Sodic amphibole exsolutions in garnet from garnet-peridotite, North Qaidam UHPM belt, NW China: Implications for ultradeep-origin and hydroxyl defects in mantle garnets

SHUGUANG SONG,¹,* LIFEI ZHANG,¹ JING CHEN,² JUHN G. LIOU,³ AND YAOLING NIU⁴

¹Key Laboratory of Orogenic Belts and Crustal Evolution, MOE, School of Earth and Space Science, Peking University, Beijing 100871, China
²Electron Microscopy Laboratory, School of Physics, Peking University, Beijing 100871, China
³Department of Geological and Environmental Sciences, Stanford University, Stanford, California 94305, U.S.A.
⁴Department of Earth Sciences, University of Durham, Durham DH1 3LE, U.K.

ABSTRACT

Two types of amphibole exsolution lamellae were discovered in garnet from a few garnet peridotites from the North Qaidam ultrahigh-pressure metamorphic belt, northern Tibet, NW China. The amphibole lamellae are strictly oriented in four directions corresponding to the isometric form {111} (i.e., octahedron planes) of garnet. Observations by transmission electron microscopy (TEM) show that amphibole lamellae are topotaxially concordant with the host garnet and possess 9.8 to 10 Å lattice “c”-spacings. Electron-microprobe analysis reveals that these exsolved amphibole lamellae are rich in Na and Ti. The TEM observations and recalculated compositions indicate that the oriented amphibole lamellae exsolved from original supersilicic majorites with high concentrations of Na2O (0.3 wt%) and hydroxyl (up to 1000 ppm by weight). These results imply that the host garnet peridotites were formed at depths greater than 200 km and that garnet can be an important reservoir of water at such depths in the mantle.

INTRODUCTION

Orogenic garnet peridotite in ultrahigh-pressure (UHP) metamorphic terranes within orogens associated with continental collision has received considerable attention due to its deep (>6 GPa) origin (Yang et al. 1993; Dobzhinetskaya et al. 1996; van Roermund and Drury 1998; Zhang et al. 2000; Song et al. 2004). As an essential phase in the upper mantle as well as in UHP rocks of subduction zones, garnet plays an important role in our understanding of plate subduction and mountain building (e.g., Liou et al. 1997).

H2O (and hydroxyl, OH) is an important component in determining the properties of minerals and melts in the Earth’s upper mantle (Smyth et al. 1991). Numerous studies have demonstrated that H2O is likely to be contained in the form of hydroxyl point defects in nominally anhydrous minerals, for example, pyrope-rich garnet from the subcontinental mantle environment (Aines and Rossman 1984; Bell and Rossman 1992a, 1992b; Matsuyuk et al. 1998). Hydroxyl-bearing garnet therefore may be one of the significant reservoirs of H in the Earth’s mantle (Bell and Rossman 1992a, 1992b).

Song et al. (2004) reported densely packed exsolution lamellae of rutile and pyroxene in garnet and of ilmenite and Al-chromite in olivine from an orogenic garnet peridotite at Lüliangshan of the North Qaidam Basin (Fig. 1), northern Tibetan Plateau. Based on the quantities and analyzed compositions of the exsolved lamellae and host phases, they concluded that this garnet-peridotite body formed at depths greater than 200 km. In this contribution, we report new findings of some unusual exsolution lamellae of sodic amphiboles in garnet from the same garnet peridotite massif in the North Qaidam UHP belt using optical microscopy, electron probe micro-analysis (EPMA), and transmission electron microscopy (TEM). The occurrence of these amphibole lamellae implies that the precursor garnet is sodic and OH-bearing and was stable only at mantle depths in excess of 200 km during a continental collision event in the early Paleozoic (~423 Ma by zircon SHRIMP dating; Song et al. 2005). These observations also have implications for the regional tectonic evolution in particular and the water budget in the Earth’s mantle in general, in the context of geochemical recycling.

