Cation-deficient phlogopitic mica exsolution in diopside from garnet peridotite in SuLu, China

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Abstract

Deep subduction and return to the surface of sediments and other continental rocks is now well known, forming terranes of ultrahigh-pressure metamorphism (UHPM). A common constituent of these terranes is garnet peridotite, mantle rock that has been brought to the surface along with the returning subducted material. Microstructures of these peridotites, especially precipitates within their constituent minerals, offer promise of providing information not only about their depth of origin but also about the subduction environment. Here we report exsolution lamellae of cation-deficient phlogopitic mica within diopside of a drill core from the UHPM terrane of SuLu, China. Detailed analysis by transmission electron microscopy (TEM) shows these precipitates to be phlogopitic mica that is highly complex (both structurally and compositionally), with a significant component of the 10 Å phase, a talc-like phase stable only at quite high pressures. Several mica polytypes are present, the simplest one, 1M, being the most cation-deficient. The presence of a significant (~30%) 10 Å phase component in the mica suggests a means of expanding the 10 Å phase “bridge” for subduction of H₂O to deep mantle depths.

1. Introduction

1.1. General background

The presence of exsolution features in the major phases of exhumed mantle rocks in regions of continental collision and ultrahigh-pressure metamorphism (UHPM) has been very important in determining their origin (Dobrzhinetskaya et al., 1996; van Roermund and Drury, 1998; Bozhilov et al., 1999; Song et al., 2004; Song et al., 2005). One significant aspect of such studies is that they may allow to trace the history and behavior of volatile components such as hydrogen and potassium under mantle conditions. The major components of mantle peridotite such as olivine, garnet, and pyroxene have been reported to accommodate moderate amounts of hydrogen and potassium in their structure under mantle conditions (Skogby and Rossman, 1989; Bell and Rossman, 1992; Harlow, 1997; Matsyuk et al., 1998; Harlow and Veblen, 1991; Katayama et al., 2000; Bindi et al., 2002; Skogby, 2006). One evidence of such incorporation of volatiles is formation of exsolution lamellae of phlogopite in clinopyroxene from marbles and pyroxenites which has been reported from the diamond-bearing UHP terranes of the Kokchetav massiv, Kazakhstan (Katayama et al., 2000; Ogawara and Aoki, 2005) and Erzgebirge, Germany (Schmadicke and Muller, 2000).

Another possibility of subduction of significant amounts of H₂O into the deep interior of Earth can be envisioned through carriers such as the 10 Å phase in peridotite. The 10 Å phase has mica structure and the composition of talc+H₂O, with the extra water residing in the interlayer site that is empty in talc but contains large monovalent cations in micas (Fumagalli et al., 2001; Comodi et al., 2005). Although the 10 Å phase has only been described from natural rocks as alteration of nanocrystalline inclusions in olivine (Khishina et al., 2001), it is well known in experiments (Poli and Schmidt, 2002; Fumagalli and Poli, 2005). Due to the close structural similarity between the 10 Å phase and K micas, one could expect potentially significant solid solution between these phases. Such a mixed phase could scavenge much of the K and H₂O in mantle rocks in which it appears and thus affect the balance and dynamics of volatiles in the mantle.

In this study we provide detailed structural and compositional characterization of phlogopitic mica exsolution in diopside from a garnet peridotite from SuLu, China. This ultra-high-pressure metamorphic (UHP) terrane in Eastern China has attracted strong interest because it represents an extensive exposure of continental rocks involved in plate collision, consequent subduction to more than 100 km (Yang and Jahn, 2000; Zheng et al., 2006), followed by return to the surface including transport of mantle garnet peridotite bodies into crustal conditions.
1.2. Polytypism in micas

Micas are characterized by their sheet structure where two tetrahedral (T) layers enclose an octahedral (O) layer and the whole packet is denoted as T–O–T layer, also known as 2:1 layer (Bailey, 1984, Ferraris and Ivaldi, 2002). The negatively charged 2:1 layers are joined together to form the mica structure by enclosing positively charged ions between them, known as interlayer cations (A). Thus, the mica structure can be described by the general formula AM$_2$–3T$_4$O$_{10}$X$_2$, where A is usually K, Na, or Ca; M=Mg, Fe, Al; T=Si and/or Al; and X=(OH), F, Cl, O.

Polytypism is a structural modification of layered structures, where the two-dimensional translations within the layers are preserved and modifications occur as differential stacking sequences along the third dimension. The pseudo-hexagonal symmetry of the tetrahedral sheets in micas stipulates that alternative stacking between the successive T–O–T packets is possible. The different stacking is expressed as relative rotation of the adjacent layers by multiples of 60° (Nespolo and Durovic, 2002).

