Olivine Pseudomorphs after Serpentinized Orthopyroxene Record Transient Oceanic Lithospheric Mantle Dehydration (Leka Ophiolite Complex, Norway)

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We examine the partial survival of high-temperature mantle microstructures throughout multi-stage hydration- and dehydration-mediated pseudomorphism at differing pressure-temperature-fluid conditions. Throughout the harzburgitic mantle section of the Leka Ophiolite Complex (Norway), finite domains of parallel olivine encompassed by mesh-textured olivine resembling ‘perfectly cleaved’ olivine grains were identified. Crystallographic orientation mapping, combined with micro-computed tomography, reveals that the parallel olivine grains are highly misoriented (up to 90°) within a crystal-preferred orientation, despite remaining parallel in three dimensions. Parallel olivine grains exhibit free dislocations with low dislocation density, whereas within mesh-textured olivine dislocations are aligned into walls. MnO is enriched (up to 1·8 wt %) and NiO depleted (0·21±0·24 wt %) within parallel olivine grains compared with mesh-textured olivine (0·29±0·14 wt % MnO; 0·38±0·19 wt % NiO). Clinopyroxene lamellae that are crystal-plastically deformed occur sandwiched in lizardite layers between every parallel olivine grain or fully enclosed within olivine. Al2O3 and Cr2O3 concentrations of clinopyroxene lamellae (2·09±0·88 wt % Al2O3; 0·79±0·27 wt % Cr2O3) overlap with those of primary clinopyroxene grains (2·43±0·69 wt % Al2O3; 0·83±0·36 wt % Cr2O3) and are distinctly different from those of secondary diopside found within the parallel olivine domains. Intragranular serpentine inclusions (XMg = 0·95±0·01), displaying elevated Al2O3 (3·92±4·10 wt %) and Cr2O3 (0·78±0·82 wt %) concentrations, are exclusively found within parallel olivine grains. Lizardite (XMg = 0·92±0·02) within the domains originates from hydration of parallel olivine and compositionally overlaps with mesh-texture lizardite. Antigorite (XMg = 0·93±0·01) replaces both types of olivine grains. Whole-rock compositions indicate a harzburgitic composition; however, microstructural and chemical observations and the current absence of primary orthopyroxene suggest that the precursor silicate of every parallel olivine domain was a single orthopyroxene grain that was initially serpentinized and later dehydrated to result in the present microstructure. Although desilicification is necessary during the transformation of orthopyroxene to olivine via a bastite stage, calculations based on whole-rock compositions imply that the released SiO2(aq) was mobile only over micrometer to centimeter scales, reacting with the surrounding olivine directly to form serpentine. Crosscutting relationships and serpentine compositions imply that dehydration occurred prior to the now evident lizardite- and antigorite-serpentinitization. Comparison with the regional geological setting indicates that dehydration may have occurred transiently within the oceanic lithosphere prior to obduction.

KEY WORDS: microstructures; ophiolite; pseudomorphism; serpentinitization; serpentine dehydration