GEOLOGICAL SETTING AND SAMPLE PETROLOGY

The North Qaidam eclogite belt lies between the Precambrian Qaidam Massif in the south and the Qilian Massif in the north. It trends NW and extends from Dulan northwestward through Xietieshan and Lüliangshan, to Yuka for about 400 km (see Fig. 1A for localities) and is truncated by the Altyn Tagh Fault, a large NE-striking left-lateral strike-slip fault in western China. Coesite has been identified as inclusions in zircon separates from paragneiss at Dulan (Song 2001; Yang et al. 2002); its occurrence and P-T estimates of the enclosing eclogite and garnet peridotite establish the North Qaidam—Altun eclogite belt as another UHP terrane exhumed from depths >80–100 km. Details of regional geology, petrology and metamorphic evolution of this belt have been described by Song et al. (2003a, 2003b).

The garnet peridotite under study occurs as a large massif (~500 to 800 m in size) within an eclogite-bearing quartzofeldspathic gneiss terrane of the North Qaidam UHPM belt (Fig. 1B). Three types of ultramafic rocks were recognized: (1) garnet lherzolite (locally garnet harzburgite) dominates with minor...
The garnet peridotite showing locations of the studied samples (modified after Bureau of Geology and Mineral Resources of Qinghai Province 1991).

FIGURE 1. (A) Geological map of the North Qaidam UHP belt and adjacent areas showing the tectonic units in the North Tibetan Plateau, NW China. (B) Geological map showing the locality of the Luliangshan garnet peridotite body. (C) Geological map of the garnet peridotite showing locations of the studied samples (modified after Bureau of Geology and Mineral Resources of Qinghai Province 1991).

Garnet lherzolite-harzburgite constitutes about 80 vol% of the massif and shows medium to coarse-grained inequigranular textures. The main constituent minerals are garnet, olivine, orthopyroxene, clinopyroxene, and Cr-rich spinel. Most garnets are porphyroblastic and vary in size from 3 to 10 mm. Garnets in the matrix are fine-grained and equigranular. Both porphyroblastic and matrix garnets are Mg-rich with 64–73 mol% pyrope, 13–23% almandine, 4–10% grossular, 0.9–1.8% spessartine, and 2–5% uvarovite. Olivine ranges from Fo84 to Fo91 and constitutes 0.8–2.0% spessartine and 3–6% uvarovite. Some garnet grains, with 69–75 mol% pyrope, 11–18% almandine, 3–8% grossular, 0.8–2.0% spessartine and 3–6% uvarovite. Some garnet grains, with 62–68 mol% pyrope, 21–24 mol% almandine, 9.5–11 mol% grossular, 1 mol% spessartine and 0.8–1.5 mol% uvarovite. Most garnets have kelyphitic Opx + Cpx + Spl rims; some break down to aggregates of high-Al orthopyroxene + clinopyroxene + Al-spinel, suggesting that these rocks have been overprinted by a late thermal event below the garnet-spinel transition pressure. Orthopyroxene ranges from En90 to En92, lower than that of orthopyroxene in garnet lherzolite/harzburgite and dunite.

AMPHIBOLE LAMELLAE IN GARNET FROM GARNET-LHERZOLITE

In contrast to the densely packed rutile and two-pyroxene exsolution phases in garnet from the garnet-lherzolite reported by Song et al. (2004), a large quantity of amphibole lamellae are observed in porphyroblastic garnets from samples 2C42 and 2C44 (Fig. 2). Figures 2a and 2b show abundant exsolved lamellae of both sodic amphibole lamellae and rutile in the porphyroblastic garnet of sample 2C42. The lamellae occur as 100–500 μm (up to 1 mm) long spindle-shaped rods in long-axis sections, and up to 15 μm thick as quadrangular, rhombohedral, or polygonal prisms in basal sections. These amphibole lamellae coexist intimately with rutile needles; their long axes are parallel to each other. Such intergrowths of both amphibole and rutile lamellae is common (Fig. 2c). Photomicrographs and back-scattered electron (BSE) images show that amphibole lamellae in some garnet grains can reach up to 5–6 vol% (Figs. 2d and 2e) with a mean of about 4.5 vol%. The amount of rutile lamellae also reaches up to about 1 vol% in the same garnet grain. All these exsolution lamellae occur in parallel groups, each being strictly oriented in one of the four directions corresponding to the isometric form {111} (i.e., octahedral planes), which show a distinct equilateral triangular lamellar pattern in Figure 2a. The high abundances and regular crystallographic distributions suggest that the rutile and amphibole lamellae in porphyroelastic garnets were developed by decompression-induced exsolution, rather than by epitaxial replacement or accidental inclusion.