Based on the mutual rotation between the 2:1 packets, mica polytypes are classified into three types: subfamily A, where angles of rotations are 2n×60°; subfamily B, where rotations are 2n+1×60°, and mixed, where both types A and B occur.

Polytypism in micas can be rationalized by describing the shift that occurs between adjacent 2:1 layers in projections onto the basal plane (001), when 2:1 layers with different orientations are stacked together (Fig. 1). The corner sharing SiO$_4$ tetrahedra form pseudo-hexagonal rings. This pseudo-symmetry allows for different stacking of the tetrahedral sheets by multiple rotations of 60°. Due to size mismatch of the tetrahedral and octahedral sheets the symmetry of the rings is not perfectly hexagonal thus the rotations are associated with mutual displacement of the rings. The projections of the displacement vectors on the (001) plane are used to characterize the structural shifts. These vectors, known also as Z symbols (Zvyagin, 1962; Zvyagin et al., 1979; Zhukhlistov et al., 1990), or OD symbols (Dornberger-Schiff, 1964) are denoted 1, 2, 3, 4, 5, and 6 according to the multiplicity (n) of rotation (n×60°) (Fig. 1) and they allow the polytypes to be described as a sequence of Z symbols representing the stacking sequence of adjacent layers.

1.3. TEM analysis of polytypes

Using HRTEM imaging, the lattice stacking of a mica crystal can be resolved and detailed polytype analysis can be performed (Amouric et al., 1978; Iijima and Buseck, 1978). From a topological point of view, two distinct general directions can be defined to rationalize the TEM
analysis: the first is $<100>-<110>-<1\overline{1}0>$ which pass through the corners of the tetrahedra, and $<010>-<310>-<3\overline{1}0>$, which pass through the centers of the tetrahedra (Fig. 1a). In the TEM, the polytype analysis is performed by imaging normal to $c^*$ and parallel to each of the special directions $<100>-<010>$. The stacking vector can be determined from the tilt of the vectors connecting equivalent points of adjacent 2:1 packets along the $c$ axis.

As shown in Fig. 2, the tilt between adjacent layers is related to the stacking vectors and each vector can be identified reliably by imaging the same crystal along two general directions. Table 1 summarizes the possible angles and sense of tilt as seen along selected directions. This approach has been successfully applied in several studies of mica polytypes (Amouric et al., 1978; Iijima and Buseck, 1978; Amouric and Baronnet, 1981; Konishi and Akai, 1991; Baronnet et al., 1993; Xu and Veblen, 1995; Kogure and Nespolo, 1999; Kogure and Banfield, 2000; Kogure and Nespolo, 2001; Kogure, 2002). The approach is demonstrated on a simulated HRTEM pattern of 2M$_1$ mica polytype shown in Fig. 3.

2. Experimental methods

The samples were prepared as standard polished petrographic thin sections. For the SEM study we have utilized an FEI-Philips XL30-PEG instrument equipped with an EDAX® EDX microanalyzer at 15 kV accelerating voltage.

The samples for the TEM study were prepared by the focused-ion-beam technique, using an FEI DuoBeam instrument and were studied at an accelerating voltage of 300 kV using an FEI-Philips CM300 TEM (objective twin-lens with spherical ($C_s$) and chromatic ($C_c$) aberration coefficients of 2.0 mm, LaB$_6$ cathode, double-tilt and rotational low-background specimen holders). Selected area electron diffraction (SAED) patterns and high-resolution (HRTEM) images were obtained from the areas of interest in order to study their structure and defects. The HRTEM images were obtained with a 50 µm diameter condenser aperture, effective objective aperture radius of 0.86 nm$^{-1}$, and beam convergence angle of 0.9 mrad. Images were recorded digitally using a Gatan 794 MultiScan CCD camera and GMS™ version 1.4 software. HRTEM image interpretation is based on comparison with published data and image simulation, which was performed using the MacTempas software version 2.1 for Mac OS X.

The compositions of all studied crystals were determined quantitatively by analytical electron microscopy (AEM) utilizing energy-dispersive X-ray spectroscopy (EDS) in the CM300 TEM operated in nano-probe mode and equipped with an EDAX Phoenix energy-dispersive spectrometer with Si(Li) detector and super-ultrathin window, which allows detection and quantification of light elements such as oxygen. The spectra were acquired with effective spot size diameter about 20 nm for 50 to 100 s. To determine the composition of the thin lamellae, the slightly defocused electron beam was distorted to elliptical shape with the condenser stigmators so that the signal was collected only from the area of interest thus minimizing the contribution of the surrounding matrix and still keeping the beam in slightly defocused state in order to minimize rapid beam damage to the specimen and prevent diffusion of the constituents. Details about the procedures for performing the EDS analyses in the TEM have been described already (Bozhilov et al., 2007).

