Occurrence, composition and growth of polyhedral serpentine

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Abstract: Occurrences, compositions and crystallization of polyhedral serpentine were investigated by SEM, AEM/TEM and μ-XANES analysis of samples from different ultramafic units. Polyhedral serpentines are identified in all of these contexts and form as an alteration product of orthopyroxene (enstatite) and as late veinin events. They are always the last serpentine type to crystallize. Their formation requires a combination of three factors: 1) open space, 2) a relatively low temperature (T < 200–300 °C), and 3) the presence of trivalent cations (Al^3+ in this study, > 0.1 atoms per serpentine formula unit). μ-XANES data at the iron K-edge indicate that Fe is predominantly ferrous and octahedrally coordinated in our Al-rich samples. This microstructure therefore cannot be systematically used as a marker of oxidizing conditions. Textural and microstructural criteria suggest that polyhedral serpentine crystallizes via a “gel” precursor first reorganized into a poorly-crystallized proto-serpentine, in which onion nucleation takes place as nested, discontinuous sheets. Grains expand radially, inwards and outwards, by a layer-by-layer mechanism. Thick layers, made of tens of serpentine sheets, propagate laterally in the (001) plane and result in a pseudo-spherical “onion-like” morphology. By analogy with available clay synthesis experiments, the relatively low temperature conditions under which polyhedral serpentine form may favor a segregation of trivalent cations in the structure. This could create locally diotahedral components in the structure that may explain the peculiar bending along (010) responsible for the faceted morphology of polyhedral serpentine.

Key-words: serpentine, AEM/TEM, gel-type precursor, growth.

Introduction

Serpentines are 1:1 trioctahedral phyllosilicates of ideal formula Mg_2Si_2O_5(OH)_4 and classical size < 1 μm. They are the trioctahedral equivalents of kaolinite group minerals. Serpentine minerals are ubiquitous in many geological systems where hydrothermal alteration of ultramafic rocks is possible, in both terrestrial (oceanic hydrothermalism, subduction zones and transform faulting) and extraterrestrial environments (Mustard et al., 2005; Schulte et al., 2006).

Serpentines display different structural types in response to a geometrical misfit between the lateral dimensions of tetrahedral (T) and octahedral (O) structural sheets. The three main types are chrysotile, antigorite and lizardite (Fig. 1). Curvature of the structure can lead to a total wrapping or a modulated structure, as for chrysotile (Fig. 1A) and antigorite (Fig. 1E), respectively. Lizardite (Fig. 1D) exhibits a planar structure (Mellini, 1982; Mellini & Zanazzi, 1987) that may be stabilized by partial substitutions for Si and/or Mg. The main possible serpentine substitutions are Al^3+ and Fe^3+ for Si in tetrahedral sites and Fe^2+, Fe^3+ and Al^3+ for Si, and sometimes, to a lesser extent, of Cr, Ni and Mn for Mg in octahedral sites. The stability field of serpentines extends over a wide temperature range (T < 600 °C) and is virtually unconstrained by pressure (cf. review in Evans, 2004). Parameters other than P, T and chemistry may contribute to the occurrence of lizardite and chrysotile, including the water/rock (W/R) ratio and reaction kinetics (Grauby et al., 1998; Normand et al., 2002; Andreani et al., 2004). This idea is in accordance with Evans (2004), who concluded that chrysotile is probably metastable relative to lizardite.

More “exotic” microstructures of serpentine have also been observed in synthesis experiments and/or natural environments. Polygonal serpentine (Fig. 1B) is another fibrous serpentine that displays a polygonal section and a much larger diameter (> 100 nm) than chrysotile. Above a critical diameter of about 100 nm, the elastic energy required for curvature (and which must be stored within the layers) is too high, preventing the radial development of chrysotile. For this reason, and because it is often associated with chrysotile, polygonal serpentine has been interpreted as a more evolved type of chrysotile that accommodates radial development of fibers by polygonization perpendicular to the wrapping axis (Baronnet et al., 1994; Baronnet & Devouard, 1996). Conical chrysotile (Fig. 1C) is also fibrous and always associated with chrysotile in magnesian synthesis experiments (Yada & Ishi, 1974;
Fig. 1. Presentation of the various serpentine microstructural types identified in natural samples. The fibrous species are: A) cylindrical chrysotile (SEM image), B) polygonal serpentine (TEM image along [100]) and C) conical chrysotile (SEM image). D) Lizardite is the planar type that classically exhibits a triangular section elongated along [001] (TEM image). E) Antigorite presents a modulated structure along [100], clearly visible along [010] with TEM. F) The newly identified polyhedral serpentine exhibits a near-spherical morphology. All these types have been reproduced in synthesis experiments except for polyhedral serpentine.

Devouard, 1995, Grauby et al., 1998), but has only been reported once in natural settings (Andreani et al., 2007).

