Serpentinite: What, Why, Where?

Bernard W. Evans1, Keiko Hattori2, and Alain Baronnet3

Rock-forming serpentine minerals form flat, cylindrical, and corrugated crystal microstructures, which reflect energetically efficient layering of alternate tetrahedral and octahedral sheets. Serpentinitization of peridotite involves internal buffering of the pore fluid, reduction of oxygen fugacity, and partial oxidation of Fe2+ to Fe3+. Sluggish MgFe diffusion in olivine causes precipitation of magnetite and release of H2. The tectonic environment of the serpentinitization process dictates the abundance of fluid-mobile elements in serpentinites. Similar enrichment patterns of fluid-mobile elements in mantle-wedge serpentinites and arc magmas suggest a linkage between the dehydration of serpentinite and arc magmatism.

Keywords: serpentinitization, antigorite, chrysotile, lizardite, buffering, subduction zone, recycling

INTRODUCTION

This article provides answers to questions that readers might have with respect to some fundamental aspects of serpentinization, our understanding of which has evolved over the last 20 years. It addresses what serpentinites are made of, why and how they formed the way they did, and where globally we find them, including how their location influences their geochemistry.

WHAT?

Serpentinites are rocks consisting mostly of serpentine-group minerals. They form by the hydration of olivine-rich ultramafic rocks at relatively low temperatures. The primary Mg-rich minerals—olivine, orthopyroxene, and clinopyroxene—are replaced by 1:1 layered Mg silicate hydrated minerals (the serpentines), magnetite, and in some cases brucite [Mg(OH)2]. The typical combination of mineral products results in a fine-grained, dark green to black rock (commonly crossed by veins of chrysotile or calcite), whose density is significantly lower than that of the primary peridotite, and whose magnetic susceptibility is up to nearly two orders of magnitude greater. A comprehensive coverage of the serpentine minerals is given in Deer et al. (2009).

The Serpentine Minerals

The serpentine minerals form under a wide range of temperatures, including Earth surface conditions and hot hydrothermal temperatures. They have the approximate formula Mg3Si2O5(OH)4. The basic structural unit is a polar layer 0.72 nm thick (Fig. 1). A Mg-rich trioctahedral sheet is tightly linked on one side to a single tetrahedral silicate sheet, notwithstanding the 3–5% larger lateral lattice dimensions of the octahedral sheet (Wicks and Whittaker 1975). The second level of organization into different serpentine species originates partly to compensate the intralayer stress due to this dimensional misfit. Good compensation results in a nearly constant layer curvature, with the larger octahedral sheet on the convex side. However, such curvature weakens the H-bonding between the layers. H-bonding tries to maintain flat layers, but this competes with the requirements of misfit compensation. As a result, the layers are locally either curved or flat.

Figure 1 Combined ball-and-stick and polyhedral atomic model of two superimposed building layers of lizardite serpentine. Oc = octahedral sheet; Te = tetrahedral sheet. Color codes of atoms are on the upper left.
The three common serpentine minerals are lizardite, chrysotile, and antigorite. Lizardite has a flat crystal structure (Fig. 2A) with the correct geometry of interlayer H-bonds. This structure is favored by coupled substitutions of Al and Fe$^{3+}$ for $^{11}$Mg and $^{14}$Si. Owing to the many different ways to stack lizardite layers, different polytypes are possible (Bailey 1988). The most common of these is the one-layer trigonal (1T) polytype, where successive layers are directly superimposed without any lateral shift. The typical habit of lizardite is a triangular plate truncated at each corner. Lizardite is the principal mineral in the “mesh” cells that commonly pseudomorph olivine (Fig. 3A, B).