To verify the AEM procedure, 25 EDS spectra were collected and analyzed from a standard phlogopite crystal. The measured concentrations of the major elements were close to the standard concentrations. The sum of the octahedral and tetrahedral cations was within 3.5% of the known values and the calculated total charge balance was always within 4% of the standard value of 0.1.

Raman characteristics were obtained with the aid of a Renishaw RM-2000 instrument at the Institute of Geology, Chinese Academy of Geological Sciences, with a confocal microscope and a 50× lens objective, giving a 1 µm sample footprint at the specimen. The laser excitation was achieved using an argon ion laser providing radiation of wavelength 514.5 nm and spectra were recorded at 2 cm$^{-1}$ resolution at several points on each measured grain in order to ensure representative signals from the heterogeneous area. Spectral accumulation times were of the order of 100 s.

Trace element analysis for B and Li was conducted by secondary ionization mass spectrometry (SIMS) using the Cameca IMS1270 ion microprobe at the University of California, Los Angeles (UCLA). Boron and Li measured intensities were normalized to $^{29}$Si. Concentrations were computed using relative sensitivity factors determined from interspersed analysis of NIST SRM 610 (Kasemann et al., 2001). Spots of diameter of about 10 µm were analyzed on petrographic thin sections of the diopside host containing mica lamellae. The concentrations in the mica lamellae were determined by comparison with analyses of the diopside host concentrations and correcting for the contribution of the host. Based on the external reproducibility on NIST SRM 610 and counting statistics of unknowns, we estimate relative

Table 1

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Negative angles denote tilt to the left, positive ones to the right (modified after Kogure, 2002).
Fig. 4. Micrographs of polished sections of garnet peridotite from a drill core from the Maobei locality. (a) Reflected light optical micrograph showing multiple diopside (Di) crystals (arrows) embedded in a large garnet crystal (light grey to white) which is surrounded by olivine and orthopyroxene. (b) Transmitted light optical micrograph of another diopside (Di) crystal in a garnet (Grt) matrix showing abundant topotactically oriented mica inclusions appearing as fine lamellae. (c) Back-scattered electron image of oriented mica lamellae (dark) in diopside host crystal.

uncertainties in trace element concentrations to be better than ~20% for Li and B.

3. Results

The host rock is a very fresh garnet peridotite from the first “pre-pilot” hole (PP-1) drilled in the Maobei locality of the SuLu ultra-high-pressure metamorphic (UHPM) belt of eastern China in preparation for the recently completed Chinese Continental Scientific Drilling (CCSD) project near Donghai that now provides 5.13 km of core (Xu et al., 2005). Fig. 4a shows a large garnet that is intricately intergrown with diopside crystals (0.5–1.5 mm diameter) which, in turn, exhibit oriented lamellae (0.5–2 µm thick by 5–20 µm diameter) of a micaceous phase along (100) planes of the diopside host (Fig. 4b,c), showing topotaxy (100)_{diopside}//(001)_{mica} (Fig. 5). The abundance of the lamellae in the diopside host, as estimated from optical and scanning electron microscopy, varies from 0.1 to 1 vol.%. The orthopyroxene, and clinopyroxene from the garnet peridotite which are not enclose silicates other than diopside. Examination by transmission electron microscopy (TEM) shows that the lamellae are interstratified trioctahedral 2:1 phyllosilicate polytypes with varying degrees of disorder and containing abundant stacking defects. Electron diffraction and high-resolution imaging reveal domains of 200 nm to 2 µm in size perpendicular to the layers with variable stacking disorder along the c⁎ axis, expressed by the typical streaking along c⁎ of hkl reflection rows for which k≠3n (Fig. 5).

Polytypes with different stacking are present, including the basic 1M polytype (Fig. 6). The unit cell parameters of the most abundant 1M polytype determined by selected area electron diffraction are: a=0.53 nm, b=0.92 nm, c=1.01 nm, β=99.5°, which is consistent with mica structure, as well as the 10 Å phase (e.g. Comodi et al., 2005). Fig. 6 gives the following cell parameters for the pure 10 Å phase: a=0.5323 (1 nm), b=0.9203(1) nm, c=1.0216(1) nm, β=99.98(1)°). Extraction of a number of lamellae from the diopside host (unavoidably contaminated by diopside) and examination by micro X-ray powder diffraction confirmed the prominent 1.0 nm d-spacing. HRTEM imaging confirms that no inter-stratification with talc, chlorite, or any other non-2:1 sheet silicate is present. SAED patterns along directions of type <010> show that reflection rows with h≠3n and k=0 (mod 3) are sharp (Fig. 6d), which suggests that the stacking disorder is due to layer rotations mostly of ±120° and ordered and disordered domains belong to subfamily A polytypes. In addition to the most abundant 1M polytype, two long-period

