text{--}20\%$  serpentinite is less dense than asthenosphere. This interpretation is supported by measured seismic P-wave speeds of  $8.1 \text{ km/s}$  for the oceanic mantle vs. a  $5.5 \text{ km/s}$  for serpentinite (Christensen and Salisbury, 1975). In any case, at least modest amounts of hydrated ultramafics are present in the uppermost parts of the lithosphere, so

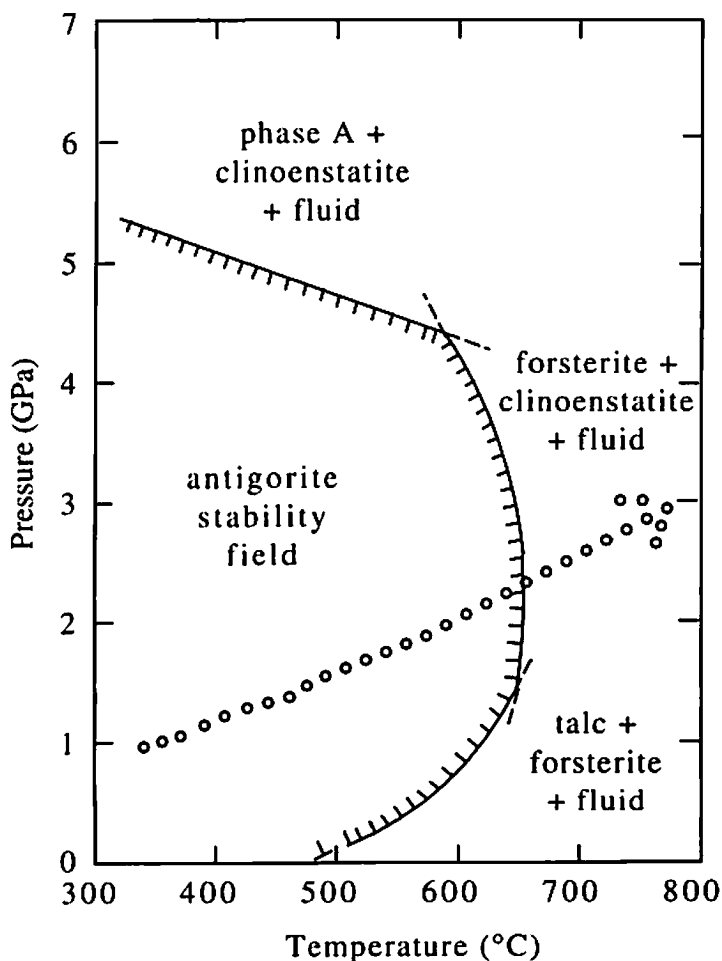


Figure 4. Typical phase diagram for the stability of antigorite, after Wunder and Schreyer (1997). See also Johannes (1975), Evans *et al.* (1976), and Ulmer and Trommsdorff (1994). The illustrated P-T trajectory for a prograde subduction-zone thermal gradient (open dots) is  $\sim 10^\circ\text{C/km}$ .



their subduction and consequent devolatilization undoubtedly contribute to the aqueous fluid flux of a descending oceanic plate (Ulmer *et al.*, 1994) prior to continental collision.

### **2.3 Metapelites and Metagraywackes**

Experimental studies of quartzofeldspathic lithologies over a wide range of laboratory conditions demonstrate that chlorites dehydrate above ~600°C, whereas potassic white micas and biotites remain stable to considerably higher temperatures—hence are present at greater subduction depths in metaclastics and orthogneisses (Le Breton and Thompson, 1988; Vielzeuf and Holloway, 1988; Vielzeuf and Montel, 1994; Gardien *et al.*, 1995; Patiño Douce and Beard, 1996; Skjerlie and Johnston, 1996; Luth, 1997; Massonne and Szpurka, 1997). A petrogenetic grid showing the phase relations for metagraywackes and pelitic schists to 2 GPa is illustrated in Fig. 5. This comprehensive treatment shows that, for peraluminous, quartz-bearing lithologies, biotite + kyanite are replaced by muscovite + garnet at pressures >1.7 GPa. For subduction-zone P–T gradients, muscovite–phengite solid solutions remain stable in gneissic units well into UHP conditions, at least to 3.5–4.0 GPa, and for metaluminous rocks, biotite persists to similar pressures, according to the various works referred to above. Because phengitic micas and biotites constitute the major, volumetrically important hydrous phases in equilibrium assemblages under UHP, quartzofeldspathic lithologies (pelitic schists + metagraywackes + gneisses) that dominate the continental crust will fail to evolve significant amounts of H<sub>2</sub>O during UHP metamorphism at depths of 100 km or more; thus they may preserve metastable, lower pressure feldspar + quartz-bearing micaceous assemblages in the absence of a catalytic aqueous fluid, failing to develop the stable prograde mineralogic assemblage of coesite + jadeite = K-spar + garnet + rutile + phengite.

