Metastability in serpentine–olivine equilibria

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Abstract

Phase equilibrium considerations derived from studies of progressively metamorphosed serpentinites combined with a theoretical analysis of the system MgO–SiO_2–H_2O by Evans *et al.* (1976) indicate that antigorite is the stable phase in olivine–serpentine reactions. Corresponding serpentine–olivine equilibria in which chrysotile is the serpentine phase are metastable relative to the antigorite analogs. I suggest that this conclusion can also be applied to reactions involving lizardite and olivine.

Metastable serpentine–olivine equilibria are inferred to be the result of combinations of crystallographic, energetic, and kinetic factors that vary for different reactions. The contrasting crystal structures of the serpentine minerals probably play an important role in determining reaction paths where kinetics are unfavorable to the attainment of stable equilibrium; *e.g.*, low temperature hydration or static dehydration. The role of crystal structure is manifested in the relative ease of nucleation of the various phases. Antigorite nucleation is hampered by its complex structure whereas lizardite–olivine reactions are favored by a topotactic relationship. Chrysotile is favored by crystallization from gels and oxides in synthetic systems and in dilation veins in serpentinites.

Introduction

This study is an outgrowth of a broader structural and petrologic project on ultramafic and mafic rocks in the Sultan-Darrington area, North Cascades, Washington (Dungan, 1974). These studies reveal a complex metamorphic and structural history for the Sultan-Darrington ultramafites (Vance, 1972; Dungan and Vance, 1972). Vance and Dungan (1977) discuss the petrology of typical metaserpentines, and demonstrate that prior to final tectonic emplacement the Sultan-Darrington primary peridotites were first serpentinized and then subjected to a prograde event which reached middle amphibolite facies. A complete gradation from incipiently recrystallized lizardite–chrysotile serpentinites through antigorite serpentinites to second-generation peridotites is present. Subsequent to emplacement, the serpentinites and peridotites were intruded by Tertiary epizonal plutons which produced small contact aureoles of limited extent and distinctive petrography.

New data from Sultan-Darrington metaserpentinites presented in this paper are petrographic descriptions and mineral analyses of some unusual rocks in which metastable deserpentinization reactions occur.
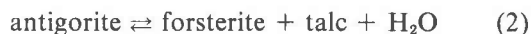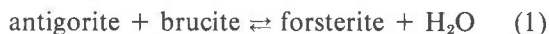
These include rocks metamorphosed in the pre-emplacement event and by Tertiary intrusions. The serpentinization of olivine and a number of experimental studies of olivine–serpentine equilibria are also discussed. The purpose of this paper is to identify some of the causes of non-equilibrium behavior in serpentinites and in relevant experimental studies.

The following section is a brief review of the basis for determining metastable and stable reactions in metaserpentinites.

Phase relations

Evans and Trommsdorff (1970) recognized that progressive metamorphism of serpentinites results in a regular sequence of mineral assemblages whose occurrence is governed by a small number of reversible dehydration reactions. This sequence begins in the prehnite–pumpelleyite facies with the incoming of antigorite as a reaction product of lizardite and chrysotile. Although the reaction to antigorite tends to be sluggish, lizardite and chrysotile are both recrystallized to antigorite prior to the appearance of new-formed olivine under equilibrium conditions. Antigorite continues to be the serpentine phase which

participates in dehydration reactions up to the middle amphibolite facies:

$$\text{antigorite} + \text{brucite} \rightleftharpoons \text{forsterite} + H_2O \quad (1)$$

$$\text{antigorite} \rightleftharpoons \text{forsterite} + \text{talc} + H_2O \quad (2)$$

Under equilibrium conditions, serpentinization reactions should be the retrograde equivalents of the dehydration reactions. In fact, there is a lack of correspondence between the serpentine mineralogy of the retrogressive pseudomorph-forming reactions and the reactions operative in progressively metamorphosed serpentinites. Trommsdorff and Evans (1972) suggest that several serpentine reactions (and experimentally-determined equilibria) in which chrysotile is the serpentine phase are metastable with respect to the stable antigorite analogs. An expanded theoretical analysis of this premise in Evans *et al.* (1976) follows in part from the petrographic observation that the reaction

$$\text{chrysotile} \rightleftharpoons \text{antigorite} + \text{brucite} \quad (3)$$

is apparently a reversible equilibria in natural serpentinites. The basis for the theoretical approach presented in Evans *et al.* (1976) is the $Mg(OH)_2$ deficiency[1] in the structural formula of antigorite as compared to the "ideal" serpentine(s) chrysotile (and lizardite). As a result of this chemography, vapor-absent reaction (3) defines the upper stability limit of chrysotile with respect to antigorite.

According to Wicks and Whittaker (1975), the various structural types within flat-layer serpentines and cylindrical serpentines can be regarded as polytypes of lizardite and chrysotile respectively. They cite the apparently overlapping compositions and equivalent structural formulae as criteria for regarding lizardite and chrysotile as polymorphs. However, the mutual phase relations remain obscure because these two minerals typically occur together in serpentinites, and they have been produced simultaneously in some experimental studies (Chernosky, 1975; Moody, 1976b). Chernosky (1971) has pointed out that the two-phase assemblage is metastable (except at the transition temperature) if the coexisting phases have identical compositions and are indeed true polymorphs (*i.e.,* the reaction boundary is characterized by a polymorphic transition). Alternatively, preferential partitioning of Al into lizardite with a resultant compositional gap between the phases would pre-

clude a polymorphic transition for aluminous bulk compositions.