Fig. 5. (a) Dark-field TEM image of mica (Mc) lamellae in diopside (Di) host. (b) [100] zone axis SAED pattern in diopside taken at the interface between mica and pyroxene revealing the topotactic orientation of the lamellae with interface parallel to the (100) in diopside. (c) [100] zone axis SAED pattern of a mica lamella demonstrating heavy streaking of reflection rows (marked) for which h≠3n and k=0 (mod 3), due to the presence of stacking disorder parallel to c⁎.

Fig. 6. Dark-field TEM micrograph and SAED patterns from mica lamellae. (a) Micrograph showing the inter-stratification of 15M and 1M mica domains. Regions with disordered mica structure are indicated by arrows. (b) SAED pattern along [100] in 15M mica polymorph, indexed in the 1M framework structure. (c) The 15-fold periodicity is clearly visible on magnified portion of the 02I reflection line. (d) [310] SAED pattern of the same crystal as (a). No streaking or splitting of reflections is visible, suggesting type A polytype. (e) SAED pattern along [100] taken from the 1M part of the crystal showing no streaking of reflections, which represents a perfect 1M 2:1 phyllosilicate structure.
Polytypes were observed which occur as domains interstratified with the basic 1M polytype and disordered domains (Figs. 6, 7, 8). The identified two long-period polytypes correspond to the 15M (Fig. 7) and 12M (Fig. 8) mica structure respectively. The 15M polytype is revealed to form narrow domains, which form thin lamellae with dimensions of 75 to 250 nm along \( c^\ast \), several microns along directions perpendicular to the \( c^\ast \) and they transect the entire mica crystal and are randomly intergrown parallel to (001) with 1M and disordered domains. (Fig. 6a). Detailed HRTEM imaging along [100] and [110] allowed the exact stacking sequence of the 15M polytype to be revealed which can be expressed as the following stacking sequence of \( Z \) vectors:

\[ ...222264264264264... \]

... corresponding to a unit cell length along the \( c \) axis of 151 Å (Fig. 7).

The 12M polytype (Fig. 8) shows occurrence and microstructure similar to that of the 15M polytype although they are not observed together in the same mica crystal. Uninterrupted 12M sequences form domains which extend from 36 to 360 nm along \( c^\ast \). As with the 15M sequences, they are intergrown with 1M polytype domains and disordered structure. The stacking sequence was revealed only partially because interpretable HRTEM images of the same region along two of the major directions could not be obtained. SAED patterns along \( <01\overline{0}> \) type directions (Fig. 8b) establish that streaking of reflections is absent, suggesting that again only rotations multiple of 2\( \times \)60° are present and only even \( Z \) vectors are present. Because interpretable HRTEM imaging could be obtained only along one zone axis, the exact \( Z \) vectors could not be determined. The stagger of the layers is represented by the sequence:

\[ ...222264264264264... \]
... + − + + + + − + + + − ... where +, −, and 0 represent the tilt of the layers clockwise, counterclockwise and 0 respectively as observed along [110] from the normal to c\(^\parallel\), which is due to stacking of layers with mutual rotations of \(±120^\circ\).

Analytical electron microscopy (AEM), consisting of energy-dispersive X-ray analysis in the TEM, cannot detect hydrogen, hence chemical analysis by this technique must be determined on a volatile-free basis. Such analysis yields compositions close to phlogopite with slightly different composition for the 1M form and the long-period polytypes. The average composition of the long-period polytypes and the interstratified disordered domains obtained from 37 spot analyses and normalized to 11 oxygen atoms is:

\[
Na_{12,(4)}K_{5.74(5)}(Mg_{2.73(11)}Fe_{0.11(5)}Al_{9.06(6)}Cr_{0.02(2)}\cdot Ti_{0.02(2)})/(Si_{12.90(10)}Al_{11.06(6)})O_{11}
\]

(1)

which sums to a total negative charge deficit of \(-0.1(5)\) per formula unit (pfu) out of 22 total charges and 86(8)% of total interlayer site occupancy. The numbers in parentheses represent the standard deviation calculated from the population of all 37 analyses. On the other hand, the regular 1M structure shows a small but significant difference in composition from 28 spot analyses, especially in K, implying significant interlayer vacancies:

\[
Na_{12,(4)}K_{5.74(5)}(Mg_{2.62(6)}Fe_{0.10(5)}Cr_{0.03(3)}\cdot Ti_{0.02(1)})/(Si_{12.84(7)}Al_{11.06(3)})O_{11}
\]

(2)

The interlayer site occupancy is only 69(9)% with a negative charge imbalance of \(-1.0(8)\) charges. This formula shows that, within the analytical uncertainty, the two compositions cannot be reliably distinguished in charge imbalance except interlayer site occupancy, which is statistically lower for the ordered 1M structure.