INTRODUCTION

Alteration and metamorphism of the Earth's oceanic lithosphere is intimately coupled to fluid-dependent mineral
replacement reactions. The most pronounced of these reactions also have fundamental repercussions for the oceanic lithosphere's geochemical and geophysical properties are the hydration (serpentinization) of mantle peridotite and dehydration (deserperminization) of serpentinites. Typically, serpentinization advances along slow-spreading ridges or bending faults during the onset of subduction, influencing oceanic plate rheology and geochemical inputs into subduction zones (e.g., Escartin et al., 2001; Rüpke et al., 2004). Upon fluid release from the subducting slab, migration upwards induces serpentinization of the forearc mantle wedge (e.g., Hyndman & Peacock, 2003). Deserperminization is thought to occur deep within the subducting slab, expelling large amounts of fluid that act as a flux for arc magmatism, and has been related to intermediate-depth earthquakes (e.g. Hacker et al., 2003; Padron-Navarta et al., 2010). Recent hydrothermal convection models, however, suggest that dehydration may also occur in situ within the oceanic plate prior to subduction and obduction (Iyer et al., 2010). Dehydration could also be promoted when partly serpentinitized peridotite is displaced along oceanic transform faults towards the hot adjacent ridge segment, potentially triggering seismicity (e.g. Rutter & Brodie, 1987). No direct observations of deserperminization at ridges or in forearc settings have been reported, possibly because meta-peridotite samples are either dredged or are taken from shallow boreholes where temperatures are insufficient to dehydrate serpentine minerals. This may be different at depth where upwelling of hot asthenosphere or magma could supply the heat required (e.g. Hyndman & Peacock, 2003; Allen & Seyfried, 2004; Behn et al., 2007). Furthermore, breakdown of hydrous minerals may occur during reactive fluid infiltration (e.g. blueschist eclogitization along a fluid conduit; Beinlich et al., 2010) or if the fluid chemistry fluctuates (e.g. changes in $\delta^18O$; e.g. Hardie, 1967).

Mantle sections of ophiolite complexes provide an extensive fossil record of the alteration processes occurring within the oceanic lithosphere. However, deciphering their potentially long alteration history is notoriously difficult. Unknown contributions of fluid flux from a subducting slab in supra-subduction zone ophiolites and possible multiple overprints in response to metamorphic events can hinder placing separate events into a geological context. The observation that serpentine is stable over a large temperature and pressure range adds to the system's complexity (e.g. Evans, 2004). Additional difficulties arise from the common lack of geochronologically relevant minerals that prevents placing microstructurally distinct events in an accurate time frame. The only exception is the indirect dating of serpentinization via hydrothermal zircons within rodingites (e.g. Dubinska et al., 2004). Stable isotope and trace element geochemistry are mainly used to constrain different fluid sources (e.g. Wenner & Taylor, 1973; Deschamps et al., 2011), whereas the crosscutting relationships of vein networks and vein to wall-rock patterns give insights into the sequence of different events (e.g. Andreani et al., 2007). However, detailed microstructural analysis in terms of mineral reaction history is a promising tool to provide valuable clues about unknown metamorphic and tectonic events occurring during the 'life-cycle' of the oceanic mantle.

Here we present an in-depth investigation of an extraordinary microstructure comprising olivine pseudomorphs after serpentined orthopyroxene grains from the mantle section of the Leka Ophiolite Complex (Norway). The microstructure records the complete polymetamorphic evolution of the mantle section, beginning with high-temperature, sub-solidus and solid-state deformation as well as mineral re-equilibriations during a hydration–dehydration–rehydration cycle. We particularly emphasize the survival of microstructures throughout multi-stage pseudomorphism during succeeding metamorphic events and use the information gained to unravel the complex mineral reaction scenarios.

