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Mineralogical and chemical effects of hydration reactions and applications to serpentinization

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Abstract

Hydration reactions occurring during retrograde metamorphism of igneous or high-grade metamorphic rocks can be expected to show systematic effects due to the lowering of water pressure (P_{H_2O}) below that of pure water at the same temperature and total (rock) pressure (P_t). These effects are: (1) Equilibrium phase relations are limited to small domains; larger domains may be characterized by more phases than are possible according to the phase rule. (2) More phases are possible in an equilibrium assemblage during retrograde metamorphism (where, generally, $P_{H_2O} < P_t$) than during prograde metamorphism of H_2O-bearing rock (where $P_{H_2O} \cong P_t$). (3) The fluid and minerals tend to be enriched in species that preferentially partition into the fluid. (4) Halides and other very soluble phases may precipitate along grain boundaries. (5) Enrichment of a rock in components that preferentially partition into the fluid is selective according to the amount of water available for hydration; partially-altered rock will show the greatest enrichment. All these features are observed in serpentinized ultramafic rocks. For example, during prograde metamorphism the sequence chrysotile → antigorite → forsterite (± brucite or talc) is common, but the retrograde sequence is typically forsterite → chrysotile (± brucite or talc). The antigorite stability field may be bypassed commonly because of low P_{H_2O}. Also serpentinites are commonly enriched in Cl, B, U, and other elements that suggest alteration by sea water. Because the fluid phase leaves a signature of its composition in the rock during hydration, we have a potential indicator of the paleocomposition of hydrothermal and metamorphic fluids.

Introduction

This paper demonstrates that a few general properties of mineral-solution equilibra lead to testable predictions concerning the compositions of minerals and fluids and the nature of mineral assemblages produced during retrograde metamorphism. These predictions are confirmed in a classic example of hydration, the serpentinization of ultramafic rocks. Because of the general nature of the derivation, the implications should be applicable to a wide variety of rocks that have undergone retrograde metamorphism.

Retrograde is used in the sense of metamorphism occurring at temperatures lower than those to which the rock was subjected at some unspecified earlier time. Included in this definition is the metamorphism of high-grade metamorphic rocks to lower grade during the waning stages of a single metamorphic event, the metamorphism of high-grade metamorphic rocks to lower grade in a later event, and the metamorphism (or alteration) of igneous rocks. Each of these processes have the common feature that the reactions are predominantly H_2O-consuming or hydration reactions.

The particular aspect of retrograde metamorphism focused on here, is the condition of P_{H_2O} less than total or rock pressure (P_t). This state can be achieved in four ways: (1) H_2O in the fluid is diluted by other volatile components such as CO_2. (2) H_2O in the fluid is diluted by dissolved solids such as NaCl. (3) No fluid phase is present; water is present as individual H_2O molecules adsorbed on the surface of mineral grains. (4) The fluid pressure is less than the total or rock pressure, as in the case where fluid pressure is governed by the height of water in an open channel system.

Thompson (1955) presented a thorough treatment of the different limiting cases for reactions involving "mobile components" such as H_2O. Equilibrium between a dilute aqueous fluid in a fissure system and the wall rock (Thompson's case 2) applies to geologic

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examples such as hydrothermal-vein ore deposits or to the parts of ultramafic bodies that are adjacent to serpentine veins. The chemical potential of species in the bulk of a rock undergoing retrograde metamorphism is, however, controlled primarily by the diffusion rate of the species through the rock (Martin and Fyfe, 1970). Thus, we are primarily interested here with conditions approaching Thompson's cases 3 and 4.