The apparent charge deficiency raises the possibility that the structure incorporates extra H\(^+\) ions or that there are other undetected positive cations present such as Li\(^+\), Be\(^{2+}\) or B\(^{3+}\). Because the utilized EDS technique cannot measure reliably low concentrations of elements with atomic number smaller than carbon, we performed Secondary Ion Mass Spectroscopy (SIMS) to investigate whether the possible charge deficiency is compensated entirely by hydrogen or whether there could be significant presence of Li or Be. The SIMS measurements for both elements in the mica lamellae revealed concentrations of \(\sim 3\) ppm which are similar to (and for Be even lower than) the corresponding concentrations measured in the diopside host, hence the electrostatic balance of the structure must be achieved by excess hydrogen or by O\(^{2-}\) vacancies. In contrast to Li and Be, no analytical determination of Be was attempted. Based on the general similarity of the geochemical behavior and abundance of Li and Be and the extremely low concentrations of Li in the diopside host, it is highly unlikely that significant Be contents are present in the host and/or inclusions. Furthermore, because WDS microanalysis can detect appreciable amounts of Be, the compositions reported in the literature for the major and accessory minerals from the Donghai peridotite can serve as a reliable indicator for the lack of significant Be in the peridotite of interest.

Unlike the presence of Li and Be, for which even qualitative analysis could provide significant information, determining the concentration of hydrogen is more challenging because only a high precision quantitative result will answer properly the question of the potential excess hydrogen content. The theoretical hydrogen content in the form of (OH) groups in end-member phlogopite amounts to 0.48 wt.%. Hypothetically, replacing 30% of the interlayer K\(^+\) by H\(^+\) would cause increase of hydrogen to 0.57 wt.%, which is about 19 wt.% difference; populating the vacant 30% interlayer sites with H\(^2+\) will increase the hydrogen content to 0.71 wt.% which would be 48 wt.% difference. We estimated that such precision in determination of the hydrogen concentration by SIMS could not be achieved due to the inherently low precision of H analysis by SIMS (±10% at best (Ottolini et al., 2002), coupled with the fact that a reference element is not straightforward to choose because the lamellae are small and invariably an unknown amount of diopside matrix will be analyzed and, in addition to this, the Si content in the mica is also variable. On top of these uncertainties, one needs to consider that there are strong orientation effects (±25%) in SIMS analysis of mica (Ottolini et al., 2002) that cannot be corrected for reliably when analyzing such small lamellae. All of these considerations led us to preclude the expensive attempt of analyzing hydrogen directly. Nevertheless, hydrogen is the only reasonable explanation for the observations.

4. Discussion

4.1. Lamellae origin

The origin of the mica lamellae in the diopside host could be due to three possible mechanisms of formation: (i) simultaneous growth of mica and diopside; (ii) replacement of diopside by mica; (iii) exsolution of mica from the diopside host.

The first scenario is highly unlikely because it requires that the garnet matrix trapped melt or fluid inclusions, which later crystallized together. This is very improbable because no diopside and mica topotactic intergrowths are observed outside the garnet host. Even if this unlikely event took place, the microstructures still do not support simultaneous growth because mica crystals would be expected both outside and inside the diopside host but only inclusions are observed, and simultaneous growth usually does not lead to topotactic orientation of the growing phases.

The second possibility, replacement, is not supported by the observed microstructures either. No clear cracks or micro-veins that could have been the potential supply routes of the volatiles such as water and potassium are observed. Furthermore, such replacement of diopside by volatiles also should affect the other early phases and it is established that pyroxene crystals not enclosed in garnet do not develop topotactically oriented mica lamellae. Also, hydrous replacement of pyroxene usually proceeds along the tetrahedral chain direction, causing formation of clearly extended narrow lamellae intersecting most or the entire host and such structures are not observed here. Instead, the lamellae are short compared to the size of the host crystals.

The third scenario, exsolution of mica lamellae from a diopside host rich in volatiles such as hydrogen and K is consistent with the observed microstructure in all respects.