A new type of serpentine, referred to as polyhedral serpentine, has been identified recently in natural samples (Zega et al., 2006; Baronnet et al., 2007; Andreani et al. 2007). It is characterized by an “onion-like”, faceted, spherical morphology (Fig. 1F) in which triangular facets consist of (001) basal planes of flat serpentine laterally continuous from one sector to another. It is somewhat similar to morphologies reported for some other layered minerals such as kaolinite (Tomura et al., 1983) or carbon (Jaszczyk, 1994). The details of its structure have been investigated by Baronnet et al. (2007) but it has not yet been produced experimentally. The conditions under which it forms relative to the other serpentine types and its growth are still unknown.

To further our understanding of serpentine microstructure significance in natural systems and the formation mechanism of spherical sheet silicates, the occurrence conditions, chemistry and crystallization mechanism of the newly discovered polyhedral serpentine will be investigated below in comparison with the other types of serpentine.

**Materials and methods**

Serpentine samples came from three different ultramafic units: 1) a serpentine unit of the Franciscan subduction complex located along the active Santa Ynez fault in the Blue Canyon, north of Santa Barbara, Central Coast Ranges (California, USA); 2) serpentinites from the Alps (Maurin, Ubaye valley, France), and 3) serpentinitized abyssal peridotites outcropping along the axial valley of the Mid-Atlantic Ridge near the Kane transform fault at 30°N (MARK area) drilled during ODP leg 153 at sites 920B and D (Cannat et al., 1995).

SEM observations were made on serpentineite broken surfaces. The samples were sonicated and then glued onto a support and covered with a 10–15-nm thick carbon coating. Images were obtained at the CRMCN (Marseille, France) using a JEOL 6320F scanning electron microscope equipped with a field-emission gun, under a 3 kV accelerating voltage for optimum image contrast. The effective resolution is decreased to nearly 10 nm under these conditions.

Thin sections, glued with Crystal Bond® thermal resin, were cut from the zone of interest. Single-hole copper TEM grids were glued with araldite on selected areas of the section and extracted from the glass substrate by heating the resin. Then the specimens were thinned by ion-beam milling (Gatan 690 Precision Ion Polishing System) and carbon-coated. TEM and HRTEM observations were performed at the CRMCN (Marseille, France) on both a JEOL JEM 3010 very high-resolution transmission electron microscope working under a 300 kV acceleration voltage and a JEOL 2000fx high-resolution transmission electron microscope at 200 kV. The latter was equipped with a Tracer Northern 5520 X-ray energy dispersive spectrometer (EDS-TEM) for major element analysis on circular areas of about 30 nm in diameter in fixed-beam mode. The geometry of this TEM was designed to optimize raw analytical data that are then processed using the Cliff Lorimer K-factors method.

Experimental K-factors were calibrated using natural and synthetic standards of layer silicates. Compositions were converted into atoms per formula unit (apfu).

Raman spectra of serpentines were collected on a volume of ~3 μm³ in a back-scattering geometry using a Dilor XY (T64000) Raman spectrometer at IFP-Paris. Sig-
nal acquisition was performed on polished thin sections at 700 mW for 120 s. The exciting radiation ($\lambda = 514$ nm) was provided by an Ar$^+$ laser focused on the sample using an optical microscope ($\times 50$ objective). Raman regions corresponding to both lattice and internal vibration modes (low-frequency: 200–1200 cm$^{-1}$) and to the stretching vibrations of the OH groups (high-frequency: 3600–3800 cm$^{-1}$) of serpentine were analyzed. The resolution of the detection system was approximately 2 cm$^{-1}$. A linear background was first subtracted over the RAMAN spectra that were then fitted by Peakfit® assuming a Voigt profile.

Iron K-edge μ-XANES mapping was carried out on a thin section using dispersive X-ray absorption spectroscopy according to the protocol described in Muñoz et al. (2006). Measurements were performed on the undulator-based dispersive-EXAFS beamline, ID24, of the European Synchrotron Radiation Facility (ESRF, Grenoble, France). XANES spectra were collected in fluorescence mode using the so-called Turbo-XAS setup. The polychromatic X-ray spot size was around 5 by 5 μm on the sample surface. The horizontal and vertical sampling step was 10 μm and the map covers a total area of 400 by 700 μm, so that 2800 spectra were collected. Data were first normalized before the mapping reconstruction, based on the XANES edge-jump and edge-position criteria.

Results

Texture and identification on a thin-section scale

A crystal with a spherical or radial arrangement has a texture with a typical and constant extinction feature under crossed polars, characterized by an extinction cross that is always parallel to polarizers (Morse & Donnay 1936). The polyhedral serpentine (Fig. 1F) clearly displays this extinction cross when the grain is significantly larger than the resolution of the optical microscope (~1 μm), as illustrated in Fig. 2A and 2B. However, smaller grain sizes identified under electron microscopes display an almost isotropic optical response that does not allow alone the identification of the serpentine type on this scale (Fig. 2C and 2D).