Certain properties of rocks are particularly favorable for creating conditions of $P_{H_2O} < P_t$ during retrograde metamorphism: (1) The amount of trapped fluid at the onset of retrograde metamorphism is small, so that hydration reactions proceed only until all trapped H_2O is consumed. (2) The rock has low permeability so that hydration reactions can locally consume H_2O from the grain boundary or pore fluid faster than H_2O can diffuse in from open fractures and veins. Thus we are considering a partly closed system in which H_2O can enter from outside the rock but is limited by the rate of diffusion. (3) The stable mineral assemblage at the retrograde conditions is more hydrous than the initial assemblage, so that the hydration reactions provide a constant sink for H_2O. These conditions are assumed to be typical of retrograde metamorphism.

In terms of "initial value" and "boundary value" components (Zen, 1963), the limiting case discussed here is that of H_2O as an "initial value component," where the amount of H_2O available for hydration is limited to that which was initially present in pores and grain boundaries in the igneous or high-grade metamorphic rock. This restriction is relaxed in order to consider H_2O as a "boundary value component," where H_2O diffuses from an external reservoir (the fluid-filled fracture system) into the part of the rock where hydration is occurring.

Analysis and predictions

Figure 1a shows a P–T diagram for a hypothetical system containing two hydrous phases or compositionally identical assemblages, H and H′, and an anhydrous phase or assemblage, A. The diagram is drawn in the conventional manner with $P_{H_2O} = P_t$. An "invariant point" (I) comprising all three phases exists at low pressure. At any particular total pressure, P_t^*, which is greater than the pressure at I, the H_2O-conserving reaction H′ = H (abbreviated HH′) is stable, and the two phases or assemblages coexist at equilibrium at temperature T_1. Also at P_t^*, the reaction H = A + H_2O (abbreviated AH) is stable, and H and A coexist at equilibrium at temperature T_2.

Under these conditions, P_{H_2O} is an independent variable. Figure 1b shows a T–P_{H_2O} section at P_t^* with $P_{H_2O} \leq P_t$. The reaction HH′ is independent of P_{H_2O} and is therefore a vertical line on the diagram at T_1. The univariant curve for reaction AH, however, decreases in temperature as water pressure decreases and intersects the curve of reaction HH′ at "invariant point" I. Clearly I is not invariant if P_{H_2O} is allowed to vary. In fact, I describes a locus of points in P_t–P_{H_2O}–T space. The projection of this curve parallel to the P_{H_2O} axis onto the P_t–T plane, coincides with curve HH′ shown in Figure 1a. As water pressure decreases, the coincidence of the three phases becomes stable at higher total pressures. Also the assemblage AH′, which is stable only at very low total pressure, where $P_{H_2O} = P_t$, becomes stable at higher total pressure where $P_{H_2O} < P_t$.

A rock undergoing prograde metamorphism will encounter H_2O-conserving reactions such as HH′ and H_2O-producing reactions such as AH. The reaction HH′ has no effect on the water pressure of the surroundings, except for the minor effect of a volume change on the pore fluid pressure. However, dehydration reactions such as AH tend to increase water pressure to a maximum where fluid (H_2O plus other dissolved components) pressure equals lithostatic pressure. Once the fluid pressure equals the lithostatic pressure, further dehydration only forces water out of the rock. If other volatile components are not present, water pressure remains equal to total pressure.

Hydration reactions have the opposite effect. Consider a rock consisting of A, which has a temperature and pressure within the stability field of H and has water in pores or grain boundaries at $P_{H_2O} = P_t$. The particular temperature–pressure path that produced these conditions in the rock is unimportant. The rock may have cooled gradually from a peak metamorphic temperature, or may have cooled abruptly by volcanism or faulting, or may have cooled to surface temperature and then been heated in a subsequent event. Regardless of the particular mechanism, a rock that has been dehydrated has reached a temperature and pressure at which a hydrated assemblage is stable. At temperatures below that of curve AH, water will be drawn from the fluid into the mineral assemblage. The fluids trapped in pores and grain boundaries will tend to be depleted in H_2O by the hydration reaction. Once the trapped pore water has been consumed, the reaction will cease if no additional water migrates into the rock from the surroundings.