COMPOSITION OF AMPHIBOLE LAMELLAE

Table 1 lists representative compositions of both matrix garnet host and exsolution lamellae determined using a JEOL JXA-8100 Electron Probe Micro-analyzer (EPMA) at Peking University. Analytical conditions were optimized for standard silicates and oxides, with 15 kV accelerating voltage, 20 nA beam current, and a focused beam spot. Considering that Na2O can be mobilized especially in hydroxyl-bearing phases, routine analyses were obtained by counting for 20 seconds at peak and 5 seconds on background. Repeated analysis of natural and synthetic standards.
**TABLE 1. Compositions of matrix minerals and exsolved lamellae in garnet peridotites**

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Host Gem</th>
<th>Ca-poor phase</th>
<th>Amphibole exsolution lamellae</th>
<th>Ca-rich phase</th>
<th>C-O Gem</th>
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<tbody>
<tr>
<td>SiO₂</td>
<td>42.11</td>
<td>41.24</td>
<td>40.65</td>
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<tr>
<td>TiO₂</td>
<td>0.18</td>
<td>2.50</td>
<td>2.68</td>
<td>3.66</td>
<td>3.76</td>
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<tr>
<td>Al₂O₃</td>
<td>22.31</td>
<td>19.52</td>
<td>19.87</td>
<td>19.57</td>
<td>19.09</td>
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<tr>
<td>Cr₂O₃</td>
<td>1.44</td>
<td>1.46</td>
<td>1.01</td>
<td>1.19</td>
<td>1.12</td>
</tr>
<tr>
<td>FeO</td>
<td>9.69</td>
<td>2.63</td>
<td>2.77</td>
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<tr>
<td>MnO</td>
<td>0.43</td>
<td>0.11</td>
<td>0.12</td>
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<tr>
<td>NiO</td>
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<td>0.33</td>
<td>0.24</td>
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<tr>
<td>MgO</td>
<td>19.57</td>
<td>22.99</td>
<td>22.64</td>
<td>22.90</td>
<td>22.61</td>
</tr>
<tr>
<td>CaO</td>
<td>4.33</td>
<td>0.31</td>
<td>1.06</td>
<td>0.11</td>
<td>0.12</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.04</td>
<td>5.52</td>
<td>5.97</td>
<td>6.69</td>
<td>7.31</td>
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<tr>
<td>K₂O</td>
<td>0.02</td>
<td>0.02</td>
<td>0.04</td>
<td>0.04</td>
<td>0.02</td>
</tr>
<tr>
<td>Total</td>
<td>100.13</td>
<td>96.63</td>
<td>97.042</td>
<td>97.01</td>
<td>97.12</td>
</tr>
<tr>
<td>O</td>
<td>12.00</td>
<td>23.00</td>
<td>23.00</td>
<td>23.00</td>
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<td>Si</td>
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<td>5.748</td>
<td>5.668</td>
<td>5.695</td>
<td>5.722</td>
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<tr>
<td>Ti</td>
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<td>0.262</td>
<td>0.281</td>
<td>0.382</td>
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<tr>
<td>Al</td>
<td>1.879</td>
<td>3.207</td>
<td>3.265</td>
<td>3.197</td>
<td>3.124</td>
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<tr>
<td>Cr</td>
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<td>0.161</td>
<td>0.111</td>
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<td>0.123</td>
</tr>
<tr>
<td>Fe</td>
<td>0.579</td>
<td>0.307</td>
<td>0.323</td>
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<td>0.151</td>
</tr>
<tr>
<td>Mn</td>
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<td>0.013</td>
<td>0.014</td>
<td>0.000</td>
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</tr>
<tr>
<td>Ni</td>
<td>0.002</td>
<td>0.037</td>
<td>0.027</td>
<td>0.020</td>
<td>0.042</td>
</tr>
<tr>
<td>Mg</td>
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<td>4.777</td>
<td>4.706</td>
<td>4.733</td>
<td>4.680</td>
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<tr>
<td>Ca</td>
<td>0.331</td>
<td>0.046</td>
<td>0.158</td>
<td>0.016</td>
<td>0.018</td>
</tr>
<tr>
<td>Na</td>
<td>0.004</td>
<td>1.492</td>
<td>1.614</td>
<td>1.798</td>
<td>1.968</td>
</tr>
<tr>
<td>K</td>
<td>0.001</td>
<td>0.004</td>
<td>0.006</td>
<td>0.007</td>
<td>0.004</td>
</tr>
</tbody>
</table>