Raman spectroscopy has been presented as an effective non-destructive method to discriminate between the main serpentine types (lizardite, chrysotile and antigorite) on the thin-section scale both in the low-frequency (200–1200 cm$^{-1}$) (Rinaudo et al., 2003) and high-frequency (3600–3800 cm$^{-1}$) vibration domains (Lemaire 2000; Auzende et al., 2004). The efficiency of this method at identifying polyhedral serpentine has been tested here on the monomineralic veins of Fig. 2 and its representative spectrum is shown in Fig. 3. In the low-frequency domain, few differences exist between the three main serpentine types and antigorite is the most distinguishable (Lemaire 2000). However, the spectrum obtained for polyhedral serpentine presents strong peaks at 230, 386 and 690 cm$^{-1}$, i.e. very close to the three main characteristic peaks of lizardite as described by Rinaudo et al. (2003). This is definitely confirmed in the high-frequency domain where the three main serpentine types have more distinct signals (Lemaire 2000; Auzende et al., 2004) and polyhedral serpentine displays the characteristic peaks of lizardite at 3682 and 3705 cm$^{-1}$. The spectrum of lizardite, obtained on monomineral lizardite veins, is given in Fig. 3 for comparison. Accordingly, polyhedral serpentine cannot be easily distinguished from lizardite on the basis of its Raman spectrum, either in low- or in high-frequency vibration domains. This attests to the high similarity of their respective structures, composed mostly of a planar arrangement of the TO sheets (Baronnet et al., 2007).

Occurrence, morphology and microstructure

The presence of this particular type of serpentine is identified in all the studied serpentinized ultramafic units in zones preserved from prograde metamorphism. They occur either as an alteration product of pyroxenes (Fig. 4) or as aggregates in veins (Fig. 2) that crosscut the background mesh and bastite texture of peridotite hydration. Occurrences as veins or altered pyroxenes are usually linked on the thin-section scale, suggesting a common formation episode. Similar textures, without identification of the microstructure, have also been occasionally reported in previous studies of calcite-serpentine segregation in kimberlites (Mitchell & Putnis, 1988) and ophiolites (Viti & Mellini 1998). Polyhedral serpentine has been clearly identified in CM chondrites (Zega et al., 2006). In all these cases, as in our samples, they always correspond to a late stage of serpentine crystallization.

The formation of polyhedral serpentine after pyroxene is preferentially linked to orthopyroxene rather than clinopyroxene alteration (Fig. 4A). This is confirmed by the orthopyroxene SEM image in Fig. 4B in which clinopyroxene exsolution lamellae are preserved, whereas the rest of the
Fig. 3. Characteristic Raman spectrum of a monomineral polyhedral serpentine vein compared with the Raman spectrum obtained for a lizardite vein. Amplitude is in arbitrary units (a.u.). The high similarity of the Raman signals, both in low- and high-frequency domains, illustrates the similarity of their structures.

Fig. 4. Polyhedral serpentine in pyroxenes. A) Comparison of alteration texture in adjacent orthopyroxene (Opx) and clinopyroxene (Cpx) grains (crossed-polar light). The Opx is preferentially transformed into polyhedral serpentine. B–D) Three-dimensional arrangement of polyhedral serpentine aggregates in Opx (SEM image). They are preferentially oriented toward relics of cpx exsolution if available; otherwise they are randomly oriented in the space between them.