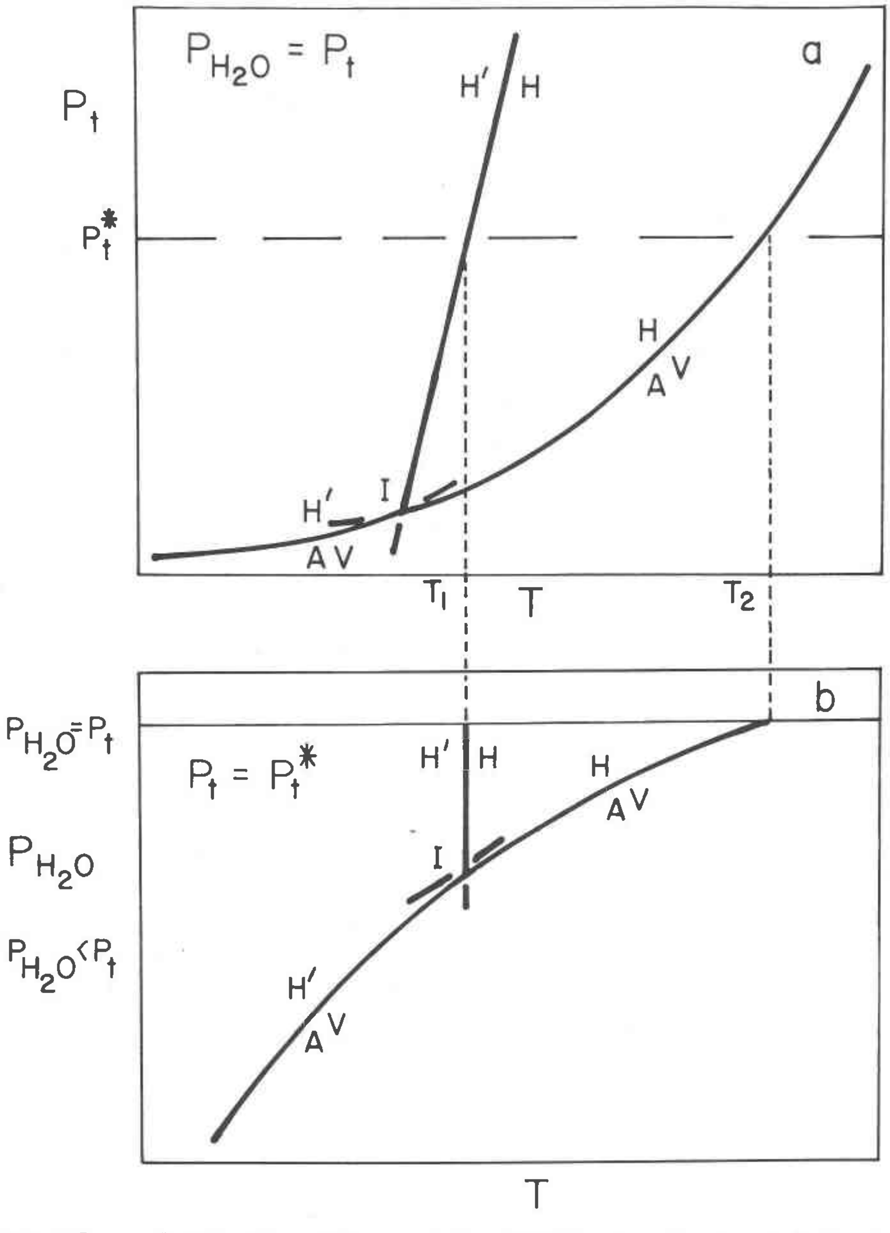

Fig. 1. P_t-T diagram at $P_{H_2O} = P_t$ (a) and P_{H_2O}-T diagram at $P_t = P_t^*$(b) for phases in a hypothetical system A-H_2O. A is an anhydrous phase or assemblage. H and H' are compositionally-equivalent hydrous phases or assemblages, V stands for vapor. Three univariant curves intersect at an "invariant point" I. In (a), I is at pressures below normal geothermal gradients. Fig. 1b shows that, if $P_{H_2O} < P_t$, "invariant point" I is geologically accessible.