Notes: Abbreviations: Grt = garnet; C-O = calculated original garnet. The original composition of garnet is calculated from 92.9% averaged garnet plus 0.8% TiO₂, 4.5% averaged amphibole and 2% pyroxene exsolutions.

**FIGURE 2.**
Photomicrographs showing rutile + amphibole exsolution lamellae in garnets from garnet peridotite sample 2C42 in the North Qaidam UHP belt. (a) Densely packed lamellae of rutile and sodic amphiboles in garnet. Note the equal-triangular patterns defined by the exsolution rods (plane-polarized transmitted light). (b) Enlarged image of a (plane-polarized transmitted light). (c) Amphibole (Amp) and rutile (Rt) lamellae and their intergrowth (plane-polarized transmitted light). (d and e) BSE images of rutile (light needles) and sodic amphibole (gray to dark) exsolutions in garnet.
yielded precisions better than ±2% for most elements. The composition of garnets from the studied rocks is fairly homogeneous without apparent zoning. High concentrations of TiO₂ (0.16–0.20 wt%) and Na₂O (up to 0.08 wt% with an average of 0.04 wt%) were detected in host porphyroblastic garnets (Table 1).

Two types of compositionally distinct amphibole rods were recognized in garnet porphyroblasts from garnet lherzolite by BSE images (Figs. 2d and 2e). The light-gray amphibole lamellae possess Ca- and Na-rich, pargasite-like compositions with the structural formula, Na_{1.28}Ca_{1.49}(Mg_{3.58}Fe_{0.24})(Al_{0.92}Ti_{0.19}Cr_{0.15})[Si_{6.08}Al_{1.92}]O_{22}(OH)₂, and characterized by high TiO₂ (1.1–2.5 wt%), CaO (9.8–10.1 wt%), Al₂O₃ (17.1–17.5 wt%), and Na₂O (4.7–4.9 wt% with a mean of 4.71 wt% for 4 analyses). The dark-gray lamellae are a Ca-poor phase (0.1–1.1 wt% CaO), but contain higher TiO₂ (2.5–3.8 wt%), Al₂O₃ (>19 wt%), MgO (~ 23 wt%), Na₂O (5.5–7.3 wt%) and hydroxyl. This dark-gray Ca-poor amphibole is compositionally similar to sodic gedrite (?) with the structural formula, (Na_{1.90}K_{0.01})(Mg_{4.81}Fe_{0.17})(Al_{1.19}Cr_{0.13})[(Si_{5.62}Ti_{0.39})Al_{2.0}]O_{22}(OH)₂. These two phases are similar in amount based on BSE image analysis. Based on the estimated amount and compositions of analyzed exsolution lamellae, we calculated the precursor garnet compositions as listed in Table 1 (see Table 1 note for the calculation procedure); it contains 0.02 more Si than the ideal value of 3 per 12 O atoms, necessitating the existence of 0.07 (Si+Ti) in octahedral coordination. It also exhibits low Al₂O₃ and high Na₂O (0.30 wt%) and TiO₂ (0.88 wt%).