The aspect of the occurrence of lizardite + chrysotile which is critical to the present study is that both phases react to antigorite at metamorphic grades below those at which reaction (1) takes place. Therefore, the lizardite analog of reaction (3) defines the upper stability limit of Al-poor lizardite, although it is not known if this is a reversible reaction. Lizardite and chrysotile in shear planes that cut antigorite–olivine metaserpentinites in the Sultan Complex, and similar occurrences elsewhere (Coleman, 1971; Mumpton and Thompson, 1975) imply real, if poorly understood, stability fields for both phases at low temperatures. However, only direct replacement of antigorite, reported for chrysotile by Evans *et al.* (1976), constitutes evidence for reversibility of the type (3) reaction. For the purpose of discussion, dehydration–hydration reactions in which low-Al lizardite is a (the) serpentine phase are treated as metastable due to the observed breakdown of this phase to antigorite prior to the first appearance of olivine by reaction (1). However, it should be emphasized that lizardite phase relations are by no means well-defined.

The serpentinization of olivine and the formation of mesh pseudomorphs

In contrast to the granoblastic-polygonal or lepidoblastic textures characteristic of olivine–antigorite assemblages, the textural relationship between olivine and mesh serpentine is indicative of retrogressive replacement. The initial step in the formation of the pseudomorphs is the growth of cross-fiber veinlets (mesh rims) along the orthogonal parting of the olivine. Where serpentinization continues beyond the rim stage, the remaining isolated grains of olivine are replaced by roughly equant mesh centers. Wicks and Zussman (1975) have shown that the predominant serpentine phase in mesh pseudomorphs is lizardite; where chrysotile is present, it occurs in subordinate amounts.

Temperatures for serpentinization derived from oxygen and hydrogen isotope studies (Wenner and Taylor, 1971, 1973, 1974) suggest that the alteration of olivine may be accomplished by meteoric waters at 85–115°C. The composition of spring waters issuing from serpentinites confirms the viability of near-surface, low-temperature serpentinization (Barnes and O'Neil, 1969), as does a study by Campbell (1975). Thus, serpentinization appears to occur at temperatures below the stability field of forsterite + H_2O so

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[1] The extent of departure of the antigorite formula from $Mg_6Si_4O_{10}|OH|_8$ is inversely proportional to the α-axis dimension, as the anomalous bridge structure is repeated along this axis.

that it is strictly retrogressive. Retrogressive antigorite is not common, and it has not been observed to form pseudomorphs after olivine. At one locality in the northern Sultan Complex the assemblage antigorite + brucite occurs in veins and shear zones (generally annealed) cutting peridotites formed by deserpentinization. This retrogressive antigorite is interpreted as an example of serpentinization of olivine near the reaction boundary of (1), suggesting that it is indeed a reversible reaction.

Simkin and Smith (1970) recognized that MnO and NiO in olivine correlate very strongly with Mg/(Mg + Fe); manganese decreasing with increasing Mg and nickel increasing. These linear trends are present in olivines from fresh and partly serpentinized peridotites (Dungan, 1974; Dungan, unpublished data). In contrast, the compositions of olivines formed by deserpentinization exhibit marked deviations from the compositions of primary olivines in terms of Mg/(Mg + Fe) as well as MnO and NiO. Metamorphic olivine in incipiently dehydrated serpentinites is enriched in MnO (by as much as an order of magnitude) and depleted in NiO relative to olivine in primary peridotites (Vance and Dungan, 1977). These olivines may also be more magnesian (Fo_{98-95}) than is characteristic of primary olivines. The lack of change in primary olivine composition in response to serpentinization indicates chemical exchange equilibrium is not attained. These compositional characteristics imply that in serpentinization, the reaction is a boundary phenomenon in which the olivine plays an essentially passive role, the serpentine growing at its expense.

Metastable deserpentinization

Several examples of unusual metamorphosed serpentinites from the Sultan-Darrington ultramafites contain olivine which has formed directly from one or both of the low-temperature serpentines. Sample 71-104 was collected from a (25 × 10 m) tectonic sliver of serpentinite which occurs approximately 30 m from the contact of a small (50 × 50 m) posttectonic granodiorite pluton. Although there is no mesoscopic indication of recrystallization of the serpentinite, the dehydration reaction in 71-104 is apparently the result of thermal metamorphism induced by this pluton, as effects of the pre-emplacement metamorphic event are absent from the rocks of the southern Sultan Complex. The thin section studied is of a serpentinite derived from an olivine-rich wehrlite parent, in which the boundaries of the original olivine and clinopyroxene grains are clearly outlined by magnetite segregations. The mesh pseudomorphs are dominated by the vein component (var. ribbon mesh after Francis, 1956). Microscopic brucite is intergrown with the mesh serpentine as small veinlets, but antigorite was not recognized in thin section or in X-ray diffraction patterns of serpentine mineral separates.