orthopyroxene grain is totally replaced by polyhedral serpentine. The incomplete basement of polyhedral grains can be oriented toward clinopyroxene lamellae (Fig. 4C and 4D). This texture is very similar to that of the associated veins where polyhedral serpentine grains homogeneously fill the available space without any preferred orientation (insert Fig. 5) except at the margins. Polyhedral serpentines form aggregates of spherical grains with a diameter that can vary in veins from one setting and zone to another, from hundreds of nm to several tens of micrometers (Fig. 2 and 5) without spatial segregation. Grains are meshed together, as illustrated in the SEM and TEM images of an isotropic vein infill in Fig. 5 (corresponding optical texture of Fig. 2D). When polyhedral serpentine grains are not tightly meshed, residual nano-metric porosity persists both in veins and in altered pyroxenes. A part of this porosity is filled by other serpentine types, essentially fibrous species such as chrysotile and polygonal serpentines (PS), that are particularly short. This latter is the most abundant serpentine and frequently displays partial closing at fiber tips by bending of the layers around an axis normal to the fiber axis [100] (Fig. 6). In polygonal serpentine, layer stacking is radial, and its tubular morphology is accommodated by bending of the layers along the ⟨100⟩ direction at sector boundaries (e.g. Baronnet & Devouard 1996). Closing at fiber tips is observed to be the result of bending along the ⟨010⟩ direction. This is also the direction along which bending from one sector to the other occurs in polyhedral serpentine (Baronnet et al., 2007).
The polyhedral serpentine grains show various degrees of anisotropy (Fig. 7) that probably reflect various growth stages. The less developed grains can present either a “shrimp-like” (Fig. 7A) or a “filled half-dome” (Fig. 7B) morphology, whereas the most complete grains are faceted spheres (Fig. 7E). The latter display a concentric “onion-like” wrapping of serpentine layers (Fig. 7E) that predominantly form non-circular sections under TEM (Fig. 5). This indicates radial overgrowth of grains by addition of new serpentine layers at the outer surface when space is available between adjacent grains. This outer layer frequently stops its growth before totally covering the polycrystalline grain, resulting in high steps that finish by a wrapping of serpentine layers (Fig. 7). Measurements of facet edges and grain diameter performed on properly oriented grains in high-magnification SEM images indicate that the edges of triangular facets tend to increase linearly with grain diameter. Rare TEM sections cutting the center of polyhedral serpentinites reveal the presence of a core similar to a short chrysotile tube, in agreement with the observations of Zega et al. (2006). Polyhedral serpentinites are locally embedded in a poorly-crystallized material discernible under SEM in the inner part of the partial domes (Fig. 7B) or between adjacent grains. This material has been identified under TEM (Fig. 8) as an assemblage of somewhat wavy, randomly oriented serpentine particles, 5–10-nm thick, displaying an incipient structural order. Halos corresponding to serpentine basal (~ 7 Å spacing) and non-basal periodicities are inferred from selected-area electron diffraction (SAED) patterns (inset, Fig. 8). This confirms both the poor crystallinity of the material and the random orientation of particles. Locally, clusters of particles are arranged with a preferred orientation (bottom left of Fig. 8) but the particles are not planar and some show an incipient wrapping (upper part of Fig. 8).

Chemical composition

AEM/TEM analyses were conducted on isolated particles of all the different serpentine types encountered in the samples from two of the ultramafic units, representative of the two main geological settings: on-land serpentinites in California and drilled oceanic serpentinites from the MARK (Atlantic). Only the major elements Mg, Si, Al and Fe are detected, with local traces of Cr. Analyses are given in atoms per formula unit in Table 1, which is deposited and available directly from the authors or the EJM editorial office in Paris, for each type of serpentine, calculated under the ferrous iron assumption (predominant in our sample – cf. the following μ-XANES results).

Measurements of proto-serpentine (Table 1) correspond to poorly-crystallized material associated with either...
Table 1. Structural formula in atoms per formula unit of the different serpentine types studied from the various deposits, calculated from EDS-TEM analyses. Fe is assumed to be divalent and calculations are done on the basis of 7 anhydrous oxygen.

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<th>Serpentine type</th>
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<th>Fe</th>
<th>Al</th>
<th>Cr</th>
<th>Tot.</th>
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chrysotile or polyhedral serpentine in samples from California (Table 1). Its composition is similar to that of the associated serpentine. The high sensitivity of protoserpentine under the TEM electron beam may reflect a high water content. Figure 9 presents the composition of the different serpentine types from all our samples plotted in a Si-(Mg+Fe\(^{2+}\))-Al cation-normalized ternary diagram. Analyses are localized in a narrow domain of the diagram along the Si-(Mg+Fe\(^{2+}\)) axis. Enlargement of the zone of interest shows that polyhedral serpentines tend to be enriched in Al with Al from 0.06 \(\text{apfu}\) up to Al = 0.22 \(\text{apfu}\). All the other serpentine types occur for Al contents below 0.1 \(\text{apfu}\). This trend is not observed for Fe, since all serpentine types are spread over the main range of Fe content (0.05 to 0.4 \(\text{apfu}\)), with exceptions for one polyhedral and two polygonal serpentine grains close to 0.6 \(\text{apfu}\).