**TEM INVESTIGATION**

To identify the microstructures of the lamellae and the topotaxial relationship between the exsolved lamellae and the host garnet, we used a Hitachi F30 high-resolution transmission electron microscope (TEM) operating at 300 kV accelerating voltage in the Electron Microscopy Laboratory, School of Physics, Peking University. The TEM is equipped with an energy-dispersive X-ray spectrometer (EDS), which has an ultra-thin-window detector, enabling the identification and measurement of elements ranging from B to U.

Electron-transparent foils were prepared by ion-beam thinning from two petrographic thin sections using a Gatan 600 DuoMill. The examined lamellae are very thin (<1 μm) and straight and have sharp boundaries with the host garnet (Figs. 3a and 3b). Energy-dispersive X-ray spectrometer (EDS) scanning (Fig. 4) reveals that their compositions are identical to those of the thick lamellae in Figure 2; they all contain considerable amounts of Na and Ti. High-resolution TEM imaging reveals that the two types of amphibole lamellae are coherently intergrown with the host garnet; this can be clearly seen in that the (100) lattice fringes of the amphibole are strictly parallel to one of the
four \{111\} directions of the host garnet (Figs. 3c and 3d). The lamellae consist of 9.8–10 Å fringes of amphibole as shown in the high-resolution TEM images. The structure of these lattice fringes was readily destroyed by the high-voltage electron beam in a short time, suggesting that the lamellae contain a high quantity of OH. The selected-area electron diffraction patterns for the host garnet and for the lamellae are shown in Figures 5a and 5b, respectively. The structure of garnet is octahedral with a space group \textit{Ia}3d. The diffraction pattern of the amphibole lamella is parallel to one direction of the host garnet.

**DISCUSSION**

Hydrous phases such as K-white mica and phlogopite have been reported as exsolution lamellae in clinopyroxene from various UHP metamorphic rocks (Schmädicke and Müller 2000; Zhu and Ogasawara 2002). Exsolved rods of quartz + amphibole also occur in clinopyroxenes of the studied garnet peridotites, suggesting the primary clinopyroxene is supersilicic and hydroxyl-enriched. However, to our knowledge, exsolution of sodic amphiboles from garnet has not yet been reported in the literature. One might interpret the two types of sodic amphibole lamellae described in the previous sections as alteration products after clinopyroxenes. However, as seen in Figure 2, all sodic amphibole lamellae distribute regularly along the host garnet \{111\} and are parallel to, or intergrown with, rutile exsolution rods. The topotaxial relationship between the lamellae and host garnet, together with their high Al and Na content, strongly suggest that these amphibole lamellae resulted from decompression-induced exsolution from a parental garnet rather than forming by epitaxial replacement during retrogression or by “along-crack” alteration after pyroxene. TEM investigation reveals clearly coherent intergrowths between the host garnet and the amphibole lamellae and corroborates their exsolution relationship.

The recognition of amphibole exsolutions in garnet porphyroblasts has twofold significance: (1) all lamellae have high Na₂O contents, suggesting a Na-rich parental majoritic garnet host; and (2) they are hydrous phases, suggesting the presence of a significant amount of hydroxyl in the parental garnet host in the form of structural effects. The latter suggests that the “protolith” of the garnet peridotite may have experienced an environment in which a fluid phase was present in its history before exsolution.

**FIGURE 4.** EDS spectra of the two types of sodic amphibole lamella by EPMA (a) and by TEM (b). The peak of Cu in b is an effect of the copper grid.