Although the mesh serpentine (see Table 1 for composition) has not been recrystallized, it is 30–70 percent replaced by small prismatic olivine grains (Fig. 1a, b). As seen in thin section, individual pseudomorphs include up to 100 olivine grains which exhibit dimensional parallelism and nearly simultaneous extinction, indicating that all these olivine grains share a single optic orientation. Nonetheless, they appear to be discrete gains rather than the two-dimensional expression of larger skeletal olivines. Olivine grains within adjoining pseudomorphs are characterized by a different aggregate orientation. Although the olivine has replaced all textural components of the mesh serpentine, nucleation appears to be favored at vein margins; magnetite grains also act as nucleation sites. Bastite serpentine in this sample lacks olivine. This may be due to its more aluminous composition or the absence of intergrown brucite. The chemical composition of olivine in 71-104 is distinct from any possible primary olivine in terms of both major and minor elements (Table 1). Vance and Dungan (1977) have shown that the combination of low iron and NiO-contents and the high MnO which characterizes the 71-104 olivines is indicative of olivine compositions formed by deserpentinization.

Sample 04-124 is a largely serpentinized cumulus peridotite consisting of alternating pyroxene-rich and olivine-rich layers. It was collected from a small tectonic slice in the northwestern Sultan Complex. Detailed study of the petrography of samples from this body has shown that the effects of the pre-emplacement metamorphism are only sporadically present, and fully recrystallized rocks containing equilibrium mineral assemblages are absent. Antigorite is present in many partially serpentinized wehrlites as veinlets or as a partial replacement product of mesh serpentine. In sample 04-124 the clinopyroxene is partially serpentinized, the olivine and orthopyroxene have been totally replaced by serpentine, and the mesh serpentine has in turn been in part replaced by newformed olivine (Fig. 1c). These metamorphic olivines crosscut mesh structures, and are texturally distinct from relict olivine grains in that they are concentrated in the vein component of the mesh rather than the centers and typically exhibit highly irregular,

Table 1. New-formed olivines and coexisting serpentines

Sample	71-104	Mesh 71-104	Bast. 71-104	04-124	71-62	Matrix 1414	Vein 1414	Antig. 1414	Chry. 1414
SiO_2	41.7	42.4	40.7	40.8	41.7	41.4	41.4	43.9	42.6
Al_2O_3	n.d.	0.44	2.3	n.d.	n.d.	n.d.	n.d.	0.92	2.6
Cr_2O_3	n.d.	0.01	0.51	n.d.	n.d.	n.d.	n.d.	0.00	0.02
FeO	2.1	3.0	2.6	5.1	2.5	6.7	6.4	2.5	2.2
MnO	0.50	0.04	0.02	1.05	0.09	0.23	0.24	0.02	0.05
MgO	54.6	41.0	40.0	51.7	54.9	51.3	51.6	40.4	39.6
CaO	0.0	n.d.	n.d.	0.05	0.04	0.00	0.00	n.d.	n.d.
NiO	0.04	0.03	0.02	0.05	0.02	0.35	0.36	0.20	0.18
Total	98.9	86.9	86.7	98.8	99.3	100.0	100.0	87.9	87.3

Cations*

Si	0.998	3.979	3.840	0.996	0.996	1.003	1.002	3.937	3.958
Al	-	0.049	0.257	-	-	-	-	0.097	0.279
Cr	-	0.001	0.038	-	-	-	-	-	0.001
Fe	0.042	0.232	0.207	0.104	0.050	0.136	0.129	0.190	0.172
Mn	0.010	0.003	0.002	0.022	0.002	0.005	0.005	0.002	0.004
Mg	1.949	5.731	5.667	1.881	1.955	1.852	1.862	5.399	5.473
Ca	-	-	-	0.001	0.001	-	-	-	-
Ni	0.001	0.002	0.002	0.001	0.000	0.006	0.006	0.014	0.013
Total	3.000	9.997	10.013	3.005	3.008	3.003	3.004	9.639	9.900
Mg/(Mg+Fe)	97.9	96.1	96.5	94.8	97.5	93.1	93.5	96.6	97.0

*Olivines calculated on the basis of 4.0 oxygens, 1414 antigorite on the basis of 13.026 oxygens and remaining serpentines on 14.000.

n.d. = not analysed.

branching shapes. As in 71-104, new-formed olivine is lacking in bastites. They are similar to the 71-104 olivines in that they follow the compositional pattern of low FeO and anomalously high MnO (Table 1). Mesh and bastite serpentines in 04-124 also exhibit compositional characteristics similar to those in 71-104 (*i.e.*, mesh = 0.75 percent Al_2O_3, 0.12 percent Cr_2O_3 *vs.* bastite = 0.6 to 1.0 Al_2O_3, 0.2–0.8 percent Cr_2O_3). In addition, all the olivine grains which occur within an individual mesh pseudomorph share the same optic orientation, whereas those in adjacent pseudomorphs are oriented differently. However, this sample contrasts with 71-104 in that fine-grained antigorite is present as rims around the new-formed olivines, which complicates interpretation of the paragenetic relationships in this sample relative to 71-104.