The metamorphic trajectory of the SuLu UHPM rocks (Wang et al., 1992; Liou et al., 1997; Liou et al., 2002; Zhang and Liou, 2003) shows that they were exhumed along a pathway of high ratio of P/T, hence the exsolution nature of the lamellae indicates that the diopside host formed at higher pressure, consistent with current knowledge that the solubility of K and H\(_2\)O in diopside increases with pressure (Shatsky et al., 1995; Harlow, 1997). There has been a report of low temperature and pressure occurrence of high K diopside in a low grade metamorphic terrane (Tsujimori and Liu, 2005) but any attempt to explain the observed microstructure by hydrothermal crystallization would suggest that the exsolution feature is due to a prograde metamorphic event which is not consistent with the regional setting of this body and furthermore it cannot explain the lack of hydrothermal textures of the garnet host and its enclosed diopside. If a prograde event were to have existed that wiped out the hydrothermal textures by recrystallization, it would also have removed the evidence of exsolution.

4.2. Interlayer cation deficiency

As described above, the structural and compositional data of the 1M polytype are consistent with phlogopitic mica with about 30% (±10%) interlayer cation deficiency. Interlayer cation-deficient micas
are not uncommon but they usually are dioctahedral micas such as muscovite and illite or Na-rich mica such as wonesite. In many cases, interlayer-deficient Mg-rich trioctahedral micas have been interpreted as containing a talc component (Grochau and Johannes, 1997), which also has been justified by IR measurements (Wunder and Melzer, 2002). Such an interpretation is well justified in the stability field of talc but under upper mantle conditions it is more realistic to expect that the high P and T analog of the talc component, namely the 10 Å phase, is present. If one were discussing solid solution in the abstract, one could talk about talc and the 10 Å phase interchangeably. However, our study takes place at the atomic level; we have verified the complete absence of talc within these lamellae, hence it is more reasonable to cast the discussion in terms of the 10 Å phase. If one were discussing solid solution in the abstract, one could talk about talc and the 10 Å phase.

By ignoring minor elements such as Na, Fe, Cr, and Ti, the combined structural and chemical data for the 1M polytype in this study can be represented as approximately as idealized solid solution in the system K₂Mg₈Si₄AlO₁₀(OH)₂. Structural and chemical data for the 1M polytype in this study can be represented approximately as idealized solid solution in the system K₂Mg₈Si₄AlO₁₀(OH)₂.

It is interesting that experiments in AI-rich bulk compositions (Fumagalli and Poli, 2005) also have produced AI enrichment of the 10 Å phase but it could not be explained by any valid solid solution mica component and the authors concluded that the AI might be present as chloride-10 Å phase inter-stratification. Such a possibility is excluded in the present case by our detailed HRTEM observations. The interlayer water molecules accommodated into the 10 Å phase can reach between 0.33 to 2.0 pfu according to experimental studies of that phase (Comodi et al., 2005).

The importance of such possibility is that it shows the potential of this phase as carrier of a considerable amount of H₂O into or out of the mantle. Significant hydrogen substitution into the cation sites of this 10 Å-related phase enhances its H₂O-carrying capacity.

Because of the variable H₂O content of the interlayer site in the 10 Å phase, it is an expandable mica (Fumagalli et al., 2001; Comodi et al., 2005). The polishing process used in our laboratory employs a final polish with a high-pH slurry containing colloidal silica. During the preparation of polished sections, larger exsolution lamellae clearly display expansion along cleavage planes, which is not typical for normal mica crystals. In particular, we have verified that the colloidal silica slurry does not lead to expansion of phlogopite. This provides additional information about the presence of a non-phlogopitic component in the phase. Further suggestion for the presence of 10 Å component is shown by comparison of the Raman spectra of this mineral with those of the 10 Å phase and phlogopite (Table 2). Not surprisingly, the correlation of Raman peaks with phlogopite is very high and other peaks show diopside interference, but this mineral also shows a weak peak at 919 cm⁻¹ that is present in the 10 Å phase (909 cm⁻¹), but absent in phlogopite or talc. This peak is associated with Si−O−Si symmetric stretching (Fumagalli et al., 2001).

From all of these observations, we conclude that the mica-like lamellae in the diopside host represent complex mixture of disordered domains and long-period polytypes with composition close to phlogopite and domains with 1M mica structure, whose composition shows significant layer cation deficiency. Within the uncertainty of the chemical analyses, this latter naturally-occurring phase can be interpreted as a solid solution primarily between phlogopite and the 10 Å phase, which has potentially important implications for mantle dynamics and the water content of deep Earth. The recent experimental demonstration that the 10 Å phase can accommodate significant excess AI in the structure (Fumagalli and Poli, 2005) is reflected by the leucophyllite component of the phase reported here. More reliable determination of the water content in such lamellae would have provided stronger evidence for the presence of the 10 Å type component but the small size of the lamellae, low content of the water component, and the large uncertainty in determining absolute hydrogen contents, applying the SIMS method precluded this.