GEOLOGICAL SETTING AND SAMPLES

The Leka Ophiolite Complex (LOC) crops out on the island of Leka (90 km$^2$), Nord-Trøndelag, Norway, located at ~65°N (Fig. 1). It is the most completely preserved ophiolite present in the Scandinavian Caledonides and represents part of the Upper or Uppermost Allochthon of the Norwegian tectonostratigraphy with an age of 497 ± 2 Ma (Dunning & Pedersen, 1988; Furnes et al., 1988). Ophiolite formation took place in a supra-subduction setting of the North Iapetus Ocean and at present exists in a pull-apart structure resulting from post-orogenic transtension (Furnes et al., 1988, 1992; Titus et al., 2002). Amphibolite-grade basement gneisses of the northern Vestrelands region crop out south and west of Leka and make up the dominant rock type of the adjacent mainland. There are no exposed contacts between the LOC and the adjacent mainland rocks, and the lack of continuity between the two implies that all contacts are of tectonic origin (Furnes et al., 1998; Titus et al., 2002). On the island of Leka mantle meta-peridotite crops out in the northern area of the island and is (1) in tectonic or transitional contact with ultramafic cumulates and (2) in tectonic contact with meta-gabbro towards the east of the island (Fig. 1b). Meta-dunite bodies of various sizes occur locally within the meta-peridotite tectonite (Albrektsen et al., 1991). The layered cumulates are dominated by dunite interlayered with meta-wehrlite and locally chromite layers. The meta-wehrlite crops out as several meter-long, lens-shaped pods within the meta-dunites. A sharp discordant boundary separates the ultramafic cumulates from the meta-gabbros toward the SW part of the island. Ordovician
metasedimentary rocks were deposited nonconformably on the ophiolite complex and metamorphosed to greenschist facies (Sturt et al., 1985). In this study we focus on samples from 10 drill cores covering the mantle tectonite (meta-peridotite) section (Fig. 1b). On the outcrop scale the mantle meta-peridotite has a homogeneous appearance with little to no variation in color (Fig. 1c); abundant millimeter- to centimeter-scale serpentine veins crosscut the meta-peridotite. Meta-peridotite is easily distinguishable from meta-dunite owing to its rougher weathering surface (Fig. 1d).

**ANALYTICAL TECHNIQUES**

Rock samples were sliced with a diamond saw and ground in a steel mill. Major and minor element concentrations of powdered rock samples were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES) using a Perkin Elmer Optima 3300R system at Royal Holloway, University of London. The analytical precision is 1% for Si, Al, Fe, Mg and Ca, and 2% for Na, K, Ti, P and Mn. Microstructures were examined in polished thin sections (≈30 μm) using polarized light microscopy. Back-scattered electron (BSE) images were acquired using a JEOL 6610-LV scanning electron microscope (SEM; Institut für Mineralogie, University of Münster, Germany). Major quantitative element analyses were obtained with a Cameca SX 100 electron microprobe (EMP; Department of Geosciences, University of Oslo, Norway). All major element analyses were acquired by wavelength-dispersive X-ray (WDX) spectrometry using an accelerating voltage of 15 kV at a beam current of 10–20 nA. A

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**Fig. 1.** (a) Geographical location and geological overview map of the central Scandinavian Caledonides showing the tectonostratigraphic position of the Leka Ophiolite Complex (LOC) and surrounding geological units [modified from Gee et al. (1985) and Bucher-Nurminen (1991)]. BS, basement; PA, para-autochthonous; LA, lower allochthonous; MA, middle allochthonous; UA, upper allochthonous; UMA, uppermost allochthonous. (b) Detailed geological map of the LOC, showing sample localities (stars), and immediately surrounding geological units [modified from Prestvik (1972)]. True north is indicated. Sample localities cover a large part of the mantle tectonic section. In some localities more than one sample was taken. (c) Field image of the LOC mantle meta-peridotite, displaying a local strong foliation. This foliation is not visible throughout the entire complex. (d) Close-up of typical rough meta-peridotite weathering crosscut by millimeter- to centimeter-scale serpentine veins.
selection of natural and synthetic minerals were used for standardization; these were albite (Na), corundum (Al), Cr₂O₃ (Cr), native Fe (Fe), NiO (Ni), MgO (Mg), orthoclase (K), pyrophyllite (Mn and Ti) and wollastonite (Ca and Si), respectively. Detection limits (3σ uncertainty) in olivine and clinopyroxene for Cr, Ni and Mn were 400–650 ppm. Mineral analyses and subsequent calculated values are reported with a 2σ standard deviation. Matrix corrections followed a routine implemented in the Cameca PAP program (Pouchou & Pichoir, 1984). Element distribution maps were obtained using operating conditions of 15 kV and 40 nA with a step size of 1 μm.