Tectonic slices of ultramafic rock in the northern Sultan Complex exhibit progressively higher degrees of recrystallization and grade of metamorphism to the east. Metaserpentinites in the northern Sultan Complex (all metamorphosed prior to middle or early Tertiary emplacement) include antigorite serpentinites, partially deserpentinized olivine–antigorite rocks, and fully dehydrated metamorphic peridotites. The Darrington peridotites, farther to the east, record the highest grade of metamorphism. They are generally completely deserpentinized and are characterized by the assemblage forsterite–talc–tremolite. Some high-grade metaserpentinites in both the Sultan and Darrington units exhibit textures which may indicate that the early stages of deserpentinization may have resulted in olivine forming directly from mesh serpentine as in 04-124. In contrast to many of the Sultan-Darrington metaserpentinites, in which deserpentinization and recrys-

Fig. 1. Three examples of new-formed olivine from Sultan-Darrington metaserpentinites. All microphotographs taken with partially crossed polars.

a. *Sample 71-104*. Cross-fiber veins of mesh serpentine oriented vertically, roughly parallel to magnetite segregations, are partially replaced by prismatic grains of new-formed olivine oriented normal to vein direction (parallel to fiber direction of the veins).

b. *Sample 71-104*. Prismatic olivine grains replacing vein and mesh center components.

c. *Sample 04-124*. New-formed olivine and antigorite have partially replaced mesh serpentine. Unrecrystallized mesh serpentine in lower left-center; olivine is light colored, and antigorite forms a fine-grained fibrous mat around the olivine. Note the unusual rectangular grain of olivine in right center which surrounds an unrecrystallized mesh center.

d. *Sample 1414*. Bifurcated chrysotile–olivine veinlet in antigorite–olivine–magnetite matrix. Linear segregation of magnetite in lower center is refracted at vein margin by dilation so that it is offset normal to the growth direction of the chrysotile–olivine assemblage.

e. *Sample 1414*. Bifurcation in chrysotile–olivine veinlet. Note curvature in olivine grains caused by rotation during growth. Olivine curvature is parallel to chrysotile fibers.

f. *Sample 1414*. Detail of olivine grains at margin of veinlet. The grain on the left is a rare example of olivine nucleation on a preexisting matrix olivine grain.

tallization were synkinematic, relict textures such as relict unrecrystallized lizardite bastites in association with antigorite plus new-formed olivine (see composition of 71-62 in Table 1) provide strong evidence for static metamorphism (Vance and Dungan, 1977). The metamorphic olivine in these statically metamorphosed rocks occurs as large mosaic grains comprised of many small individuals which have nearly the same optic orientation (Fig. 2a, b). In some examples the boundaries of these composite grains coincide with magnetite segregations marking relict mesh pseudomorph outlines as well as the boundaries of the relict bastites. Thus, they appear to be higher grade equivalents of metaserpentinites (*e.g.,* 04-124 or 71-104) in which new-formed olivine grew directly from lizardite in mesh serpentine rather than from antigorite + brucite (reaction 1).

Sample 1414 is an antigorite–forsterite metaserpentinite from the Darrington peridotite that is petrographically distinct from the samples discussed above. It consists primarily of a fine-grained aggregate of antigorite intimately intergrown with smaller needles of new-formed olivine (0.05–0.1 mm in length). The features of interest are several subparallel veinlets (1–0.5 mm in width) consisting of intergrowths of chrysotile fibers and olivine (identification of chrysotile was made by SEM). The olivine occurs as tablets and needles oriented normal to the margins of the veins. The long-dimensional axes of

the olivines are oriented parallel to the chrysotile fiber direction, and where the olivine occurs as small needles, the two phases are intimately intergrown. This textural relationship is the result of the simultaneous growth of the two phases at the time of formation of the veins. Although olivine has nucleated on preexisting matrix olivine grains where the vein margins transect them (Fig. 1f), the scarcity of olivine in the matrix antigorite indicates that most of the olivine in the veins did not form in this manner. Linear segregations of magnetite which intersect the veins at oblique angles are offset parallel to the chrysotile fiber direction (Fig. 1d), indicating that the veins formed by dilation rather than *in situ* replacement of the preexisting antigorite–olivine host. Microprobe analyses (Table 1) of serpentine–olivine pairs in the antigorite matrix and in the veins show that the olivines have similar $Mg/(Mg + Fe)$, as do the two serpentines. This relationship suggests that both olivine–serpentine pairs achieved at least an approach to Mg–Fe exchange equilibrium under similar conditions.

The olivine in the three metaserpentinites described above is interpreted to have formed by metastable deserpentinization reactions within the stability field of antigorite or antigorite + forsterite. Differences in serpentine mineralogy among the samples indicate that the olivine formed via various reaction paths. In sample 71-104 the reaction is
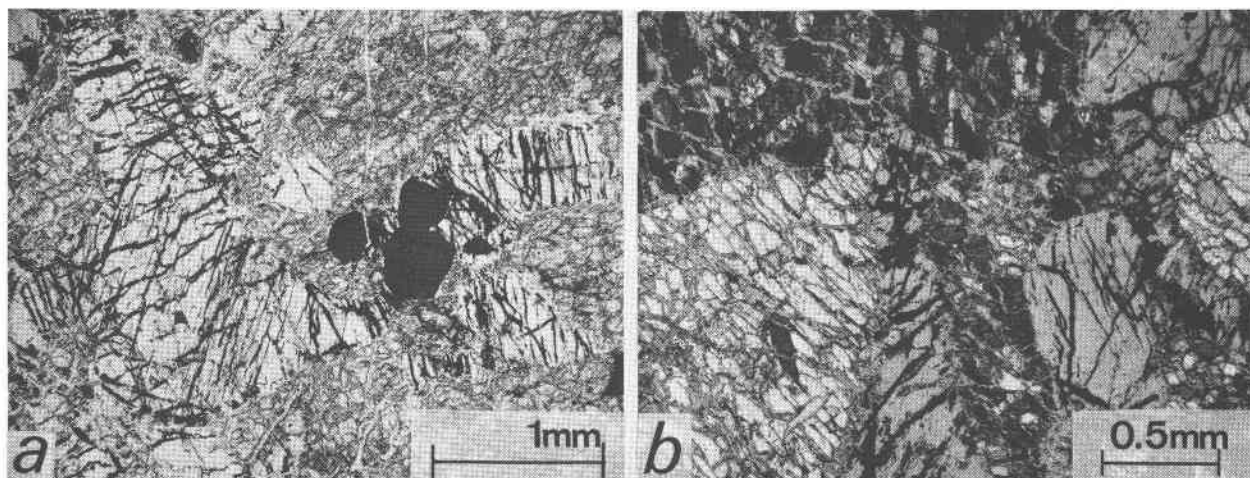