Although discovery of this phase exsolved in diopside of one mantle rock does not prove the existence of a stability regime for this solid solution, the possibility that a relative of the 10 Å phase exists in natural rocks could dramatically affect the constraints currently envisioned on subduction of significant amounts of H₂O into the deep interior of Earth. The 10 Å phase potentially provides a “hydrological” bridge between the stabilities of antigorite and phase A under subduction zone conditions (Poli and Schmidt, 2002), allowing water to be carried to great depths in Earth in warm subduction zones. Our suggestion that the 10 Å phase forms extensive solid solution with K micas may significantly expand such a bridge because it should scavenge all of the K and H₂O in mantle rocks in which it appears and thereby have a significantly expanded stability field, further relaxing the temperature restriction on subduction of hydrous phases.

4.3. Petrologic significance

Thus, in subducting lithosphere, significant amounts of H₂O could be carried across this “bridge” in a phase comparable to that described here, with the K content highly variable, dependent on the bulk chemistry of the rock (see Fig. 1 of Poli and Schmidt, 2002 for subduction context). This could also provide a mechanism for recycling of K back into the deep mantle, with implications for Earth’s thermal budget. Moreover, the microstructural context in which this phase is found suggests that it may have been brought to the surface from depths significantly greater than the stability of mica and the 10 Å phase. Specifically, the presence of the diopside along grain boundaries enclosed in polycrystalline garnet (Fig. 4) suggests that the diopside itself also might be an exsolution product, from supersilicic (majoritic) garnet at very high pressure. Pyroxenes dissolve progressively into garnets between 6 and 15 GPa (Ringwood, 1991) and we have confirmed that decomposition of such majoritic garnets from 14 GPa yields exsolation of diopside along grain boundaries (Dobrzynieckaya et al., 2004). Similar exsolution of enstatite from garnet at lower pressures has been observed in peridotite xenoliths from kimberlite (Haggerty and Sautter, 1990), in peridotite from

<p>| Table 2 |
| Raman peaks (cm⁻¹) of SuLu mica-like lamellae compared to reference minerals (Fumagalli et al., 2001). |</p>
<table>
<thead>
<tr>
<th>SuLu phase</th>
<th>Phlogopite</th>
<th>Talc</th>
<th>10 Å phase</th>
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<td>116</td>
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<td>453</td>
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Norway (van Roermund and Drury, 1998; Spengler et al., 2006) and in our experiments at lower pressures (8–5 GPa) (Dobrzhinetskaya et al., 2004). It is therefore possible that the K and H2O in the mica described here are inherited from an original majoritic garnet, indicating the presence of these components in the mantle transition zone. The dominant minerals of the transition zone, wadsleyite and ringwoodite, exhibit very high solubility of water (Young et al., 1993; Kohlstedt et al., 1996), hence even a small amount of water present in majoritic garnet could indicate a significant bulk content in the parent rock. Such a conclusion must be considered speculative, but our direct observation of a phase known to be important for enabling subduction of significant amounts of H2O to great depth is a significant step forward and points to future direct information on this subject to be gleaned from ultra-high-pressure metamorphic rocks.

4.4. Polytype origin

The origin of the polytypes observed in the phlogopite are more difficult to interpret. There is no uniform theory of polytype formation in micas (Baronnet, 1992; Kogure, 2002; Nespolo and Durovic, 2002), although there is general understanding that most long-period polytypes probably do not possess a strictly-defined thermodynamic field of stability. They usually form aggregates and interstratified intergrowths with common short-range polytypes or disordered structures. Usually, long-period polytypes are considered as a result of the kinetics of growth (Baronnet, 1992; Kogure, 2002). This interpretation has been brought forward as a consequence of prevailing observations that long-period polytypes occur with identical compositions as that of the short-range polytypes they are associated or intergrown with (Ross et al., 1966; Baronnet and Kang, 1989; Baronnet, 1992; Baronnet et al., 1993; Kogure and Nespolo, 1999).

The 12M, 15M, and the interstratified mica crystals enclosed in these pyroxenes from the Sulu garnet peridotite differ from most mica polytype occurrences in that they have on average slightly different composition compared to the 1M phlogopite they are intergrown with, where the 1M polytype has about 20% lower K content. The difference in composition is not very large and its statistical significance is not easy to evaluate, given the inherent imprecision of AEM analyses and the small number of mica crystals analyzed.