**FIGURE 5.** Selected-area electron diffraction (SAED) patterns for the host garnet (a) and the sodic amphibole lamella (b) that are shown in Figure 2d.
The maximum 6 vol% with a mean of 4.5 vol% of exsolved amphibole lamellae (see above) suggests the presence of ~0.25–0.35 wt% Na2O and >0.1 wt% (>1000 ppm by weight) hydroxyl in their parental garnet crystals. Available experiments and field observations demonstrate that the solubility of pyroxene in garnet increases with increasing pressure (Irfune et al. 1986; Ono and Yasuda 1996), and Na and Ti (including P) concentrations of garnet also display a positive correlation with pressure (Tompson 1975; Zhang et al. 2003; Okamoto and Maruyama 2004). The high concentration of rutile and sodic amphibole exsolution lamellae in garnets suggests the existence of (CaNa2)Ti3Si2O12 and (CaNa)(AlTi)SiO3 components in the garnet structure (see Zhang and Liou 2003), which may have the same function as majoritic garnet through the substitution Na + Ti = Ca + Al at ultrahigh pressures.

As expected, Na and Ti contents of bulk garnet peridotite are much lower than those in eclogites metamorphosed from basaltic rocks. The estimated Na2O (~0.30 wt%) and octahedral Si + Ti (~0.07) contents of the original majoritic garnets in our studied samples (Table 1), however, are similar to or higher than those of the synthetic garnets at 7 GPa and 1000 °C using starting material of a natural eclogite from Dabieshan (Okamoto and Maruyama 1998), at 7 GPa and 1400 °C using an N-MORB composition (Ono and Yasuda 1996), and at 10 GPa and 1200 °C using a continental crust composition (Irfune et al. 1994). On the other hand, most inclusions of majoritic garnet in diamond associated with peridotites contain relatively lower Na2O than in diamond associated with eclogites; those majorities with more than 0.5 wt% Na2O are believed to have crystallized in the mantle transition zone (i.e., 410–660 km) (Irfune et al. 1989; Moore et al. 1991). The calculated Na2O content (0.30 wt%) in our sample is higher than that of most natural inclusions in diamonds and experimental peridotite garnets formed at P > 10 GPa. This high Na2O content is most probably because high hydroxyl content may facilitate Na dissolution in majoritic garnet. The analyzed garnet also contains a measurable amount of K2O (about 1 wt%), which is believed to be dissolved into the garnet structure only at very high pressures (Wang and Takahashi 1999). Considering the very high Na2O and octahedral Si + Ti contents in the original garnet plus all the above observations, we interpret that the original majoritic garnet from garnet peridotite in the North Qaidam UHP belt may have been formed at P > 7 GPa. That is, the garnet peridotite body may have been exhumed from mantle depths in excess of 200 km.

Previous studies revealed that OH abundances in garnet are closely linked to their host rock paragenesis (e.g., Bell and Rossman 1992b). Garnets in both garnet peridotite and eclogite from the subcontinental mantle occurring as xenoliths in kimberlite pipes have hydroxyl contents ranging from less than 1 up to 200 ppm by weight (Bell and Rossman 1992b; Matsuysk et al. 1998). However, no report of the OH content of garnet from orogenic peridotites in continental collision belts is available.

Experimental studies have demonstrated that the hydroxyl content of nominally anhydrous minerals dramatically increases with pressure, and the maximum solubility of water in pyrope is 200–1000 ppm by weight at P of 5–10 GPa, above which pyrope starts to dehydrate (Geiger et al. 1991; Lu and Keppler 1997; Withers et al. 1998). MgSiO3-majorite, a deeper mantle phase stabilized in the transition zone (410–660 km), can contain a significant amount of water, as high as 670 ppm by weight (Bolfan-Casanova et al. 2000). High OH concentrations in peridotitic garnets occur preferentially in those of Ti-rich composition (Bell and Rossman 1992); this implies that Ti and OH likely have a positive correlation. These results are consistent with our estimate of hydroxyl contents (>1000 ppm by weight) in garnet that formed at depths greater than 200 km. Therefore, it is reasonable to conclude that garnets from orogenic garnet peridotite in the cold, water-saturated conditions of subduction zones can contain higher amounts of hydroxyl than those from hot subcontinental mantle and therefore could contribute to the water cycling of the Earth during plate subduction.

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