### **2.4 Evolution of H<sub>2</sub>O at UHP**

Although most downgoing low-grade metamorphic rocks lose important amounts of volatiles at shallow subduction depths (Fig. 1), by the time they reach HP/UHP conditions, micaceous quartzofeldspathic and metapelitic lithologies should be relatively deficient in H<sub>2</sub>O-producing phases. Thus, the amphibole-bearing oceanic crust and serpentized peridotite—not mica-bearing sialic crust—are the most significant dehydrating rock type at depths approaching or exceeding 100 km. If so, the closure of an ocean basin prior to continental collision provides the greatest proportion of deep-seated aqueous fluid rising through the subduction channel as well as diffusing into the hanging-wall mantle wedge. The fluid flux at UHP is probably curtailed or terminated at depth by the arrival, profound underflow, and suturing of continental crust.

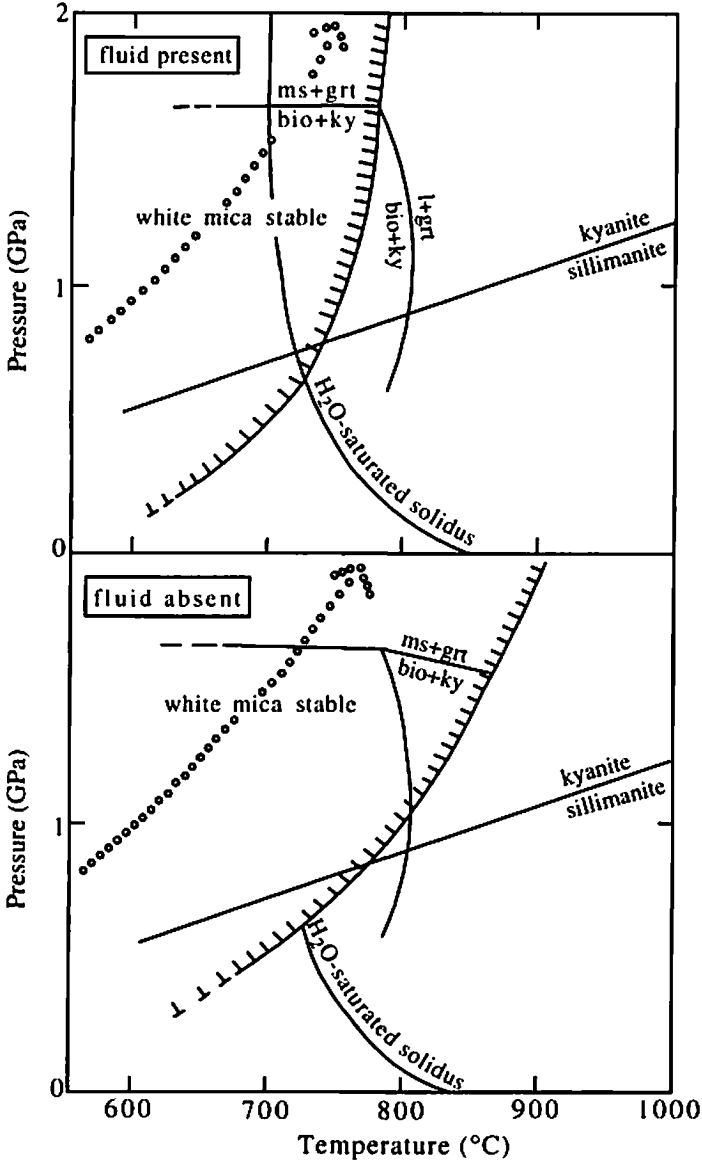


Figure 5. Experimentally determined and computed petrogenetic grid under fluid-present and fluid-absent conditions for quartzose metagraywackes + pelitic schists possessing intermediate bulk-rock Fe/Mg ratios, simplified after Vielzeuf and Holloway (1988). Abbreviations: bio, biotite; grt, garnet; ms, white mica. Phengitic micas are stable to pressures in excess of 3.5–4.0 GPa in quartzofeldspathic rock types (Le Breton and Thompson, 1988; Vielzeuf and Montel, 1994; Gardien *et al.*, 1995; Patiño Douce and Beard, 1996; Skjervlie and Johnston, 1996; Massonne and Szpurka, 1997). Biotite is stable for simplified metaluminous bulk compositions up to ~9 GPa (Luth, 1997). The illustrated P–T trajectory for a prograde subduction-zone thermal gradient (open dots) is ~10°C/km.

### 3. KINETIC CONSTRAINTS

The principal evidence testifying to the existence of UHP recrystallization of continental crust now exposed at Earth's surface resides in the fragmentary preservation of UHP silicate phases and yet rarer diamond. The persistence of such mineralogic relics is a reflection of initial prograde P–T conditions and even more importantly, sluggish rates of backreaction during ascent and decompression. What do we know about the kinetics of such transformations?

#### 3.1 Rate of Graphitization of Diamond

Experiments on the anhydrous transformation of diamond → graphite show that the rate of graphitization can be estimated by the expression:

$$d\xi/dt = C \exp^{-(\Delta E + P\Delta V)/RT}$$