The new assemblage of hydrous (H) and anhydrous (A) phases defines an equilibrium value of $P_{H_2O} < P_t$. In a partly-closed system, the influx of H_2O is limited. The alteration rim of hydrous minerals that forms around grains of anhydrous phases tends to restrict the flux of water to the anhydrous assemblage. Locally, at the contact between hydrous and anhydrous phases, P_{H_2O} may be buffered close to an equilibrium value that is less than P_t. This lowering of P_{H_2O} provides the driving force for diffusion of H_2O to the site of the reaction, the interface between hydrous and anhydrous phases. Lower flux of water tends to favor a closer approach to equilibrium at the hydrous-anhydrous phase boundary.

If high permeability allows substantial water to permeate the rock, the hydration reaction continues until the anhydrous assemblage is consumed. However, in many retrograde metamorphic rocks, the hydration reactions have not gone to completion.

The equilibrium value of P_{H_2O}, whether attained on a local scale at the hydrous-anhydrous mineral contact or attained on a broader macroscopic scale, may be achieved by several mechanisms, as mentioned above. Water may be diluted by other volatile components, the fluid may become concentrated in salts, or a fluid phase may be absent and H_2O present as individual molecules or a thin film adsorbed on grain boundaries. Regardless of the nature of the H_2O present, its activity has an equilibrium value defined by the assemblage of hydrous and anhydrous minerals.

In small systems where P_{H_2O} is the equilibrium value defined by the hydrous and anhydrous mineral assemblages, lower temperatures result in lower P_{H_2O} at constant P_t. This is illustrated by the reaction curve AH in Figure 1b. Figure 1b also shows that, in the hypothetical system, AH′ is a stable assemblage at lower temperatures. At low P_{H_2O}, A can react directly to H′ by the reaction $H' = A + H_2O$ (abbreviated AH′). Thus an assemblage that is not found as a prograde metamorphic assemblage, where $P_{H_2O} \cong P_t$, can be found in stable equilibrium during retrograde metamorphism where $P_{H_2O} < P_t$. There is one more degree of freedom for systems in which $P_{H_2O} < P_t$ than for those with $P_{H_2O} = P_t$. Therefore one more phase is possible in any assemblage at equilibrium in a system having $P_{H_2O} < P_t$.

Because the water pressure may be lowered by different amounts and buffered at different values depending on the bulk composition of the system and the availability of water, we may also expect localized regions of a rock to have different mutually incompatible assemblages. The actual number of phases in a rock of hand-specimen size, for example, may be expected to be greater than the maximum number allowed by the phase rule.

Fluids in rocks undergoing retrograde metamorphism (hydration) will tend to be concentrated in dissolved components, because H_2O is removed from the fluid. This process is strictly analogous to Thompson's (1970) "experiment" in which the H_2O content of a brine is progressively decreased and the solute concentration increased as the (externally imposed) chemical potential of H_2O is decreased. In this case, the chemical potential of H_2O is lowered by mineral reactions rather than by dilution of H_2O by alcohol in an external reservoir.

Exchange reactions between mineral components and dissolved components will tend to enrich the minerals in those species that are preferentially partitioned into the fluid. For example, exchange reactions between a hydroxyl end member (X–OH) and a (hypothetical) chloride end member (X–Cl) of a binary series may be written:

$$\text{X–OH} + \text{Cl}^-(\text{aq}) = \text{X–Cl} + \text{OH}^-(\text{aq})$$

$$\text{X–OH} + \text{HCl}(\text{aq}) = \text{X–Cl} + \text{H}_2\text{O}(\text{aq})$$

Similarly, reactions may be written for isotopic exchange between a mineral and a coexisting fluid, for example:

$$\text{X–}^{18}\text{O} + \text{H}_2{}^{16}\text{O}(\text{aq}) = \text{X–}^{16}\text{O} + \text{H}_2{}^{18}\text{O}(\text{aq})$$

Because chloride and ^{16}O are preferentially enriched in the fluid, components such as these tend to become more concentrated in the fluid during hydration of the rock. The increase of these components in the fluid drives the above exchange reactions to the right and increases Cl/OH and $^{16}O/^{18}O$, for example, in the minerals.