Fig. 2a. *Sample 71-62.* Relict lizardite bastites in a new-formed peridotite. Bastites include magnetite segregations parallel to pyroxene cleavage. Note relict chromite grains in right center of photograph. Matrix consists of granular olivine (Fo_{97}) plus minor antigorite and back-reaction serpentine. Plane polarized light.

b. *Sample 71-62.* Detail under partially crossed nicols showing mosaic of olivine grains which have replaced individual mesh pseudomorphs. All the small grains within the boundaries of single mesh pseudomorph have nearly the same optic orientation. Grains at upper left at extinction contrast with grains in lower left and center right. Note the sharp boundaries between serpentine in bastites and the new-formed olivine.

lizardite ($\pm$ chrysotile) + brucite

$$\rightleftharpoons \text{forsterite} + H_2O.$$

Sample 04-124 lacks brucite, but antigorite is present. Olivine may have formed as in 71-104 until brucite in the rock was exhausted, with the antigorite forming independently from lizardite and/or chrysotile. Alternatively, olivine formation may have proceeded by the lower-temperature metastable reaction

lizardite or chrysotile $\rightleftharpoons$ antigorite

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

The close association of the antigorite with the new-formed olivine suggests that (4) was operative.

The reaction which produced the vein assemblage in 1414 is impossible to discern because the vein did not form by direct replacement of a preexisting assemblage. Textural relationships are equivocal, although the mineral compositions suggest that the veins formed at the same temperature as the antigorite–olivine matrix.

Stability and metastability in experimental studies of serpentine phase relations

Johannes (1975; see also in Evans *et al.,* 1976) has produced experimental brackets for (2) at water pressures from 2 to 15 kbar. This study is the first experimental reversal of an antigorite-dehydration reaction. As noted in Evans *et al.* (1976), the temperatures at which reversals were determined are compatible with temperatures for this reaction inferred from field-petrologic studies (Trommsdorff and Evans, 1972). In previous experimental studies, antigorite was not synthesized because serpentine mineralogy is strongly dependent on the nature of the starting materials. Salient points of previous experimental studies are briefly summarized below.

(1) Most early experimenters employed mixtures of oxides or gels as starting materials with the result that chrysotile was formed rapidly and generally to the exclusion of other phases (Bowen and Tuttle, 1949; and others). Due to the apparently fast reaction rates, short run-times were considered adequate for attainment of equilibrium.

(2) Johannes (1968) employed crystalline starting materials (serpentine phase = synthetic chrysotile) and discovered that the previous attempts to bracket reaction boundaries were hampered by disequilibrium crystallization of chrysotile in the stability fields of forsterite + H_2O. These synthesis experiments resulted in estimations of reaction temperatures which

were 50–100°C too high (see Fig. 2 of Moody, 1976a). Similar results were obtained by Scarfe and Wyllie (1967) and Chernosky (1973) for the reaction chr = fo + ta + H_2O. Chrysotile was the synthetic serpentine phase present in the reactants and products of experiments conducted by Johannes and Chernosky as well as Scarfe and Wyllie.

(3) Dietrich and Peters (1971) attempted to define the phase relationships between chrysotile and antigorite, using natural serpentines as starting materials. Despite extremely long run times (up to 270 days), no change occurred in the proportions of the minerals after hydrothermal treatment at temperatures below 490°C. At higher temperatures and with run times $\geq$60 days, chrysotile disappeared, and forsterite and talc appeared. Antigorite may have grown at the expense of chrysotile, but it was only present in the products of runs in which it was also included in the starting mix. Thus, there is no direct confirmation that antigorite formed from chrysotile, even though experiments were conducted within the stability field of antigorite.

(4) Syntheses of antigorite by Iishi and Saito (1973) were achieved by using starting gels which were deficient in MgO and H_2O relative to $Mg_6Si_4O_{10}(OH)_8$. Experiments were conducted within the stability field of antigorite (300–500°C). Antigorite was formed in subordinate amounts relative to chrysotile, its abundance increasing with increasing degree of MgO and H_2O deficiency and increasing P and T. Apparently antigorite grew from the $Mg(OH)_2$-deficient residuum which remained after MgO, SiO_2, and H_2O had been exhausted in the proportions necessary for the stoichiometry of ideal serpentine by the formation of abundant chrysotile ($\pm$minor lizardite).

(5) Moody (1976b) performed olivine-hydration experiments in which natural and synthetic olivines plus H_2O were reacted under conditions of buffered oxygen fugacity (iron–magnetite at 300–400°C and 0.5–2.0 kbar). These runs resulted in the formation of lizardite + brucite + magnetite by direct replacement of olivine. Examination of the run products by scanning electron microscope showed that with increased run times chrysotile fibers replaced lizardite platelets. Synthetic olivine plus serpentine and brucite formed by the hydration of olivine were used as reactants in attempts to reverse the reaction, with the result that olivine grew from the hydrated phases.