Nevertheless, as far as our observations are concerned, it can be speculated that in the Sulu phlogopite the 1M polytype is stabilized by its specific composition. Whether the interlayer cation deficiency is due to interlayer vacancies or the presence of solid solution component with the 10 Å phase structure is of less significance in this aspect because both would lead to stronger local distortions of the tetrahedral and octahedral sites as compared to interlayer sites fully populated by K and/or Na. Such local distortions could reduce the equivalency of the adjacent rotated T–O–T layers, which can restrict the formation of long-period polytypes. The fact that phlogopite with significant interlayer deficiency is stabilized at high pressure (Comodi et al., 2004) can be related to the current observation of interlayer-deficient Sulu phlogopite which also is exsolved at high pressure and temperature. The observed turbostratic stacking and long-range polytypes may be considered as stabilized by either their specific composition or due to kinetics of growth. Kinetic factors, such as growth controlled by screw dislocations, is often cited to explain long-range polytype formation (Baronnet et al., 1981; Baronnet, 1992; Takeda and Ross, 1995; Kogure and Nespolo, 1999). The important detail is that such growth usually occurs during growth from liquid or vapor phase, whereas in the present case we have most probably solid state transformation. The “periodic slip mechanism” (Mardix et al., 1968) for polytype formation has been proposed as the most likely mechanism under the conditions of solid state replacement where interface controlled growth and tectonic disturbances are prominent factors and can cause development of stacking faults. However, the periodic slip mechanism is not likely to cause the development of very long-range polytypes such as are observed here, nor can it account for the observed difference in composition between long-range polytypes and simple ones. Moreover, origin as exsolution lamellae in an undeformed host crystal severely restricts the possibility of slip. Another proposed mechanism for development of long-range polytypes is the Jagodzinski disorder hypothesis (Jagodzinski, 1954) where random distribution of stacking defects is induced and stabilized by local minimization of the free energy induced by variation in composition and local arrangement. The vagueness of this hypothesis makes it difficult to rule out but also renders it non-testable and nonproductive as an explanation.

None of these models easily fits our observations. However, the screw-dislocation model is the only one that seems credible as an explanation for repetition of the long-range sequences observed here. We hypothesize that screw dislocations were introduced into the growing lamellae and they led to the long-range polytypes observed, in an analogous manner to that proposed by earlier workers, except that the ions being assembled into the lamellae arrived at the site by diffusion from the diopside host rather than from a fluid. Such dislocations could have been present in the host diopside and were preferentially used as nucleation sites for the lamellae. Our observation that the 15M and 12M polytypes are formed by successive layer rotations of predominately ±120° about the axis of the hypothetical screw dislocation is also consistent with this argument. If this is the case then there are four different possible scenarios for development of the observed two different compositions and structures.

The first possibility would require primary exsolution and growth of the 1M polytype in solid solution with the 10 Å phase, followed at later stage by replacement of interlayer water molecules by K in selected domains, which were transformed consequently into long-range polytypes and disordered structures by re-crystallization. This might have been caused either by later K infiltration or by differential rate of exsolution of K and H from the host diopside.

The second possibility would be simultaneous growth of two stable mica compositions, one with 1M structure and appreciable amount of solid solution with the 10 Å phase and another with composition closer to phlogopite, which developed the long-range polytypes and the disordered domains by the screw-dislocation growth mechanism. The domains with significant 10 Å phase component could not develop long-range polytypes, although they also might have nucleated under the screw-dislocation mechanism, due to fact that more significant distortions of the interlayer sites caused by the presence of the 10 Å component as mentioned above could not develop stable symmetrically equivalent configurations necessary to form polytypes.

The third possibility is that the primary mica phase exsolved had variable composition presumably controlled by the kinetics of the process and grew by the screw-dislocation mechanism developing long-range polytypes and disordered domains. At later stage, the 1M polytype, which was the stable structure for that specific composition evolved by slow conversion of the metastable original crystals, whereas some of the original long-range polytypes were preserved due to their specific composition.

The fourth possibility involves primary exsolution of K-rich composition that grew under the screw-dislocation mechanism. Later replacement of K by water molecules led to development of the 10 Å phase solid solution and collapse of the long-range polytypes. The water could have come from external sources or from the host diopside caused again by differential rate of release of K and H from the pyroxene structure.

Which one of the four possibilities actually took place is difficult to decide. Some of these hypothetical cases might be tested by experimental synthesis, but they might be impossible to reproduce on laboratory time scale due to the slow kinetics of natural processes. The possibility for unraveling the mystery of the possible scenarios for polytype formation and the variable composition of the mica crystals by thermodynamic considerations also seems remote.
References