Chrysotile forms multiwall nanotubes or nanoscrolls (Fig. 2B). An undeformed chrysotile fiber is $<$100 nm in outer diameter and $\pm$4 nm in inner diameter, and it may reach several centimeters in length. Fibers are achiral, being rolled up around the $a$-axis (normal chrysotile) or, less commonly, around the $b$-axis (parachrysotile). Cylindrical polytypes exist for chrysotile, resulting from tube-in-tube layer glides having circumferential and/or axial components. Across the tube wall, there is a radial gradient of stored elastic energy (Baronnet and Devouard 1996). This tubular structure as a whole obeys five-fold symmetry (Cressey and Whittaker 1993) and is a one-dimensional crystal in that it is periodic only along its axis. The core of the fibers may be empty or filled by amorphous matter. Chrysotile is poor in Al and total Fe and occurs mainly as a filling of fractures that crosscut serpentinite (Fig. 3C). Its parallel fiber orientation (cross, oblique, or slip) is mostly determined by the repeated opening of fractures (Fig. 3C). Chrysotile is the main constituent of commercial

**Figure 2** (A) High-resolution transmission electron microscopy (TEM) micrograph of the flat lizardite microstructure in which the basic structural unit is 0.72 nm thick. Inserts: enlarged part of a polyhedral presentation of the lizardite microstructure at the same scale. The microscope image shows only Mg and Si atoms without O atoms. The small distance between Mg atoms makes them appear as a continuous dark band, and each pair of Si atoms shows up as a dark blob (right insert). (B) High-resolution TEM image of the cross section of a chrysotile nanotube with a hollow core. Inset: polyhedral model of the tube-in-tube cylindrical structure. Bar scale = 10 nm. (C) High-resolution TEM image of the wavy structure of antigorite along its $b$-axis. Insert: approximate structure represented as a polyhedral model at the same scale showing the rows of Mg and Si atoms.
asbestos, a material with outstanding electric, thermal, and phononic insulation properties, but its fine dust is thought to be deleterious to human health (Fubini and Fenoglio 2007).

Antigorite displays curved, wavy layers similar to Roman tiles on a roof (FIG. 2c). The octahedral sheet is continuous and wavy, whereas the tetrahedral sheet undergoes periodic reversals along the a-axis so that it connects to the concave half-waves of adjacent octahedral sheets (Capitani and Mellini 2004). The reversals allow serpentine layers to be bound through strong, mainly covalent Si–O bonds. This explains the lack of easy cleavage and the enhanced hardness and seismic velocities of antigorite compared to those of lizardite and chrysotile. The antigorite structure is an as-grown modulated structure, and the wavelength along the a-axis can be indicative of the composition and P–T conditions of the metamorphic rocks containing the mineral (Mellini et al. 1987). Antigorite has a triperiodic unit cell, that is, it is a “normal crystal” like lizardite. Antigorite contains Al and Fe⁢⁺³ and is enriched in Si due to the “talc-like” chemical contribution of its reversals. Antigorite is considered to be a high-temperature phase of serpentine. It commonly occurs in partially recrystallized and metamorphosed serpentinite. There, antigorite commonly forms interlocking, elongated, blade-shaped crystals that overprint earlier-formed serpentine (FIG. 3o).

In addition to these three familiar members, some microstructures have been recognized only recently with the transmission electron microscope. Polygonal serpentine reported by Mitchell and Putnis (1988) contains curved and flat parts along individual layers, resulting in a microstructure with 15 (FIG. 4) or 30 sectors. It may be viewed as a less metastable microstructure than that of chrysotile (Mitchell and Putnis 1988). Polyhedral serpentine as faceted, onion-like nanospherules (Baronnet et al. 2007) form from altered pyroxene in Al- and Fe⁢⁺³-bearing media at T < 300 °C and P₂⁢H₂⁢O = 0.7 kbar. Conical serpentine nanofibers have recently been recognized in optically isotropic veins of serpentinite (Andreani et al. 2007). They are all scrofis with apical angles of 30°. Cones exhibit a further loss of control of the layer curvature with respect to cylindrical chrysotile, having an evolving curvature along their length. This suggests that cone-shaped serpentine may be even more metastable than chrysotile.