Previous studies of Zega et al. (2006) report abundant Fe\(^{3+}\) content in Fe-rich (up to 8 atomic %, i.e. Fe\(^{3+}/\text{Fe}^{\text{tot}} \sim 0.7\) polyhedral serpentine and propose that these microstructures may be potential markers of oxidizing conditions. In order to test if this hypothesis is valid for our Al-enriched and Fe-poor samples, we first performed \(\mu\)-XANES mapping tests at the iron K-edge on a selected area of a thin section containing a polyhedral serpentine vein (V2, Fig. 10A), representative of Californian samples. This deposit was selected because of its internal content in Fe and Al (average Fe \(\sim 0.23 \text{apfu}\) and Al \(\sim 0.17 \text{apfu}\)). The mapping area was also selected because it offered the possibility of a direct comparison between polyhedral serpentine and fibrous serpentine (chrysotile + polygonal serpentine) that fill an older vein (V1, Fig. 10A). Color contrasts in Fig. 10A are based on the height of the edge-jump of the XANES spectra, which is correlated to the total iron content distribution in the sample (Muñoz et al., 2005). This map shows that iron is between 1.5 and 2 times more abundant in V1 than in V2, with average edge-jump values of around 0.3 and 0.5, respectively. This is consistent with the EDS analyses of the serpentine grains from these veins (Table 1 – California). Red regions of the map indicate a very high, localized iron content that most likely corresponds to magnetite inclusions. Color contrasts in Fig. 10B correspond to the energy-position of the Fe K-edge determined with an arctangent fit. This map (Fig. 10B) displays a difference of around 0.3 eV between V1 and V2, with edge-positions of 7120.1 eV and 7120.4 eV, respectively. Note that because of sample heterogeneity, such small changes in XANES spectra could be insignificant for point analyses but become statistically significant for a 2D mapping exploration. This shift of a few eV can be attributed to: i) changes in the oxidation state of iron (the Fermi level being shifted by a few electron-volts with increased oxidation of cations; e.g., Ankudinov et al., 1998) and/or ii) structural changes (iron local geometry) and/or iii) crystallographic orientation with respect to the linearly polarized incident X-ray beam (Mancau et al., 1988; Dyar et al., 2002). In the present case, serpentine crystals present no preferential orientation (e.g. Fig. 5) so that the effect of polarization can be spayed. To accurately identify the origin of this edge-position shift (Fig. 10B), XANES spectra were integrated for the two main regions of interest, i.e. V1 and V2, in order to improve the signal-to-noise ratio and extract specific speciation information from the pre-edge region. The averaged spectra are presented in Fig. 10C.

The pre-edge extraction and normalization (feature a; zoom inset in Fig. 10C) clearly shows a variation in height with negligible changes in position. Indeed, results obtained from deconvolution (dashed lines) based on the method presented by Wilke et al. (2001) provide similar centroid values of 7112.82 eV and 7112.81 eV for V1 and V2 pre-edges, respectively. In contrast, the integrated intensities of V1 and V2 pre-edges, 0.071 and 0.055, respectively, vary significantly. Compared with standard values obtained from almandine and andradite (Fig. 10C), similar centroid positions for V1 and V2 suggest that changes in iron oxidation state between them are not significant, and that both minerals are mainly Fe\(^{3+}\)-free. However, the difference in pre-edge intensities reflects a significant change in the averaged symmetry degree of iron site between the two types of serpentine. Slight differences for features b and c, with feature b slightly lower and feature c slightly higher for polyhedral (V2) compared with fibrous serpentine (V1), could also result from this difference in averaged local structure around iron. Complementary EXAFS (Extended X-ray Absorption Fine Structure) experiments are required to accurately derive changes of the Fe–O distances and Fe-averaged coordination numbers. Red and orange regions in Fig. 10B coincide with magnetite clusters and assemblages of serpentine + magnetite in the mesh texture of the host rock that are most likely enriched in Fe\(^{3+}\).

**Discussion**

**The role of temperature, chemistry and system openness with regard to occurrence conditions**

Polyhedral serpentines always correspond to the last stage of serpentine crystallization, which suggests that their
formation occurs in the lower part of the serpentine stability field, only restricted by \( T < 600 \) °C (cf. review in Evans, 2004). Mitchell & Putnis (1988) suggest crystallization of similar textures in kimberlite voids at \( T < 400 \) °C. In previous descriptions of the pyroxene hydration process (Le Gleuher et al., 1990; Viti et al., 2005), replacement leading to a bastite texture occurs in the first stage of pyroxene hydration. Since textural criteria indicate that polyhedral serpentine crystallization postdates mesh and bastite formation, it should accompany the last stage of pyroxene hydration, proposed by these authors to occur at \( T < 300 \) °C. Note that Le Gleuher et al. (1990) describe “triangular structures intergrown with polygonal fibers” in regions of non-topotactic replacement in pyroxenes, that may correspond to polyhedral serpentine (see their Fig. 8). A complete study of the serpentinitization history in the MARK area suggests that the last generation of hydrothermal veins filled with polyhedral serpentine forms below 200 °C (Andreani et al., 2007), which restricts their temperature domain of occurrence. Their absence in MSH syntheses conducted at 300 °C by Grauby et al. (1998), where all the other types have been identified, supports this temperature range. However, the purely magnesian system used for these experiments may not favor polyhedral serpentine formation and polyhedral serpentines may be formed under this temperature in chemically different systems.

Another important characteristic of polyhedral serpentines is their systematic enrichment in trivalent cations: only \( \text{Al}^{3+} \) in this study or \( \text{Fe}^{3+} \) in Zega et al. (2006).