Eventually, after much water is withdrawn, the solution may become saturated in halide and similar compounds. We might expect a sequence of salt precipitates like those found in evaporite deposits. These would probably exist as submicroscopic grains concentrated along grain boundaries.

We can assess the degree and distribution of enrichment in a rock by considering the details of the reaction. If the water available for reaction is only that which was initially trapped in pore spaces (H_2O is an "initial value component"), then alteration and enrichment will be slight. Maximum halide enrichment will occur when the amount of trapped and introduced water is just enough to completely hydrate the rock (a special case of H_2O as a "boundary value component"). If more than enough water is available (*i.e.*, where $P_{H_2O} \cong P_t$), then halides will tend to be dissolved and the altered rock will be depleted in halides. Thus halides will tend to be as poor in veins and fractures as in the unaltered rock, and will be most concentrated where there is restricted outflow of fluid and where the hydration reaction has gone only partly to completion.

Thus we can summarize the features that could be expected from hydration reactions during retrograde metamorphism:

(1) Equilibrium phase relations are limited to very small domains. Larger regions are characterized by more phases than are possible according to the phase rule.

(2) Assemblages that are not stable products of prograde metamorphism can be stable as a result of retrograde metamorphism and lowered water pressure.

(3) Minerals are enriched in halides and other species that preferentially partition into the fluid.

(4) Halides and other very soluble phases may precipitate, probably as submicroscopic grains along grain boundaries.

(5) Enrichment of a rock in halides is selective according to the amount of water locally available for hydration and the relative inflow and outflow of water. Partially-altered rock will show the greatest enrichment.

Applications to serpentinization

Although many hydrated rocks may show these features, serpentinized ultramafic rocks are particularly suitable for testing these predictions because of the large amounts of water necessary for hydration (about 13% by weight) and the relatively simple chemistry and mineralogy.

(1) A multiplicity of phases is common in serpentinized ultramafic rocks. Relict olivine and pyroxene are commonly found in the same thin section as a variety of serpentine minerals plus brucite and amphiboles. Some of the many examples of overdefined assemblages are discussed by Wicks and Whittaker (1977).

(2) Experimental studies at $P_{H_2O} = P_t$ combined with field data from progressively metamorphosed terrane have shown that the chrysotile and forsterite stability fields are separated by antigorite + brucite at geologically reasonable pressures (Evans *et al.*, 1976). Although antigorite breaks down to form olivine during prograde metamorphism (Trommsdorf and Evans, 1972), antigorite rarely replaces olivine during retrograde metamorphism. Instead, olivine commonly hydrates directly to chrysotile and/or lizardite (Wicks and Whittaker, 1977). These observations are easily explained by variations in H_2O activity.

In Figure 1, if we replace H′ by chrysotile, H by antigorite + brucite, and A by forsterite, then the curve HH′ is replaced by a curve for the reaction