where  $\xi$  is the proportion converted,  $t$  time,  $C$  a constant,  $\Delta E$  the activation energy,  $\Delta V$  the activation volume, and  $R$  the universal gas constant (Davies and Evans, 1972). The low activation volume for graphitization ( $\sim 10 \text{ cm}^3 \text{ mol}^{-1}$ ) indicates that the influence of pressure is small and that the rate of graphitization depends largely on temperature (Pearson *et al.*, 1995). Experimentally determined activation energies for graphitization of diamond are lowest for {110} faces,  $760 \text{ kJ mol}^{-1}$ , and highest for {111} faces,  $1060 \text{ kJ mol}^{-1}$  (Pearson and Nixon, 1996). Using the activation energy for the graphitization of {110} faces under anhydrous conditions, Pearson *et al.* (1995) calculated that the complete conversion of a diamond octahedron ( $\sim 10 \text{ mm}$  edge length) to graphite requires about 1 m.y. at  $1200^\circ\text{C}$  or 1 b.y. at  $1000^\circ\text{C}$ .

In the Kokchetav Complex of northern Kazakhstan, where inclusions of variably graphitized microdiamond are well documented (Sobolev and Sobolev, 1980; Sobolev *et al.*, 1990), the ascent to midcrustal levels seemingly took about 20 m.y., indicating an average exhumation rate of 5–6 mm/year (Ernst *et al.*, 1997). Ascent from mantle depths of the garnet lherzolite and eclogite complex at Alpe Arami, central Alps, took place at  $>20 \text{ mm/year}$ , according to SHRIMP dating by Gebauer (1996). In the eclogites of the Western Gneiss Region of southwestern Norway (Dobrzhinetskaya *et al.*, 1995), and the Dabie Shan of east-central China (Xu *et al.*, 1992), exceedingly rare microdiamonds have been reported, but not generally confirmed; in these putative occurrences, the average exhumation rates to crustal depths are poorly constrained, but are comparable to the previously cited occurrences at approximately 1–4 mm/year (Ernst *et al.*, 1997). Kinetic studies on the graphitization of diamond require orders-of-magnitude slower exhumation rates and higher temperatures than are thought to have occurred in the petrotectonic evolution of these UHP complexes, suggesting

that no diamonds in UHP metamorphic rocks should be altered to graphite. In fact, diamond is preserved in the Kokchetav Complex (and apparently in the Western Gneiss Region, and the Dabie Shan) under only very special conditions, chiefly as armored micro-inclusions in nonreactive, strong pressure vessels such as garnet or zircon. Re-equilibration that occurred during the exhumation history of these UHP rocks probably caused the complete graphitization of any diamond that was present in the matrix. Calculated rates of graphitization based on experiments are slower than nature probably because the dry graphitization experiments do not take into account the presence of aqueous fluids and other experimentally verified rate-enhancing constituents (Tagiri and Oba, 1986). The preferential preservation of these tiny inclusions of diamond relative to coesite micro-inclusions in northern Kazakhstan (Sobolev and Sobolev, 1980; Sobolev *et al.*, 1990) reflects the fact that at high temperatures ( $\sim 900^\circ\text{C}$ ), coesite backreacts much more rapidly than diamond on decompression.