Fig. 10. \( \mu \)-XANES mapping at the iron \( K \)-edge on a selected area of a thin section (California sample) containing a polyhedral serpentine vein (V2) and an older fibrous serpentine vein (chrysotile + polygonal serpentine: V1). A) Total iron content distribution in the sample, proportional to the height of the edge-jump of the XANES spectra. B) Distribution of the energy-position of the Fe \( K \)-edge. Note the electron-volt shift of the edge energy that can be attributed to changes in the oxidation state of iron and/or to structural changes (iron local geometry). C) Averaged XANES spectra for the V1 and V2 regions, as well as almandine and andradite standard compounds used for pre-edge calibration (the zoom inset shows the deconvolution of V1 and V2 pre-edges).

Lizardite can attain a similar substitution rate with high \( \text{Al}^{3+} \) and/or \( \text{Fe}^{3+} \) contents (e.g. Le Gleuher et al., 1990; O’Hanley & Dyar, 1993; Fuchs et al., 1998). Thus, abundant trivalent substitutions are a general trend for planar as opposed to curved microstructures and cannot explain alone the occurrence of lizardite rather than polyhedral serpentine in natural systems. This is in accordance with their similar RAMAN spectra (Fig. 3) that attest to a structural short-range similarity between these two microstructures, even if a minimum trivalent substitution of 0.1 \( \text{apfu} \) seems to be required for polyhedral serpentine, whereas lizardite can be purely magnesian. On the other hand, the faceted morphology of polyhedral serpentine results from an unusual regular bending of layers along the (010) direction (Baronnet et al., 2007) that may correspond to a long-range dissimilarity. This has also been proposed by Fuchs et al. (1998) when comparing lizardite and chrysotile. Previous work on other sheet silicates shows that the minimum energy structure corresponds theoretically to an ordered distribution of cations that tend to mix and are maximally dispersed in the structure (Sainz-Diaz et al. 2003). However, clay minerals synthesized with different proportions of \( \text{Al}^{3+}, \text{Fe}^{3+} \) and \( \text{Mg}^{2+} \) reveal a clustering tendency when the temperature decreases to below \( \sim 150–200 \) °C (Decarreau et al., 1992), in agreement with natural observations of low-temperature clay minerals (e.g. Manceau & Calas 1985). These cations can display various arrangements in the octahedral sheet: \( \text{Al}^{3+} \) and \( \text{Fe}^{3+} \) tend to mix, whereas \( \text{Mg}^{2+} \) and \( \text{Fe}^{3+} \) or \( \text{Mg}^{2+} \) and \( \text{Al}^{3+} \) tend to segregate.
Polyhedral serpentine

(Decarreau et al., 1992; Grauby et al., 1993), which separates dioctahedral from trioctahedral components. In the proposed temperature range for polyhedral serpentine formation, clustering of trivalent cations can be expected. This should lead to creation, locally, of dioctahedral environments within the tri-octahedral structure of serpentine that may explain the regular specific bending along (010). Indeed, in equivalent dioctahedral minerals such as halloysite, bending usually occurs along (010) (Giese, 1991). Scanning TEM mapping of a 15-sector polygonal serpentine by Uehara & Wicks (2006) illustrates such potential chemical heterogeneity within serpentine microstructures on a nanometric scale.

The last parameter in common for the occurrence of polyhedral serpentines is system openness, since they preferentially form in open fractures or in the space between clinopyroxene exsolution lamellae. The degree of system openness, controlling the water-to-rock ratio and residence time of the fluid, affects topotactical relationships and has already been proposed as a parameter determining the mode of pyroxene alteration (Le Gleuher et al., 1990) and of serpentinization in general (Baronnet & Boudier 2001). Pseudomorphosis occurs via solid-state reactions under a reduced water-to-rock ratio and usually favors the formation of oriented flat lizardite or other sheet silicates at the interface. These conditions may prevent spherical polyhedral serpentine from forming despite the availability of Al, Fe or Cr (especially in pyroxenes). If polyhedral serpentine does not crystallize in tight environments, lizardite crystals can fill open veins (Viti & Mellini 1997; Andreani et al., 2007) under T conditions similar to those favoring polyhedral serpentine, but are poorer in Al (last hydrothermal vein generation; Andreani et al., 2007).

In summary, it seems that the three parameters mentioned below, i.e. 1) low T conditions, 2) the presence of trivalent cations (Al³⁺ in this study), and 3) system openness, are required to form polyhedral serpentines.