$$\text{chrysotile} = \text{antigorite} + \text{brucite} \qquad (1)$$

curve AH is replaced by a curve for

$$\text{antigorite} + \text{brucite} = \text{forsterite} + H_2O \qquad (2)$$

and curve AH′ is replaced by two reaction curves

$$\text{chryostile} + \text{brucite} = \text{forsterite} + H_2O \qquad (3)$$

and

$$\text{chrysotile} = \text{forsterite} + \text{antigorite} + H_2O \qquad (4)$$

Phase relations in the Al- and Fe-free system MgO–SiO_2–H_2O are shown in Figure 2. Evans *et al.* (1976) estimate that the H_2O-conserving reaction (1) is near 300°C, and Hemley *et al.* (1977) place it at 325°C. "Invariant point" I is probably at pressures below those of normal geothermal gradients, if water pressure equals total pressure. Hemley *et al.* point out that P_{H_2O} causes the dehydration reactions to occur at lower temperatures and causes the assemblage of point I to occur at higher total pressures. On the basis of the general discussion of water pressure during hydration, we may expect that serpentinization would cause the water pressure to be buffered by reaction 2, for example (Fig. 2b). At temperatures and water pressures below point I, forsterite would be directly replaced by chrysotile and water pressure would be buffered by reaction 3 or 4.

In Al- and Fe-bearing natural serpentinites, lizardite and chlorite are important minerals in addition to those discussed above (*e.g.*, Wicks and Whittaker, 1977; Caruso and Chernosky, 1979). Although the details of lizardite phase relations are not completely understood, experimental work by Caruso and Chernosky has shown that increasing Al content of the serpentinite tends to stabilize lizardite at increasingly higher temperatures and that at low pressure lizardite may be stable above the upper thermal stability limit of antigorite. Thus forsterite + lizardite can coexist stably where $P_{H_2O} = P_t$. Therefore, whereas forsterite + chrysotile may suggest conditions where $P_{H_2O} < P_t$, the assemblage forsterite + lizardite is completely ambiguous in this regard.

The reactions of forsterite to chrysotile are metastable at pressures where they have been located experimentally (Evans *et al.*, 1976). According to Evans *et al.* and Hemley *et al.* (1977), the lower thermal stability limit for forsterite + water is at higher temperatures than the upper limit of chrysotile except at extremely low pressures. The occurrence of the assemblage forsterite + chrysotile has been explained by the difficulty of nucleating antigorite relative to chrysotile (Dungan, 1977). Although such an explanation has a reasonable basis, particularly from hydrothermal experiments, the present interpretation is a more general explanation that may have wider applicability to other mineral assemblages where nucleation kinetics are not a problem. Because the reaction of olivine to chrysotile is not necessarily metastable, the difficulty of nucleation is not necessary to