### 3.2 Rate of Transformation of Silicates

Evidence of widespread disequilibrium during eclogite-facies metamorphism (e.g., Rubie, 1990; Hacker, 1996; Austrheim, this volume) highlights the need for more quantitative experimental data on reaction rates. It has become increasingly clear from natural examples that availability of fluid, rather than P-T-induced thermodynamic changes, chiefly control the rate at which reactions occur. Although the catalytic effect of  $\text{H}_2\text{O}$  is well known and some specific catalytic mechanisms have been proposed (e.g., Rubie, 1986), little is known quantitatively from experiments about the dependence of reaction rates and mechanisms on fluid concentration in systems with low fluid:rock ratios—the most likely condition for large massifs of subducting continental crust.

Of primary concern in the present case are the kinetics of three types of transformation: polymorphic, multiphase solid–solid, and dehydration reactions. In particular, for quartzofeldspathic lithologies, quartz is expected to transform polymorphically to coesite, plagioclase should break down to form any of a series of denser phase assemblages, and phengite should dehydrate at high temperature. Below we consider the rather limited database on the kinetics of these three categories of reaction (cf. Hacker and Peacock, 1994).

### 3.3 Polymorphic Reactions

Preliminary results on quartz  $\rightarrow$  coesite kinetics (Mosenfelder and Bohlen, 1995) as well as experimental data on the reverse transformation (Mosenfelder and Bohlen, 1997) suggest that this reaction is rapid in both directions at UHP conditions. This hypothesis is compatible with textural evidence from natural UHP metagranitoids. For instance, the undeformed UHP Brossasco metagranite

(Biino and Compagnoni, 1992) contains granoblastic quartz aggregates pseudomorphing original euhedral igneous quartz; the most probable explanation for this texture is a complete reversion from coesite. However, two factors have not been satisfactorily addressed in experimental studies. First, nucleation in laboratory experiments may be much faster than in nature because of the presence of cracks or other structural damage in starting materials. Second, trace amounts of H<sub>2</sub>O in synthetic phases can further accelerate reaction (Mosenfelder and Bohlen, 1997).

Backreaction of UHP phases during exhumation presents a different problem because transformation may be inhibited by a number of factors. In particular, coesite and diamond included in other phases can be protected by an "overpressure" from the host phase until cracking occurs at lower temperatures (Gillet *et al.*, 1984). Furthermore, the effect of fluids, or lack thereof, may be especially important at lower temperatures during exhumation.

### 3.4 Multiphase Solid–Solid Reactions

At UHP conditions in a quartzofeldspathic system, plagioclase should ultimately break down via the discontinuous reaction plagioclase → jadeite + grossular + kyanite + quartz. Sufficient data to predict the kinetics of complex, multiphase, solid–solid reactions are unavailable. Such reactions, both prograde and retrograde, are expected to be considerably slower than polymorphic transformations because they are probably controlled by diffusion of several species, potentially along complex pathways, rather than by the diffusion of a single ion across an interface. A number of studies of natural rocks (e.g., Wayte *et al.*, 1989; Rubie, 1990; Biino and Compagnoni, 1992; Wain, 1997; Austrheim, this volume), have inferred that plagioclase breaks down only in the presence of an aqueous fluid, even at relatively high temperatures and large pressure oversteps. This suggests that extreme nucleation barriers exist for these reactions, a hypothesis which needs to be tested experimentally and theoretically.

### 3.5 Dehydration Reactions

It is commonly assumed that dehydration reactions either occur rapidly or are controlled by the rate of enthalpy production (Ridley, 1985). Most experiments, employing powdered starting materials, yield rates which are rapid when extrapolated to geologic conditions (e.g., Wegner and Ernst, 1983; Schramke *et al.*, 1987; Jové and Hacker, 1997). However, work on dehydration reactions employing solid rocks as starting materials yields slower rates and different mechanisms (Brearley, 1987; Rubie and Brearley, 1987; Brearley and Rubie, 1990; Hacker, 1990; Hacker and Christie, 1991). In these studies, metastable dehydration melting commonly occurs, which actually inhibits stable dehydration

reactions. Extrapolation of these results to longer timescales and temperatures close to equilibrium is uncertain at present. Nevertheless, it seems clear that, because dehydration reactions generate a rate-enhancing constituent ( $H_2O$ ), prograde transformations will proceed more rapidly than the equivalent backreaction. This phenomenon, and the fact that mafic lithologies carry substantial amounts of a pressure-limited hydrous phase, whereas felsic rocks are not so constrained, constitute the thrust of this paper.