(6) The occurrence of lizardite in natural and synthetic systems may also be in part dependent on composition. Roy and Roy (1955), Gillery (1959),

and Chernosky (1975) have synthesized chrysotile–lizardite mixtures in the system MgO–Al_2O_3–SiO_2–H_2O, and noted the tendency for increased Al-content to favor formation of greater proportions of lizardite. The crystallographic rationale for this behavior was first recognized by Radoslovich (1963), who suggested that substitution of Al in lizardite reduced the mismatch in size between the octahedral and tetrahedral sheets, thereby reducing intralattice strain and enhancing lizardite stability (see also Chernosky, 1975 and Wicks and Whittaker, 1975). The tendency for greater thermal stability in Al-lizardite is expressed by the persistence of aluminous lizardite bastites in metaserpentinites of the Sultan-Darrington area (*e.g.*, Fig. 2a, b). The restriction of these relict bastites to statically recrystallized metaserpentinites suggests that this mode of occurrence could reflect metastable persistence. However, the role of compositional effects on serpentine phase relations is a subject which requires study, as it may be one of several critical factors which determine their mutual stability fields.

Discussion

Given the assumption that reactions (1) and (2) are stable equilibria and that the analogous reactions in which the serpentine phase is lizardite or chrysotile are metastable, causes for the metastability have been examined for both natural and synthetic occurrences. Four modes of occurrence are discussed: (1) persistence of lizardite and chrysotile into the stability field of antigorite in progressively metamorphosed serpentinites; (2) formation of the low-temperature phases in experimental studies within the antigorite stability field; (3) the hydration of olivine to form mesh pseudomorphs; and (4) the dehydration of lizardite and chrysotile to form olivine. The widespread metastability associated with serpentine equilibria is inferred to be at least in part the result of a combination of crystallographic, energetic, and kinetic factors.

Although antigorite appears in metaserpentinites at low metamorphic grade, lizardite and chrysotile commonly persist as metastable relics to much higher metamorphic grade than the first appearance of antigorite (upper prehnite–pumpelleyite facies or lowest greenschist facies). Evans *et al.* (1976) suggest that this sluggishness is largely attributable to the small ΔS associated with the water-absent antigorite-forming reactions.

The low ΔS inherent in the antigorite-forming reaction apparently promotes thermal overstepping in

experimental studies as well. Here the short run times and lack of strain energy allow chrysotile or lizardite dehydration reactions to proceed by virtue of the relatively large ΔS associated with the liberation of H_2O-vapor. The study of Dietrich and Peters (1971) in which antigorite failed to form from a chrysotile-only starting mixture, despite relatively long run times (>60 days), illustrates the problem of forming antigorite from another serpentine phase.

The thermal regime associated with the formation of olivine in sample 71-104 is a natural analog of the experimental studies which record serpentine dehydration without antigorite-formation. In this serpentinite, olivine was formed by purely thermal metamorphism induced by a small pluton, which would be unable to maintain high temperatures in its aureole for a prolonged period. The relatively rapid rise in temperature produced by an igneous intrusion into cold country rocks more nearly simulates raising the temperature of an experimental charge several hundred degrees from room temperature than does the thermal regime associated with regional metamorphism. Apparently the serpentinite at this locality was heated so rapidly above the temperature required for the reaction lizardite ($\pm$ chrysotile) + brucite $\leftrightarrows$ forsterite + H_2O that the dehydration reaction occurred before antigorite was able to nucleate and grow.

Thermal overstepping of reaction boundaries occurs in all metamorphic equilibria because the activation energy associated with the nucleation of the new phase(s) must be overcome before crystallization can commence. Consequently the magnitude of the activation energy is important in low ΔS reactions in which one serpentine phase forms from another. In the case of the less kinetically favorable retrograde reactions, its importance may be even greater. I propose that the relative ease of nucleation of the various serpentine phases plays a very important role in producing metastability in serpentine–olivine equilibria. The effect is pronounced because the complex crystal structure of antigorite acts as a nucleation barrier (*i.e.*, large activation energy), while the topotactic nature of intergrowths between chrysotile and olivine and especially lizardite and olivine result in a lower activation energy and greater relative ease of nucleation.

The distinctive antigorite crystal structure is characterized by (1) an unusually long *a* dimension (20-120A) and (2) a curved "alternating half-wave" structure (Kunze, 1961). The half-waves are joined at an inflection point by a unique bridge structure which is the cause of $Mg(OH)_2$ deficiency in antigorite. The

tetrahedral sheets on either side of the inflection have opposite polarity. Kunze (1961) recognized that the bridge structure represents a barrier to the nucleation of antigorite, because the nuclei must consist specifically of the unique bridge structure from which the half-waves spontaneously radiate outward. Nuclei in which a single tetrahedral polarity occurred would be forced to propagate as a stoichiometric serpentine, either as a cylindrical (chrysotile) or as a flat-layer structure (lizardite).

Olivine-hydration experiments by Moody (1976b) demonstrate preferential replacement by lizardite. This tendency is also characteristic of mesh pseudomorphs. Although mesh pseudomorphs are multiphase assemblages (lizardite ± chrysotile ± brucite ± magnetite) and are texturally composite as well, their coherent pattern of extinction suggests that some preferred orientation is inherited by the serpentine from olivine. Wicks (1969) determined that intergrown lizardite and brucite in a mesh serpentine veinlet were mutually oriented with the lizardite (001) parallel to the brucite basal plane. He inferred that this correspondence was controlled by the nature of the olivine replacement mechanism; i.e., the reaction was topotactic. The hydration of olivine in basalts (iddingsitization) results in pseudomorphs composed of sheet silicates and iron oxides. Brown and Stephen (1959) and others have shown that olivine exerts a topotactic control over the replacement products.