Nucleation and growth

Polyhedral serpentine grains are locally embedded in relics of a poorly-crystallized proto-serpentine (Fig. 7B, C), consisting of small crystallites made of a few serpentine layers (Fig. 8). These observations suggest that polyhedral serpentine grows from the proto-serpentine in which the nanometer crystallites of serpentine can act as nuclei. Similar materials have already been observed in nature as precursors of: i) crystallization of fibrous serpentine in veins (Andreani et al., 2004), ii) lizardite formation during the first stage of non-topotactic olivine serpentinization (Rumori et al., 2004), and iii) the last stage of non-topotactic orthopyroxene alteration (Viti et al., 2005). The presence of a short nanotube in the center of some polyhedral serpentine grains suggests that short chrysoctyles can appear first and serve as a nuclei to either polygonal or polyhedral serpentine. Nonetheless, both thin curved crystallites and wider flat serpentine layers are observed within the proto-serpentine (Fig. 8). Thus, polyhedral serpentine may be able to form directly from these short-range ordered particles without tubular nuclei. This proposition is also reinforced by SEM images of well-developed partial domes (Fig. 7D) that display an empty interior without evidence of a central tube. Polyhedral serpentine nucleation can also be assisted locally by a substrate such as clinopyroxene exsolution lamellae, if available (Fig. 4). The observed linear increase in edge size with polyhedral grain diameter suggests that the number of facets remains constant during growth and is probably determined very early in the growth history of the mineral. Radial development is accommodated by a layer-by-layer mechanism with the nucleation of a thick series of layers (Fig. 7E). They then grow laterally in the (001) plane with regular bending at facet edges until they cover the whole grain surface and form partial polyhedral caps. Proto-serpentine and its transformation products have similar chemical compositions (Table 1) that attest to its isochemical evolution. Our observations show that spherical polyhedral serpentine is the final product of proto-serpentine transformation, i.e. the most stable product (Ostwald step rule) under these conditions. The two possible evolution scenarios (1) and (2) probably reflect local kinetic heterogeneities, with chrysotile being occasionally a metastable intermediate (cf. review in Evans, 2004):

1) proto-serpentine → chrysotile → polyhedral serpentine
2) proto-serpentine → polyhedral serpentine.

The characteristics of proto-serpentine (potential high water content, homogeneity, low crystallinity) are very similar to those of a gel, which is defined as a substance of colloidal dimensions that contains a continuous solid skeleton (polymers or aggregates linked together to form a network) enclosing a continuous liquid phase (cf. Brinker & Scherer 1990). A gel is amorphous, which is not the case for the proto-serpentine; however, proto-serpentine can represent the first stage of reorganization of a “gel-type” phase into serpentine domains. This suggests that polyhedral serpentine could crystallize as a result of a “gel” ageing process rather than direct crystallization from a solution. This recalls the development of lizardite at the expense of olivine in mesh texture studied by Rumori et al. (2004). Similar phenomena were observed in an experiment concerning the hydrothermal synthesis of spherical kaolinite from aluminosilicate gels (Fiore et al., 1995; Huertas et al., 2004). The authors describe a first stage of in-situ transformation of the gel accompanied by the production of metastable spherical particles in amounts not correlated with the saturation degree of the solution (Huertas et al., 1999; 2004). Diffusion-controlled growth may be dominant in gels (Henisch, 1970). Nevertheless, assuming a H₂O-enriched precursor phase, serpentine crystallization should lead to a release of excess water and an increase in porosity. This would be consistent with the porous final texture. Consequently, the diffusion-controlled growth of serpentine crystals may evolve gradually toward a surface-controlled process in solution.

The hypothesis of a “gel” precursor to polyhedral serpentine crystallization is of particular interest with regard to the observed effect of trivalent cations on its occurrence.
Studies on multicomponent gels show that molecular scale homogeneity, linked to element coordination, is influenced by the physico-chemical conditions (essentially $T$, pH and salinity) during gel formation and that the different elements can be more or less uniformly incorporated (cf. Brinker & Scherer 1990 and references therein). Satokawa et al. (1994) propose that the morphology of synthetic kaolinite can be attributed to the structure of the starting gel material, which is mainly controlled by the pH in their experiments. This suggests that in the case of a gel phase precursor, pH conditions may also initiate a specific distribution of the trivalent cations in the first stage of gel transformation that may favor polyhedral serpentine formation, in addition to the low T conditions invoked in the preceding part (Decarreau et al., 1992). The available experimental data on aluminous phyllosilicates cannot be directly applied to magnesian systems. Thus, experimental studies on the respective roles of pH and $T$ in magnesian gel transformation may help constrain cation ordering during hydrothermal crystallization of serpentine.