Stability and Metastability of Serpentine

In the MgO–SiO₂–H₂O system, lizardite is more stable than chrysotile at 200 and 300 °C and 0.7 kbar (Grauby et al. 1998). Laboratory syntheses suggest that chrysotile might be more stable than lizardite above 400 °C, and chrysotile is certainly more common in recrystallized or tectonized serpentinite (O’Hanley 1996). However, antigorite grows from lizardite and chrysotile with increasing grade of metamorphism at T above about 320 °C. A calculated transition from lizardite to antigorite + brucite with a steep negative dP/dT slope takes place at approximately 300 °C (FIG. 5). This renders chrysotile entirely metastable at any temperature. This conclusion is ironic given that, for many years, chrysotile was the only Mg serpentine with listed thermodynamic properties—notwithstanding the uncertainties caused by elastic strain-energy differences among the layers in the structure.

Reversed laboratory experiments have shown that antigorite breaks down at 640 °C and 2 GPa in the pure system and at ~700 °C when Al saturated; these conditions correspond to a change in the dP/dT slope of the breakdown curve. At this point, the reaction volume changes sign, although the solid volume change stays negative. The reaction at high pressure produces olivine + orthopyroxene and large quantities of H₂O; consequently it is of great interest in the context of subduction zone seismicity and arc magma generation via fluid-fluxed melting. The P–T phase diagram (FIG. 5) shows that the reaction terminal to the stability field of forsterite + H₂O at low T yields antigorite + brucite (at 380 °C and 2 kbar, for example). This implies that the almost universal formation of lizardite from olivine during serpentinitization signifies (1) major (down-T) overstepping of the reaction, (2) a failure of antigorite to nucleate and grow, or (3) errors in the thermodynamic data. In natural systems with Al, Cr, Fe⁢⁺², and Fe⁢⁺³, we have to contend with possible reversals from the stability order of serpentines in the simple system. This perhaps explains the many conflicting field observations in the literature of mutual replacements among the serpentine minerals. The Gibbs free energy, entropy, and volume differences among the

**Figure 4** High-resolution TEM image of the cross section of a fifteen-sectored fiber of polygonal serpentine surrounded by chrysotile fibers. Flat lizardite-like layers inside sectors are linked by curved layers at their boundaries.

**Figure 5** A possible phase diagram for the MgO–SiO₂–H₂O system. To illustrate the uncertainty, two steep H₂O-conserved reactions are shown as wide gray bands (modified after Evans 2004). Mineral compatibilities in the divariant fields are shown on the MgO–SiO₂ binary line after projection from H₂O. Abbreviations: A, Atg = antigorite; B, Brc = brucite; F, Fo = forsterite; L, Liz = lizardite; T, Tlc = talc.
serpentine minerals are small, and so impurities matter. There seems to be some consensus that chrysotile growth is favored in fluid-filled voids.

**WHY?**

It has long been clear that the process of serpentinization involves some oxidation of iron. At the same time, the pore fluid becomes more reducing. This seems like a paradox, but it isn't. We try to clarify this below.

**The Oxidation–Reduction Paradox**

H₂O gains pervasive access to peridotite along joints, fractures, and grain boundaries. These openings may be thermal in origin (cooling), tectonic, or hierarchical (due to volume expansion). The hydration of olivine is accompanied by the oxidation of Fe²⁺ to Fe³⁺ and the release of H₂ gas:

\[
\text{MgFe olivine} + \text{H}_2\text{O} \rightarrow \text{MgFe serpentine} + \text{magnetite} + \text{MgFe brucite} + H_2.
\]

Most of the ferric iron resides in magnetite, but a sizeable proportion is also in the serpentinite, which in most instances is the lizardite variety. Typically 50 to 90% of the Fe in lizardite is Fe³⁺, and it is for this reason that advanced serpentinization (>10 wt% whole-rock H₂O) is commonly associated with whole-rock Fe³+/Fe²⁺ ratios in many cases in excess of 2, which is larger than the ratio commonly associated with whole-rock Fe³+/Fe²⁺ ratios in most cases.