Raleigh and Paterson (1965) performed non-equilibrium dehydration experiments on natural serpentinites. Under certain run conditions, several of the lizardite–chrysotile serpentinites contained fine-grained new-formed olivine produced by deserpentinization of mesh pseudomorphs. This olivine is more magnesian[2] than the olivine ($\approx Fo_{90}$) which characterizes the parent sample, and the elongate grains within an individual pseudomorph share a single optic orientation. A significant point is that where relict olivine is present in the serpentinites, the new-formed olivines are in optical continuity with the adjacent preexisting grains. Thus, secondary olivine formed from serpentine duplicates the orientation of the primary olivine from which the serpentine formed. These textural relationships imply that there is a

single preferred structural correspondence between olivine and serpentine and/or intergrown brucite. The textures and olivine compositions produced by Raleigh and Paterson bear a striking resemblance to the new-formed olivine in 71-104 and to a lesser extent 04-124. Although there is no relict olivine in the latter samples with which to compare optic orientations, the origin of the preferred orientations of olivines in the deserpentinized rocks is here inferred to be inherited from preexisting serpentine by virtue of some topotaxial intergrowth. A possibly important implication of Raleigh and Paterson's experimental results, exemplified by the olivine–serpentine relationships exhibited in 71-104, 04-124 and 71-62, is that peridotites formed by deserpentinization could be characterized by topotactically induced preferred olivine orientations identical to those present in the parental peridotites. Miers (1970) has measured fabric orientations in some statically deserpentinized Darrington peridotites which are similar to those observed in syntectonically recrystallized primary peridotites.

Experimental dehydration studies of serpentines by Aruja (1943) and Hey and Bannister (1948) demonstrated that the resultant forsterite was oriented with respect to the serpentine. Brindley and Zussman (1957) and Ball and Taylor (1963) performed additional experiments in order to better define the nature of the topotaxy and to model the reaction mechanism. While this work provides support for the topotactic nature of the olivine–serpentine reactions, the experimental techniques indicate that their results should be extrapolated with reservation to natural and synthetic equilibria. The starting mixtures for these experiments were serpentine powders or in a few cases bundles of chrysotile fibers. Brucite was not included.

Brindley and Zussman (1957) examined the thermal decomposition of chrysotile, 6-layer serpentine, lizardite, and antigorite in air at one-atmosphere in the temperature range 500–800°C. Talc was not produced in any experiments. X-ray determinations of the mutual intergrowths indicated that all serpentine phases yielded the same rather strong preferred olivine orientation with respect to the parent serpentine, except for chrysotile, which showed a second weakly developed orientation as well. The results of these X-ray measurements are as follows: $(010)_f$ and $(013)_f$ parallel to $(100)_s$, $(001)_f$ and $(011)_f$ parallel to $(010)_s$, and by implication $(100)_f$ is parallel to c_s.

Brindley (1963) noted that the replacement relationship for the orthoserpentine lizardite could be

[2] Raleigh and Paterson determined olivine compositions by the X-ray method of Hotz and Jackson (1963). They recorded compositions of Fo_{96} and Fo_{102}, the latter obviously in error. They suggest that the anomalous compositions result in part from substitutions of additional cations not present in large quantities in the olivines used to calibrate the curves. Microprobe analyses of new-formed olivines suggest that the extraneous cation is probably Mn.

recast in the following notation in terms of crystal-lographic axes and unit-cell parameters

$$b_{fo} \; // \; a_{liz} \qquad b_{fo}(10.2A) = 2a_{liz}(10.6A)$$

$$c_{fo} \; // \; b_{liz} \qquad 3c_{fo}(18.0A) = 2b_{liz}(18.4A)$$

$$a_{fo} \; // \; c_{liz} \qquad 3a_{fo}(14.4A) = c_{liz}(14.6A)$$

As Brindley (1963) and Wicks (1969) have noted, this type of replacement in which unit-cell dimensions are inherited implies that the close-packed oxygen framework of the parent phase remains relatively undisturbed and cations are free to migrate. Indeed, if forsterite were to replace lizardite as prescribed by this volume relationship, substantial addition of magnesium from an external source would be required.

Ball and Taylor (1963) performed dehydration experiments on chrysotile fibers under hydrothermal conditions (400–830°C and 0–1.4 kbar P_{H_2O}). Above 500°C forsterite was formed with a strong preferred orientation, and the talc produced in some runs likewise exhibited a strong orientation with respect to the serpentine. Several orientations for olivine which apparently were dependent on the presence or absence of H_2O and the specific P,T conditions were found, although several runs contained mixtures of several orientations. A tendency for a decrease in the strength of the preferred orientation was recorded in hydrothermal runs with $P_{H_2O} > 0.6$ kbar, suggesting a decreasingly important role for oriented nucleation as reaction rates increase with increasing pressure. In all types of preferred orientations between chrysotile and olivine, the forsterite a-axis was normal to (001) of chrysotile. This indicates that the planes of close-packed oxygens within the mutually intergrown phases are parallel. Ball and Taylor (1963) also reproduced the lizardite–olivine relationship recognized by Brindley and Zussman (1957) under hydrothermal conditions (520°C and 0.5 kbar). Brindley and Ali (1950) found a similar relationship between chlorite and olivine.