For serpentine phase and brucite identification Raman spectra were collected with a high-resolution Jobin Yvon T6400 Raman spectrometer, which used the 532 nm line of a 14 mW Nd:YAG laser as excitation source (Norwegian Center for Raman Spectroscopy, University of Oslo, Norway). The scattered Raman light was collected in 180° backscattering geometry and dispersed by a 1800 grooves mm⁻¹ grating after travelling through a 100 μm entrance slit. The spectrometer was calibrated using the first-order Raman band of silica at 520 cm⁻¹ and the epoxy resin was analyzed to check for contributions to the mineral analyses. Raman peak positions were fitted using the FITFYK software (Wojdyr, 2010). Acquired serpentine and brucite spectra were compared with published referencespectra (Dawson et al., 1973; Rinaldo et al., 2003; Groppo et al., 2006). In addition, all spectra were compared with the RRUFF Project database (Downs, 2006).

Quantitative crystallographic orientation data for olivine, clinopyroxene and magnetite were acquired via automatically indexed electron backscatter diffraction (EBSD) patterns collected using a Philips XL-30 field-emission (FE-)SEM equipped with an Oxford Nordlys II EBSD detector (Department of Geological Sciences, Stockholm University, Sweden). Thin sections for EBSD analysis were SYTON®-polished and not coated with carbon. Working conditions during acquisition of EBSD patterns were 25 kV accelerating voltage, ~0.8 nA beam current, 20-4 mm working distance, 70° sample tilt and low-vacuum mode (~0.7 mbar). EBSD patterns were acquired on rectangular grids by moving the electron beam at a regular step size of 0.7–1 μm. EBSD pattern indexing was executed using the HKL CHANNEL5 software. This software was also used for EBSD data processing, by applying a noise reduction filter that replaces non-indexed solutions by the most common neighbor orientation (Prior et al., 2002; Bestmann & Prior, 2003). A modified Kuwahara filter was applied once (3 × 3 filter with 5° smoothing and 1° artifact angle).

Oxidation decoration was used to gain an insight into the olivine dislocation density and arrangement (Kohlstedt et al., 1976). This technique uses oxidation of Fe present in the olivine and subsequent precipitation of iron oxides at lattice distortions to identify the dislocation sub-structures on a microscopic scale. Single dislocations are visible as points and dislocation walls (i.e. subgrain boundaries) as lines. For this technique a polished rock slab was heated at 900°C for 45 min in air. Subsequently, a 30 μm thin section was prepared from the polished side and examined using an SEM in BSE mode (Karato, 1987).

For micro-computed X-ray tomography (μCT) a cylinder (1 cm × 0.7 cm) was cut from a rock sample that showed the required microstructure in thin section. μCT was executed using a XRADIA MicroXCT-400 at an acceleration voltage of 100 kV and a tube current of 100 μA (Australian Centre for Microscopy & Microanalysis, University of Sydney, Australia). For the measurement, 1200 projections (40 s integration time per projection) were acquired during a 180° rotation of the sample, resulting in a spatial resolution of ~2.5 μm per voxel. Three-dimensional (3-D) visualization was carried out using the Visualization Sciences Group (VSG) Avizo Fire® program. A Hessian-based multi-scale enhancement filter (Frangi et al., 1998; computed in MATLAB) was used to extract the serpentine vein locations from the μCT-data.

Mineral abbreviations follow those of Whitney & Evans (2010).