**Significance for geological processes in serpentinites**

In the case of oceanic-type serpentinites, i.e. samples from the Atlantic (MARK) and the Alps, polyhedral serpentine formation is clearly linked to the last stage of hydrothermal alteration observed in pyroxene and veins. The chemical composition of these veins is slightly different from that of the host rock since polyhedral serpentines are systemati
cally enriched in trivalent cations. The chemical study of the MARK area by Andreani et al. (2007) shows that veins of polyhedral serpentine accompany the last stage of peridotite hydration with a dominant contribution of Al/Fe/Cr-rich magnesian minerals such as pyroxenes and spinel (chromite). Transfer of these elements to the vein can occur via diffusion from the host rock and/or via an advecting fluid enriched in trivalent cations. The smoothed margins of these veins (e.g. Fig. 2C) suggest that the host rock has undergone dissolution and that these veins represent ancient fluid pathways. Thus, polyhedral serpentine veins form in two stages, i.e. dissolution and precipitation. In oceanic settings, this can be related to changes in fluid properties due to depth variation and/or reactions with host rocks along its course. Crystallization in open veins usually forms blocky textures with one stage of nucleation on the margins and subsequent growth in solution. Growth competition is also a characteristic of such veins, which leads to a preferred orientation of grains perpendicular to the margins (e.g. Oliver & Bons, 2001). This does not correspond to the highly homogeneous crystallization texture of polyhedral serpentine, which requires either several stages of nucleation linked to incremental opening of the vein or distributed grain nucleation in an isotropic media. The first hypothesis would result in a zoned or banded crystallization texture across the vein, which is not the case here. Similar homogeneous textures are formed by spherulitic grains resulting from crystallization of viscous magmas at a high degree of supercooling or from devitrification of glasses (e.g. Keith & Padden 1963; Lofgren, 1971). Under hydrothermal conditions, a hydrous “gel-type” phase is a more appropriate isotropic precursor than a glass. These textural criteria reinforce the hypothesis of a “gel” precursor for polyhedral serpentine crystallization, as proposed in the previous section. Gels are seldom observed in nature, but experiments have suggested that siliceous gels may result from different processes such as: i) weathering of volcanic glasses, marked, for example, by allophane formation in volcanic soils (Wada, 1989), ii) hydrothermal alteration of crystalline silicates through formation of an amorphous leached layer (e.g. Hellmann et al., 1990), and iii) rapid precipitation from high-concentration hydrothermal fluids undergoing a sudden drop in temperature (e.g. Oehler, 1976; Herrington & Wilkinson, 1993). Processes ii) and iii) can be considered in our settings. According to the low solubility of phyllosilicates, instantaneous filling of a vein (as in iii), even with a low density phase, would not seem realistic with the limited amount of matter carried by the fluid in the vein. Instead, we propose a gradual process of dissolution at the margins, similar to ii), which can lead to a “gel” diffusive layer containing elements from the dissolved host rock and from the moving fluid. In the hypothesis of a water-enriched “gel”, this latter should occupy a larger volume than the corresponding dissolved rock, allowing gradual filling of the vein. Then, recrystallization of the “gel” into proto-serpentine and polyhedral serpentine would be accommodated by diffusive mass transfer between the host serpentine and the vein.

In the particular case of Californian samples, the proximity of the active Santa Ynez fault and presence of polyhedral serpentine veins along fault planes suggest a possible role of slip in the formation of these veins. This point requires a specific study that is beyond the scope of this article. Note, however, that silica gel layers have been described along fault planes in high-speed slip experiments (> 0.01 m s$^{-1}$) under humid conditions (Goldsbey & Tullis 2002; Di Toro et al., 2004). Such a layer leads to the abrupt decrease in shear strength at near-seismic slip rates. The hypothesis of a gel precursor to polyhedral serpentine formation may have implications on our understanding of coseismic processes in serpentinites. Such a gel-type phase may result, under these conditions, either from partial dehydration of the serpentine background or by high-pressure fluid injection along faults. Recrystallization into polyhedral serpentine creates a layer of sub-spherical serpentine grains on the fault plane, with mechanical properties that are still unknown.

**Conclusions**

Polyhedral serpentine is ubiquitous in serpentinites from various settings such as slow-spreading ridges, ophiolites, ultramafic remnants in subduction complexes and meteorites. The general lack of polyhedral serpentinite reported in previous serpentine studies probably results from the wide variety of their textures, easily confused with lizardite lamellae or large polygonal serpentine under both petrographic and transmission electron microscopes.
The wide field of investigation of this study in terms of serpentinite deposits made it possible to determine the three main factors controlling the formation of polyhedral serpentine in natural settings: 1) open space, 2) a relatively low temperature (T < 200–300 °C), and 3) the presence of trivalent cations with a minimum value of 0.1 apfu μ-XANES data show that Fe is ferrous in our samples. Thus, Al³⁺ is the only trivalent cation and polyhedral serpentine cannot be systematically used as a marker of oxidizing conditions. By analogy with experimental synthesis of other phyllosilicates, the low temperature conditions of polyhedral serpentine crystallization should favor segregation of trivalent cations during their incorporation in the sheet structure. This would result in the creation of a dioctahedral environment within the trioctahedral structures of serpentine, and may explain the bending along (010) at facet edges. Our results also indicate that polyhedral serpentine grows from a poorly-crystallized material (proto-serpentine) made of flat or slightly curved 7 Å-periodicity crystallites that act as nuclei to polyhedral serpentine which develops closer to equilibrium. Structural and textural criteria suggest that proto-serpentine may represent the first stage of reorganization of a “gel-type” phase that could form by alteration of vein margins during hydrothermal fluid circulation, and possibly during slip on serpentine fault planes. Polyhedral serpentine could therefore be the final product of a gel transformation process rather than the result of a direct crystallization from a supersaturated solution.

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