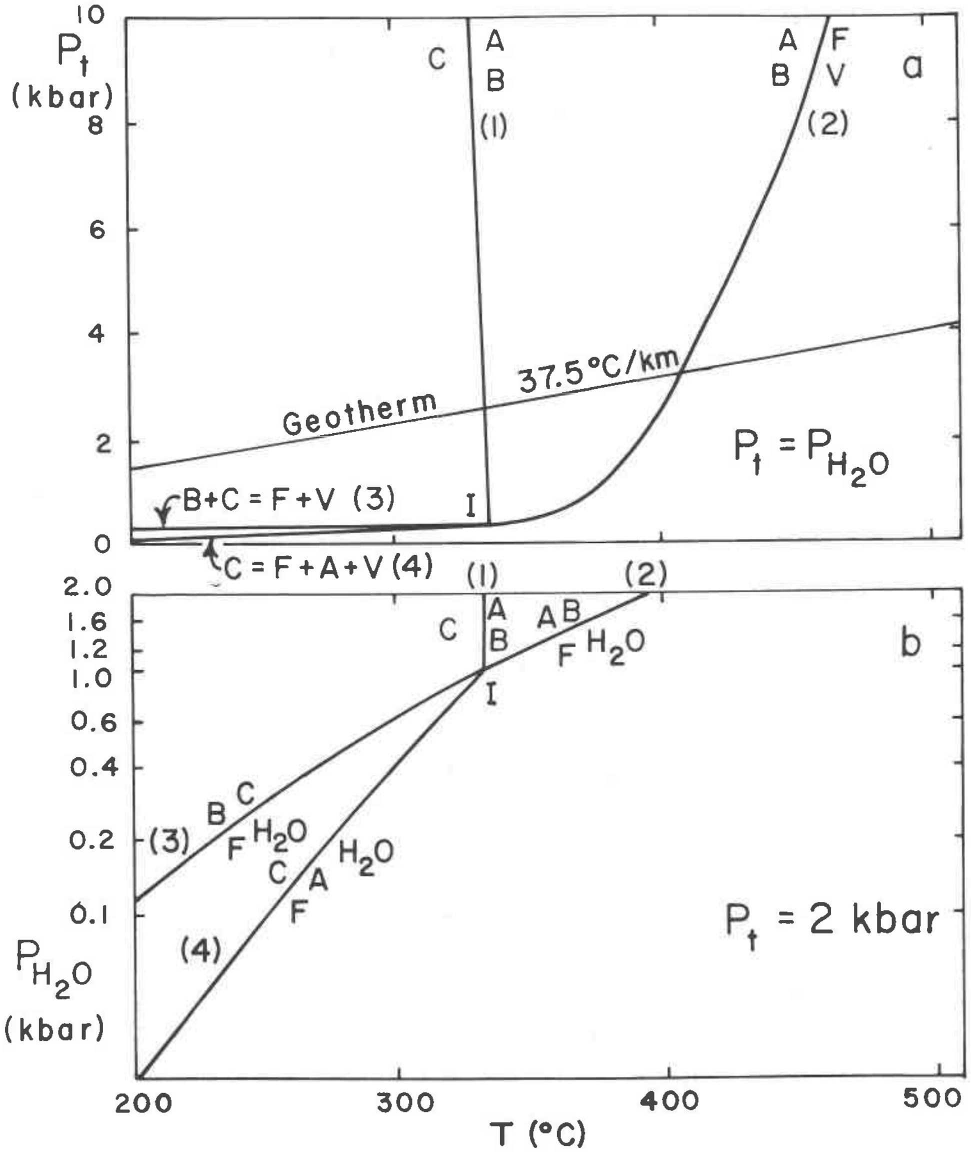

Fig. 2. Relations in the system $MgO-SiO_2-H_2O$ among the phases brucite (B), chrysotile (C), antigorite (A), forsterite (F), and vapor (V). The numbers (1) to (4) refer to reactions described in the text. (a) P_t–T relations at $P_t = P_{H_2O}$; (b) P_{H_2O}–T relations at $P_t = 2$ kbar. Numerical values are approximate. The assemblage F + C occurs at geologically unreasonable pressures (<300 bars at about 300°C) at $P_{H_2O} = P_t$, but, if $P_{H_2O} < P_t$, F + C is stable at high pressures.

account for the absence of antigorite. Even if the absence of antigorite is due to its failure to nucleate, serpentinization along the metastable extension of reaction 3, for example, would tend to lower P_{H_2O} to values below that of point I (Fig. 2b) where reaction (3) is stable.

(3) and (4): Relative to unaltered ultramafic rocks, serpentinites are commonly enriched in chlorine (Kuroda and Sandell, 1953; Early, 1958; Stueber *et al.*, 1968; Rucklidge, 1972; Rucklidge and Patterson, 1977; Wicks and Plant, 1979), in boron (Faust *et al.*, 1956; Faust, 1963; Varlakov and Zhuzhgova, 1964; Thompson and Melson, 1970; Seitz and Hart, 1973; Moody, 1976), in uranium (Seitz and Hart, 1973), and possibly in fluorine (Stueber *et al.*, 1968). Most of these authors agree that these elements were enriched during serpentinization. Points (3) and (4) will be discussed together, because whether the trace elements are in the serpentine structure or whether they are present as separate phases can be difficult to determine.

Stueber *et al.* showed that average unaltered ultramafic rocks contain a mean value of 88 ppm Cl, but similar rocks with more than 10% serpentine contain 300 ppm Cl on the average. Cl contents as high as 7000 ppm have been reported for serpentinites (Early, 1958).