Paradoxically, the oxidizing serpentinization reaction takes place at very low oxygen fugacity and correspondingly high hydrogen partial pressures. These conditions, which allow the precipitation of native metals, such as awaruite (Ni₃Fe) and wairauite (CoFe), are reached by means of down-T (e.g. down to ~200 °C) mineral buffering of the grain-boundary fluid. The principal driver of this buffer trend is the isobarically univariant redox reaction written conventionally as:

\[
\text{MgFe olivine} + \text{H}_2\text{O} + O_2 + \text{SiO}_2\text{aq} \rightarrow \text{MgFe serpentine} + \text{magnetite}.
\]

The d log fO₂ versus T slope of this reaction on the phase diagram is much steeper than the familiar curves for experimental redox-buffer assemblages such as FMQ (fayalite-magnetite-quartz) and MI (magnetite-iron). With falling temperature, the reaction can proceed by the release of H₂ or by the addition of O₂, but the extent of the reaction in nature may be trivial despite the major decline in log fO₂. By contrast, the culminating serpentinization reaction involves substantial progress at temperatures probably several tens of degrees Celsius (for kinetic reasons) below the stable isobaric invariant point where brucite joins the mineral assemblage. The “paradox” is thus explained by the internal (buffer) control of Fe oxidation, instead of exposure to an external oxidizing fluid.

**Low Silica Activities**

An isobaric phase diagram with aSiO₂ shows that very low silica activities also attend serpentinization (Frost and Beard 2007), as witnessed by the formation of minerals such as brucite, awaruite, hydrogarnet, and, in rare cases, diaspore, corundum, and perovskite. Again, the drive towards low values of aSiO₂ is the persistence to low T of MgFe olivine together with aqueous pore fluid. The buffering reaction in the MgO–SiO₂–H₂O system is analogous to the previous reaction:

\[
3\text{Mg olivine} + 4\text{H}_2\text{O} + \text{SiO}_2\text{aq} \rightarrow 2\text{Mg serpentine}.
\]

In both cases, higher-T buffering reactions involving talc rather than serpentine could also have been operative.

**The Pore Fluid**

The predictive success of the isobaric T–activity diagrams suggests a general model for serpentinization involving internal (mineral assemblage) control of the geochemistry of the aqueous pore fluid. The unique fluid chemistry created during serpentinization (high Ca, low Mg, high pH, high fH₂, and low aSiO₂) has been recognized in many active continental and oceanic hydrothermal systems. The pore fluid's geochemistry reflects mineral buffering. By addition of Ca and extraction of Si and Na, this fluid is responsible for converting mafic dike rocks enclosed in serpentinite into rodingite, a conspicuous pink or white rock containing hydrogrossular, diopside, prehnite, chlorite, clinozoisite, vesuvianite, and/or wollastonite (Frost and Beard 2007).

**Mg–Fe Partitioning**

We can take the buffering logic further and argue that the reacting mineral assemblage (principally olivine) also controls the chemical potentials of Mg and Fe²⁺ in the pore fluid (Evans 2008). Thus, serpentine growing at the olivine crystal surface is likely to be Mg rich because its composition is guided by Mg/Fe²⁺ partitioning in olivine–serpentine pairs. We assume that the partition coefficient, K₆, including its dependence on composition, is to a first approximation the same as for olivine + antigorite pairs in fully recrystallized serpentinite (Fig. 7). Thus, an approach to Mg/Fe²⁺ exchange equilibrium explains why the Mg# (i.e. Mg/(Mg + Fe)) of the serpentinite is generally greater than that of olivine and orthopyroxene. Vein chrysotile, derived by intergranular diffusion of aqueous Mg and Si from host serpentinite, provides a geochemical test of this model by showing a peak frequency at Mg# = 97 (Evans et al. 2012, Fig. 14). Lizardite compositions have a similarly placed frequency maximum (Mg# = 96–97), but in contrast to chrysotile the histogram has a broad tail extending to an Mg# of 86. The tail reflects the major and variable presence of Fe³⁺ in lizardite. These high Mg#s are not a reflection of any intrinsic, crystal-chemical limitation on Fe uptake in serpentine; they are a response to local heterogeneous phase equilibrium in a system of mantle-peridotite composition. With more Fe-rich olivine, such as in layered mafic intrusions, we can find a much more Fe-rich lizardite (probably rich in Fe³⁺).
Partitioning of total Fe and Mg (as XFe) between coexisting olivine and antigorite in metamorphosed serpentinites. Roughly 10–20% of Fe in antigorite is Fe3+.