**GEOCHEMICAL CHARACTER OF THE LEKA MANTLE SECTION AND THE PROTOLITHS OF THE LEKA SERPENTINITES**

Analyses of whole-rock compositions and previously published whole-rock data (Maaloe, 2005; Iyer et al., 2008a) clearly identify the meta-peridotites of the mantle tectonite section as harzburgite with an average normative primary mineralogy of 77±8% olivine, 22±8% orthopyroxene and 1±1% clinopyroxene (Fig. 2a). Whole-rock compositions of dunites that are identifiable in the field (e.g. Albrektsen et al., 1991) are also plotted in Fig. 2a for comparison. Average whole-rock compositions of harzburgite and dunite are given in Table 1. Mg/Si and Al/Si whole-rock element ratios, which are tracers for the protolith of the serpentinite (Hattori & Guillot, 2007), are close to the element ratios of serpentinites from the Mariana Trench and the Greater Antilles (Fig. 2b) consistent with previous geochemical investigations, which indicate an evolution within a supra-subduction zone setting (Furnes et al., 1992). This is also supported by the composition of primary Cr-spinel grains (Fig. 2c). Based on whole-rock compositions and the extensive alteration we use the name meta-peridotite when referring to rocks with a harzburgitic geochemistry.
MICROSTRUCTURES AND MINERAL CHEMISTRY OF THE LOC META-PERIDOTITE

On the basis of microstructural and microchemical analysis of the samples, three domains can be identified throughout the LOC meta-peridotite, which are schematically illustrated in Fig. 3.

Domain I is made up of elongated, parallel olivine grains (domains of parallel olivine: DPO) with a characteristic spacing, which are separated by thin clinopyroxene lamellae that are generally enclosed in lizardite. Diopside aggregates and elongated magnetite grains occur interstitially. Antigorite locally overprints the DPOs.

Domain II comprises the matrix and is composed of mesh-textured olivine grains that are partially hydrated to form lizardite with interstitial magnetite. Isolated antigorite replaces mesh-textured olivine relicts to varying degrees. In addition, large augitic clinopyroxene and primary spinel grains occur.

Domain III is represented by continuous areas of massive interpenetrating antigorite blades extending for several millimeters across thin sections, obliterating all previous microstructures.

Detailed chemical analysis of olivine, clinopyroxene, the serpentine varieties and oxides are given in Tables 2 and 3.

Domain I: detailed characterization

In total 30 DPOs in 20 thin sections were investigated in detail. All display consistent microstructural and microchemical characteristics.

Microstructures

Within a single thin section DPOs make up ~7–10% relative to mesh-textured olivine, excluding areas of massive antigorite-serpentinization (Domain III). Isolated DPOs, measuring ~1–5 mm in diameter, are surrounded by Domain II textures, producing an appearance similar to a porphyroblast (Fig. 4a and b). Olivine grains in the DPOs have complex undulose extinction patterns where single for comparison. (b) Weight ratios of Mg/Si vs Al/Si in peridotites of various origins in comparison with meta-harzburgites and meta-dunites from the Leka ophiolite [modified from Hattori & Guillot (2007) and Saumur et al. (2010)]. Meta-harzburgites and meta-dunites from Leka plot within the field of forearc mantle peridotites and are similar in composition to forearc serpentinites along the Zaza fault in Cuba (Hattori & Guillot, 2007) and Puerto Rico Trench serpentinites (Bowin et al., 1966). (c) Comparison of Cr# vs XMg of Cr-spinel grains from the LOC upper mantle section. Data are taken from Furnes et al. (1992) and Iyer et al. (2008a). Each point represents the composition of the core of one grain. The field of abyssal peridotite includes abyssal spinel peridotite and plagioclase peridotite (Dick & Bullen, 1984). The forearc mantle peridotite field is defined by Cr-spinel data from serpentinized peridotites exhumaed in the Mariana forearc (Ishii et al., 1992). All data points, except for one, plot in the field of forearc peridotite.