Chlorine exists in serpentinites both in halide minerals and within the serpentine structure. Kohls and Rodda (1967) and Wicks and Plant (1979) found iowaite [$4Mg(OH)_2 \cdot FeCl \cdot xH_2O$], and Jambor (1975) found $NiCl_2 \cdot 6H_2O$ in serpentinized ultramafic rocks. Poty *et al.* (1972) experimentally produced $Mg_2(OH)_3Cl$. Rucklidge (1972) considered Cl to reside in the serpentine structure, but in a later paper Rucklidge and Patterson (1977) suggested that Cl occurred as an Fe analog to $Mg_2(OH)_3Cl$, $Fe_2(OH)_3Cl$. Miura *et al.* (1979 and in preparation) showed, using transmission electron microscopy, that the Cl in serpentinites studied by Rucklidge and Patterson exists within the serpentine structure. Specifically Cl resides in the very fine-grained (<10 nm) serpentine immediately adjacent to relict olivine grains, but not in the coarser-grained (50–300 nm) serpentine in veins. This fine-grained serpentine is also enriched in Fe, Ca, Ni, and Mn and contains discrete grains of awaruite ($FeNi_3$). Wicks and Plant (1979) observed that Cl was more commonly associated with retrograde serpentine varieties than with prograde types.

Several authors (Sahama, 1945; Faust *et al.*, 1956; Varlakov and Zhuzhgova, 1964; Thompson and Melson, 1970; Seitz and Hart, 1973) have noted higher B concentrations in serpentinites than in unaltered ultramafic rocks and have concluded that B is introduced during serpentinization. Typical results are those of Seitz and Hart, who observed B concentrations in relict orthopyroxene from partially altered oceanic ultramafic rocks in the range 0.4–0.7 ppm compared with values as high as 155 ppm in the adjacent serpentinite.

Uranium in unaltered relict minerals of partially altered oceanic ultramafic rocks ranges from 0.4 ppb in orthopyroxene to 7.0 ppb in olivine, whereas the altered parts of these rocks contain 0.5 to 2.4 ppm U (Seitz and Hartz, 1973), about a thousand-fold increase in concentration.

Fluorine shows greatest concentration (as much as 1550 ppm) in a few serpentinites from alpine ultramafic bodies, but most serpentinites have no more F than the unaltered ultramafic rock (<8–58 ppm) according to Stueber *et al.* (1968), who analyzed 55 ultramafic rocks from various sources.

(5) Selective enrichment of Cl in partially serpentinized ultramafic rock is well illustrated by the observations of Rucklidge and Patterson (1977) and Miura *et al.* (1979 and in preparation). Relict unaltered dunite and veins of serpentine are poor in chlorine. However, chlorine is clearly enriched in the fine-grained serpentine that immediately surrounds relict olivine grains. Similarly B is concentrated in serpentine adjacent to relict orthopyroxene grains (Seitz and Hart, 1973).

Thus all the evidence is consistent with the predictions that follow from treating water pressure as a variable independent of total pressure.

Because components that partition into the fluid are enriched in the hydrated rock, this chemical signature can be useful in determining the nature of the hydrating fluid during retrograde metamorphism. Most authors who have studied Cl in serpentinites have concluded that the hydrating fluid is sea water. Enrichment of serpentinite in B, U, and Ca, and lack of enrichment in F, is also consistent with sea-water alteration. Fe, Ni, and Mn, which are enriched in the fine-grained serpentine studied by Miura *et al.* (1979 and in preparation), could have been concentrated from sea water, but the relatively large amounts of these elements in the original rock suggests that most Fe, Ni, and Mn was merely remobilized and redistributed. Quantitative calculation of the original fluid composition is not feasible, because refluxing of the fluid tends to enrich the rock in the least soluble species and deplete it in the more soluble species, and because the retention of ions by the rock is selective according to the ability of serpentine or other phases to accomodate the ions in their crystal structures. However, the example of serpentinization shows that alteration fluids leave recognizable fingerprints of their paleocompositions.

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