**Figure 7**

### Why Magnetite and Hydrogen?

If the serpentinization reaction goes to completion, why doesn’t the Mg# of lizardite end up being the same as the Mg# of the original olivine, around 90? (Forget brucite for the moment.) This would be the textbook model for a solid-solution reaction, as depicted (oxygen conserved) in a closed, isobaric $T$–$X_{Mg}$ phase loop. What happens is that residual olivine retains its primary composition (Mg#) until it is completely consumed, and a result of this is that lizardite is similarly restricted in its content of ferrous iron. This behavior can be attributed to the very slow rate of MgFe diffusion in olivine at low temperatures (Evans 2010). Such diffusion is required in the textbook model; both olivine and lizardite should become Fe enriched in unison as their modal amounts change reciprocally. The resulting problem of Fe mass balance is resolved by the precipitation of magnetite, and the attendant oxidation is enabled by the liberation of H2 gas. The modal amount of magnetite and the release of H2 will be greatest when brucite, whose Mg# is less than that of olivine, does not form (e.g. in harzburgite, a rock rich in orthopyroxene). Growth of Fe3+-rich lizardite will reduce the amount of magnetite but will have little effect on hydrogen production.

### Kinetics of Serpentinization

The progress of the serpentinization reaction can be readily measured in the laboratory. The reaction may be sluggish even at hydrothermal temperatures and occurs at temperatures lower than the equilibrium temperature by as much as 50–60 °C. It is common to observe sizeable changes over days or weeks, although rates fall off sharply with declining temperature. These kinetics highlight the problem that hydrous fluid has in nature to penetrate cracks and grain boundaries towards its “target” in the temperature window for reaction. Incompletely serpentinized peridotite and the nearby co-occurrence of little-altered and highly altered peridotite are both commonly observed. When we add to these limitations those of MgFe diffusion in olivine, we must recognize that slow $T$-serpentinization of peridotite does not proceed in nature under equilibrium conditions. Equilibrium is both local and partial, and the extent of serpentinization is generally limited by an insufficient supply of H2O at the grain scale.

A two-step process of serpentinization has been suggested by a number of authors, based upon petrographic study of natural samples; an initial growth of brucite is reversed with further serpentinization, and low-Fe lizardite and magnetite are formed instead. This observation finds support in the upward curvature of data points on the graph of magnetic susceptibility relative to density (e.g. Beard et al. 2009). Rather than separate steps, we may be witnessing enhanced diffusion between olivine and pyroxene microdomains, as cracks are opened by volume expansion or tectonic deformation. Mg and Si are exchanged across boundaries towards its “target” in the temperature window, and water/rock ratio. The uptake of Fe3+ in lizardite can take the form of a Mg cronstedtite component (a coupled replacement by Fe3+ of Mg and Si on the M sites), a vacancy-balanced M-site substitution, or a process of deprotonation. Mg cronstedtite substitution can be expected in SiO2-poor rocks containing brucite or olivine, whereas the M-vacancy trend should occur in rocks with talc or pyroxene and in partially carbonated peridotites (Streit et al. 2012). Mg cronstedtite substitution shows as an inverse correlation (with slope approaching –0.5) between T-site atoms (Si + Al/2 + Cr/2) and total Fe afpu. On the other hand, an increase in the cation occupancy ratio, $T/(T + M)$, with an increase in Fe signifies M-vacancy substitution. Oxidation of Fe2+ by deprotonation may well be favored at the high pH associated with serpentinizing fluids. The Mg cronstedtite substitution is probably the dominant mode of Fe3+ uptake in serpentine. A mixed-volatility reaction linking oxidized and reduced Fe in Fe serpentines suggests that low $T$ should favor the formation of the Mg cronstedtite component:

$$6\text{ cronstedtite} + \text{ H}_2 = 3\text{ Fe}^{3+}\text{ serpentine} + 5\text{ magnetite} + 7\text{ H}_2\text{O}.$$
Dehydration of Serpentinite

The prograde metamorphism of serpentinite ultimately brings about the loss of H2O and growth of secondary olivine and talc (alternatively, orthopyroxene at high pressure). Strict reversal of the serpentinization reaction would require the reintroduction of hydrogen, something that seems unlikely. Does this mean that metamorphosed serpentinite retains its high Fe3+/Fe2+ ratio (Fig. 6)? Field accounts of thermally deserpentinized ultramafic rock from diverse tectonic environments reveal in many cases the presence of newly generated olivine with a Mg# in the unusual range of 98 to 93, together with abundant magnetite. Although the data are sparse, the Mg# of prograde olivine correlates well with analyzed whole-rock Fe3+ contents, and so it can serve as a proxy indicator of the extent of reduction in metaperidotite. Given the very dilute concentration of O2 in the aqueous fluid and the mass of potential magnetite reactant, any reduction in Fe3+ simply by release of O2 is likely to be very small. So there may in some cases be a kind of hysteresis in petrophysical properties in the peridotite–serpentinite cycle.

However, there are also field examples of prograde-metamorphosed serpentinite where the reduction of Fe3+ apparently did take place and olivine compositions were restored to mantle values (Mg# = 92–89). In these cases we have to ask if there were sufficient modal amounts of graphite and/or sulfide in the average serpentinite to react with magnetite and release CO2 and SO2 in some form into the fluid, or was an oxidizing fluid introduced? In practice, we don’t always know the redox ratio (or the degree of serpentinization) of the original serpentinite. This issue is deserving of further study in regard to what kind of released H2O fluid we can expect from the eventual high-pressure dehydration of antigorite serpentinite in subduction zones.

WHERE?

Serpentinites are volumetrically minor, but they occur in all ancient orogenic belts. A suite of rocks consisting of serpentinite, mafic volcanic rocks, and minor chert is known in many mountain belts, and they are collectively referred to as ophiolites. Serpentinites are also produced at present in a variety of geological settings.

Locations of Present-Day Serpentinitization

Peridotites are hydrated by seawater under a variety of conditions, from the cool seafloor to hot ridge hydrothermal systems. Low-temperature seafloor serpentinitization is common at the surface of oceanic lithosphere produced at slow- to ultraslow-spread ing ridges (Fig. 1 in Guillot and Hattori 2013 this issue). Here, magma-starved oceanic lithosphere exposes mantle peridotite on the seafloor (Cannat et al. 2010). Because the Mid-Atlantic Ridge has a slow spreading rate of ~2 cm/y, serpentinites are exposed at numerous sites on the Atlantic Ocean floor. Well-studied examples include the Kane area of the Mid-Atlantic Ridge (MARK, ~15°20’ N), the Atlantic Massif (~30° N), and the Iberian-margin serpentinites. Seawater is able to penetrate to deep levels, forming serpentinite down to ~7 km. Oceanic lithosphere at fast-spreading ridges, such as the East Pacific Rise, is commonly covered by basaltic rocks, although serpentinites are exposed along major transform faults, fractures in trenches, and local rifts. The serpentinites in the Hess Deep in the Pacific Ocean are a good example. Another place for serpentinization is along faults at outer rises near trenches, where incoming oceanic plates are bent, producing deep fractures (Ranero et al. 2003). Serpentinization at low temperatures on and near the seafloor is commonly accompanied by the formation of carbonates and sulfides through microbial reduction of marine sulfate within serpentinites (e.g. Alt et al. 2012).