Martin and Fyfe (1970) attempted to evaluate the kinetics of forsterite hydration by means of experimental reaction-rate studies, using synthetic and natural olivines as starting materials. The identity of the serpentine mineral was not established, but the results of Moody (1976b) suggest that it was lizardite. Initially, very fast reaction rates were recorded. This was interpreted as evidence for a heterogeneous reaction characterized by a small activation energy. Topotaxy between serpentine and brucite was suggested as the factor promoting serpentine nucleation but

topotaxy among all three phases appears equally possible. After a portion of the olivine was hydrated to serpentine + brucite the reaction rates decreased, indicating that the diffusion rate of H_2O to the reaction interface may have become the rate-controlling step.

Processes relating to diffusion and nucleation may operate differently in powder aggregates versus rocks, due to the greater pore space and surface area present in the former. Consequently, where reaction kinetics are a function of diffusion and nucleation, and nucleation and growth rates are strongly dependent on the character of topotaxial intergrowths, comparisons between experimental studies and natural rock systems such as those made in this paper are somewhat tenuous. Additional degrees of complexity not considered in detail in this paper (or in some experimental studies cited above) are the roles of other phases such as brucite, talc, and magnetite in promoting oriented transformations in specific reactions. Although experimental results corroborate the petrographic interpretation that some of the reactions regarded as metastable proceed as oriented transformations, more data are needed concerning the mutual orientation relationships among the constituent phases in natural and synthetic serpentine–olivine equilibria. Topotaxy and the ease of nucleation inherent in this type of reaction is inferred to be an important factor in determining the mineralogy of serpentine–olivine equilibria under conditions in which activation energy becomes a proportionally significant amount of the energy budget.

As was noted above, the mesh-forming process can take place at temperatures as low as 25–115°C. Under these conditions, nucleation effects may play an important role in the replacement mechanism. The experiments conducted by Martin and Fyfe (1970) may provide insight into the consistent two-stage development of the mesh texture. In the incipient stages of serpentinization, fluids find easy access to reaction surfaces on olivine along its parting surfaces, and the orthogonal pattern of cross-fiber veinlets is formed. When the fractures are sealed by serpentine (± brucite) the reaction rate (and possibly the mechanism of nucleation and/or growth) changes, as diffusion of H_2O to the reaction interface is impeded by the veins. This second stage coincides with the formation of the mesh centers. In the reverse case, where olivine forms by deserpentinization of mesh pseudomorphs (*e.g.*, 71-104), nucleation of olivine is probably enhanced by topotactic relationships between the olivine and phases of the pseudomorph. A similar mechanism

may account for reversals of metastable equilibria in analogous experimental systems.

The chrysotile–olivine assemblage in the 1414 veins contrasts with these other examples in that it did not form by replacement of a preexisting substrate. The textural evidence for dilation indicates that the two-phase vein assemblage grew by precipitation from a vapor phase. The nature of the intergrowth between olivine and chrysotile in these veins is unknown, but the olivine is apparently not constrained by a rigid three dimensional orientation with respect to the chrysotile. The presence of chrysotile rather than antigorite is remarkable in that the chrysotile has nucleated on antigorite. The exclusion of antigorite from the vein in favor of chrysotile suggests that this occurrence is similar to synthetic systems in which chrysotile is produced by crystallization of gels or oxide mixes as opposed to a starting mixture composed of silicate minerals.

Conclusions

Metastability in serpentine dehydration reactions occurs under conditions of thermal upgrading where synkinematic recrystallization is lacking. Metastability is also characteristic of olivine hydration reactions which proceed under static conditions; most notably the formation of mesh pseudomorphs which also occurs at relatively low temperatures. Under these conditions, nucleation effects are a potentially significant factor in promoting the occurrence of metastable phases and reactions (*e.g.*, Spry, 1969, p. 86–95). It is postulated that the peculiarities and large superlattice dimensions of the antigorite crystal structure act to retard the formation of this phase, particularly from other serpentines due to the low ΔS associated with the reaction. The difficulty with which antigorite nuclei form is compounded by the ease with which the other serpentine phases, lizardite and chrysotile, nucleate from appropriate starting materials. The role of oriented transformations between olivine and lizardite and to a lesser extent olivine and chrysotile has been advanced here as a significant factor in promoting metastable hydration and dehydration in natural and synthetic equilibria. Both the petrography of some metastable reactions in serpentinites and the results of a variety of experimental studies support the existence of topotactic intergrowths between olivine and lizardite-chrysotile. Although a general tendency for the development of oriented intergrowths in olivine–serpentine reactions and their potential for inducing formation of metastable mineral assemblages is supported by the available data, it is not suggested that one simple reaction model accounts for all observed metastable behavior. In fact, the actual reaction mechanisms involved in the several different equilibria discussed above are not known in detail, particularly with regard to the potential roles of additional phases such as brucite, magnetite, and talc. Although topotactic relationships between serpentines or olivine and these phases would not materially alter the concept of nucleation controlled reaction paths, they obviously modify the detailed interpretation of the reaction mechanism. The first step in testing the general model proposed here is to determine the nature of multiphase intergrowths produced in metastable serpentine equilibria by X-ray or electron microscope techniques.

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