#### 4. DISCUSSION

The ease with which aqueous fluids gain access to—or egress from—subducting and ascending sialic masses is a complex function of rock composition, permeability, extent of deformation, grain size, and availability of volatiles. These quantities reflect the histories and ongoing dynamics of the lithotectonic units at the convergent plate junction. What we know reasonably well, based on computational thermal modelling (Peacock, 1992; Peacock, 1995; Ernst and Peacock, 1996) and laboratory phase-equilibrium studies (Vielzeuf and Holloway, 1988; Massonne, 1995; Schreyer, 1995; Liu *et al.*, 1996; Patiño Douce and McCarthy, this volume), is the evolving P–T structure of a continental collision zone and the P–T stability fields of the mineral assemblages for the major rock types. What we do not know with any degree of certainty is the rates at which mineralogic transformations take place, and therefore, the conditions and tectonic realms under which volatile constituents are evolved and consumed. Given the proper (anhydrous) circumstances, low-pressure assemblages can be retained under prograde UHP conditions, and UHP relics can be preserved under retrograde low-pressure conditions. Quantification of the kinetics for the controlling reactions is the key, and as briefly described above, these data are not yet available except for a few, chemically simple mineral systems.

#### 5. CONCLUSIONS

The examination of UHP rocks exhumed from depths of >100 km, combined with experimental phase-equilibrium data, and available kinetic information, allows the following conclusions:

- 1) Subduction of oceanic and/or sialic massifs at moderate depths results in the partial hydration of relatively dry units and in the evolution of volatiles from “juicier” lithologies (Fig. 1).
- 2) Under typical deep-seated subduction-zone P–T trajectories, clinoamphiboles dehydrate at pressures <2 GPa (Fig. 2); amphibole-bearing rocks such as metabasalts expel aqueous fluids during eclogitization, and

recrystallize readily to the stable HP/UHP garnet + omphacite + rutile ± white mica (eclogite-facies) assemblage. Similar to clinoamphiboles, antigorite in serpentinized peridotites dehydrates at comparable to slightly higher pressures (Fig. 4).

3) For such P–T subduction paths, phengitic micas and biotites are stable to far greater pressures than characterise clinoamphiboles and antigorite (Fig. 5); accordingly, interlayered mica-rich lithologies (metagranitoids, gneisses, metagraywackes, and metashales) may fail to evolve significant amounts of H<sub>2</sub>O under UHP conditions. Thus quartzose felsic units probably transform much less completely to eclogitic phase assemblages (coesite + jadeite = K-spar + garnet + rutile + phengite) than do spatially associated mafic rocks.

4) Volatile evolution is maximized during the subduction of amphibole-rich oceanic crust and associated serpentinized mantle prior to continental collision; once large volumes of micaceous quartzofeldspathic rock enter the subduction zone, dehydration may virtually cease at depths ≥100 km. If sialic crust is carried down substantially farther, mica-bearing units must eventually dehydrate due to higher pressures and temperatures.

5) Attending prograde evolution of volatiles, some H<sub>2</sub>O diffuses into the overlying, nonsubducted lithospheric hanging wall, while the rest of the aqueous fluid migrates back up the subduction channel, depending on the permeabilities of the lithologic units involved.

6) As segments of a sialic massif are exhumed, propelled chiefly by buoyancy along the subduction zone acting as a stress guide, cooling takes place; the degree of retrograde rehydration depends on the nature of the units involved and on the availability of aqueous fluids.

7) During thermal relaxation and decompression (wet or dry), the rates of backreaction of silicates such as coesite exceed that of the diamond → graphite transition.

## ACKNOWLEDGMENTS

Discussions with numerous researchers investigating intracontinental HP/UHP terranes helped lead us to the ideas expressed here. Our manuscript was reviewed and materially improved by John Holloway, Douglas Rumble III, and Werner Schreyer as well as the editors of this volume, B. R. Hacker and J. G. Liou. Sandy Keiser drafted the illustrations. We thank the above workers and both Stanford University and the Carnegie Institution of Washington for support.

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