Ocean-ridge hydrothermal activity results in the hydration of abyssal peridotite near the seafloor at moderately high temperatures (e.g. 350 °C). The Mid-Atlantic Ridge hydrothermal systems of Logatchev and Lost City have been well reported since their discovery (e.g. Früh-Green et al. 2003). Serpentinites formed by such hot fluids commonly show positive Eu anomalies because of dissolution of plagioclase in mafic igneous rocks during hydrothermal activity.

Forearc mantle peridotite is hydrated by water expelled from the subducting slab, forming a layer of serpentinite near the base of the mantle wedge. The existence of such a hydrated layer is suggested by the low and anisotropic seismic velocities in that location (Hirth and Guillot 2013 this issue).

Serpentinites in Orogenic Belts

Orogenic belts commonly contain bodies and lenses of serpentinite (the classic Alpine serpentinites). Although minor in volume, they provide information useful for elucidating the history of orogenic belts. The protoliths of these serpentinites have various origins; for example, they may represent cumulates from a variety of mafic melts or residual-mantle peridotites. Residual (i.e. depleted)-mantle peridotites comprise abyssal and mantle-wedge peridotites. The latter show a refractory geochemical signature since they underwent a high degree of partial melting. The absence of primary mantle minerals and the mobility of most petrogenetically useful elements make it difficult to characterize the protoliths. However, plots of the major elements Mg, Al, and Si commonly provide information related to the protoliths because the serpentinization is primarily isochemical, except for Ca (e.g. Hattori and Guillot 2007). During partial melting, the Al/Si ratio decreases and the Mg/Si ratio increases in residual peridotites. This approach, however, is not useful for evaluating the origin of hydrated dunite, whether of cumulate or residual-mantle origin. The abundance of platinum-group elements (PGEs) is found to be effective in differentiating cumulates from residual-mantle dunite because partial melting fractionates PGEs due to the different compatibilities of these elements.

Almost all large bodies of serpentinite are hydrated mantle peridotite, but serpentinite produced by the hydration of ultramafic cumulates form large blocks in massifs (Hattori and Guillot 2007). Good examples are the base of the Drakkarpo unit and the Nidar ophiolite in the western Himalayas, and the Pelvas d’Abriès serpentinite in the western Alps.

The abundance of immobile elements in bulk rocks and the chemistry of relict Cr spinel have been successfully used to discriminate abyssal serpentinite from mantle-wedge serpentinite. Cr spinel is a robust mineral that
commonly retains its primary composition in the cores of grains, even in fully hydrated and deformed peridotite. These studies show that regionally extensive serpentinites are mostly composed of hydrated abyssal peridotite. They were hydrated on or near the seafloor and obducted onto the continents. Examples include the Jurassic Apennine ophiolite, the Tertiary Alpine serpentinites, and the Late Cretaceous to Mid-Eocene Northern Serpentinite Belt in Cuba and Hispaniola.

Mantle-wedge serpentinites are found in forearcs, along major deformation zones in subduction zones, and in trenches. Their buoyancy (2.6 g/cm³ relative to 3.2 g/cm³ for anhydrous peridotite) allows them to rise from the base of the mantle wedge to the surface (Saumur et al. 2010). As they ascend, they commonly bring with them fragments of rocks, such as high-pressure rocks (e.g. Fryer et al. 2006; Saumur et al. 2010). These serpentinites are characterized by distinctly low concentrations of immobile, incompatible elements compared to serpentinites formed from oceanic mantle peridotite. Examples of mantle-wedge serpentinites are the Mariana forearc serpentinites and the serpentinites along major shear zones in Cuba and the Dominican Republic (e.g. Hattori and Guillot 2007; Saumur et al. 2010).

Role of Serpentinite in the Recycling of Elements
Mantle peridotite loses incompatible elements during partial melting, but the concentrations of these elements generally increase during the progressive hydration of peridotite. In a system with a low water/rock ratio, the concentrations of soluble elements are enriched in the fluid as H₂O is consumed by the hydration. Those elements dissolved in the fluid are eventually incorporated in the serpentinite. The composition of serpentinite is therefore affected by the nature of the fluid and by the water/rock ratio. For example, seawater contains high concentrations of B, U, and S as sulfate, so that serpentinite formed in a marine environment has high contents of these elements. As an example, serpentinites in the MARK area are enriched in B (up to 136 ppm) and U (up to 7 ppm) (Vils et al. 2008). These values may be compared to primitive mantle values of 0.3 and 0.0203 ppm, respectively.

In subduction zones, sediments and altered oceanic lithosphere release water and fluid-mobile elements; this leads to the enrichment of serpentinite in the overlying mantle wedge in As, Sb, Pb, and Sr (e.g. Hattori and Guillot 2007). When the speciation of As and the presence of pseudomorphic textures, mantle-wedge serpentinites are interpreted to show early incorporation of As at shallow depths and later incorporation of Sb, Pb, and Sr at deeper levels (Hattori et al. 2005; Deschamps et al. 2012).

Among these elements, As⁵⁺ replaces Si⁴⁺ in the tetrahedral site of serpentine (Hattori et al. 2005). The distribution of B also suggests residence in the tetrahedral site (Pabst et al. 2011): Some elements form distinct phases, such as sulfides. Among the fluid-mobile elements, alkalis are not enriched in serpentinite (Hattori and Guillot 2007). Their ionic radii are too large for them to be incorporated into the serpentinite structure, except for Li⁺, which has an ionic radius similar to Mg²⁺. Furthermore, in a subduction setting, alkalis are not released from the subducting slab and then incorporated in serpentinite because they are retained in phengite, a mineral that is stable at a depth exceeding 300 km.

Relations with Arc Magmas
It is well known that arc volcanoes are distributed in a curve parallel to the trench, with a conspicuous lack of volcanoes between the volcanic front and the trench. Also, arc magmas contain high concentrations of fluid-mobile elements, such as As, Sr, and Pb (Fig. 8; Noll et al. 1996). There had been considerable debate regarding the formation of volcanic fronts. Hattori and Guillot (2003) showed that the enrichment pattern of fluid-mobile elements in arc magmas is similar to that of mantle-wedge serpentinites (Fig. 8). The data explain both the lack of volcanoes in the forearc and the occurrence of a volcanic front where the subducted slab is around 100 km deep. Serpentinite retains water in forearc mantle and transports fluid-mobile elements incorporated at shallow depth to deep mantle depths. Eventual dehydration of the serpentinite releases water and fluid-mobile elements to the hot interior of the mantle wedge, leading to partial melting and arc magmatism (Hattori and Guillot 2003).

Abyssal serpentinites formed at ridges and on the ocean floor move to subduction zones by plate motion, which results in the transfer of fluid-mobile elements from ocean water to subduction zones (Vils et al. 2008; Deschamps et al. 2012). Oceanic serpentinites and serpentinites in mantle wedges are eventually dehydrated, releasing water and fluid-mobile elements to the interior of the mantle wedges. Thus, serpentinites play an important role in the recycling of elements from the surface to the deep lithosphere and back to the surface via mantle wedges and arc magmas.
CONCLUSIONS

Serpentinites have relevance to several important subjects in the geosciences, including geodynamics, prebiotic life, and the global recycling of elements, as this issue of Elements shows. Future progress in understanding serpentinites will be enhanced when cutting-edge techniques, such as TEM, reaction-path modeling, isotope geochemistry, and mineral spectroscopy, focus in fully integrated fashion on the diversity of natural serpentinites from well-located locations. These studies will illuminate the roles of mineral buffering, kinetics, deformation, and the constraints of local and partial equilibrium.

ACKNOWLEDGMENTS

We thank H. Austrheim, P. Kelemen, and G. Calas for their critical reviews.

REFERENCES