Fig. 2. Geochemical characteristics of the LOC meta-peridotites and meta-dunites. (a) Streckeisen triangular plot for the classification of ultramafic rocks, showing the primary modal composition of LOC meta-peridotites and meta-dunites calculated on a water-free basis. DPO-bearing rocks are located within the harzburgite field, exhibiting a natural spread in composition with no major trend towards a dunitic composition. Calculated mineral abundances from the whole-rock geochemistry of the meta-dunites from Leka clearly show the difference between the meta-dunites and the DPO-bearing rocks. Whole-rock compositions originate from this study and from Iyer et al. (2008) as well as average (av.) compositions from Maaløe (2005).
Table 1: Average whole-rock geochemical compositions of investigated meta-peridotites and meta-dunites

<table>
<thead>
<tr>
<th>Rock type:</th>
<th>Meta-peridotite</th>
<th>Meta-dunite</th>
</tr>
</thead>
<tbody>
<tr>
<td>n:</td>
<td>16</td>
<td>9</td>
</tr>
</tbody>
</table>

wt %

Table:<br>SiO₂ 39.06 (1.09) 35.66 (1.62)<br> TiO₂ 0.00 (0.01) 0.00 (0.01)<br> Al₂O₃ 0.61 (0.40) 0.20 (0.30)<br> Fe₂O₃ 7.12 (1.64) 9.28 (1.35)<br> FeO(rec) 6.41 (1.47) 8.35 (1.21)<br> MgO 46.28 (1.66) 48.40 (2.44)<br> MnO 0.12 (0.04) 0.16 (0.03)<br> CaO 0.42 (0.65) 0.30 (0.82)<br> Na₂O 0.01 (0.01) 0.01 (0.02)<br> K₂O 0.01 (0.03) 0.01 (0.02)<br> P₂O₅ 0.00 (0.01) 0.00 (0.01)<br> LOI 10.38 (1.33) 9.96 (3.25)<br>Total 98.43 (0.61) 98.06 (1.63)<br><br>Recalculated on water-free basis:<br>SiO₂ 44.37 (1.54) 40.37 (0.84)<br> TiO₂ 0.00 (0.01) 0.00 (0.01)<br> Al₂O₃ 0.69 (0.46) 0.22 (0.35)<br> Fe₂O₃ 8.09 (1.78) 10.53 (1.49)<br> FeO(rec) 7.28 (1.60) 9.48 (1.34)<br> MgO 46.28 (1.66) 48.40 (2.44)<br> MnO 0.12 (0.04) 0.16 (0.03)<br> CaO 0.42 (0.65) 0.30 (0.82)<br> Na₂O 0.01 (0.03) 0.01 (0.02)<br> K₂O 0.01 (0.03) 0.01 (0.02)<br> P₂O₅ 0.00 (0.01) 0.00 (0.01)<br>Total 100 100<br>Mg/Si (wt %) 1.044 (0.059) 1.199 (0.074)<br>Al/Si (wt %) 0.016 (0.010) 0.006 (0.009)<br><br>Values are average and 2σ, including loss on ignition (LOI) and recalculated on a water-free basis. Data from this study and Iyer et al. (2008a). n, number of analyses; rec, recalculated.

Fig. 3. Simplified thin-section sketch showing the main millimeter-scale spatial mineralogical associations in the investigated samples. Samples can be divided into three domains depending on their mineralogy and microstructures; Domain I consists solely of DPOs occurring as individual areas throughout the thin section and minor overprinting antigorite (Atg), Domain II comprises olivine (Ol) grains that are partially replaced by lizardite to form a mesh texture, antigorite patches replacing mesh-textured olivine, single large clinopyroxene (Cpx) grains and primary spinel (Spl) grains. Domain III encompasses massive antigorite occurrences that overprint all previous microstructures.

Areas do not extinguish concurrently (Fig. 4c). Figure 4c illustrates the parallel alignment of the elongated olivine grains, which have a characteristic periodic spacing of 16 ± 4 µm (n = 100). Orientation data expressed as a misorientation map of a representative central DPO area (Fig. 5a) display no correlation between crystallographic orientation and the parallelism of the olivine grains (Fig. 5b). Instead, neighboring parallel olivine grains are highly misoriented with respect to one another, with misorientation angles of up to 90° to a fixed reference point (star in Fig. 5b). Furthermore, high misorientations are observed either (1) in extension of an elongated olivine grain (arrow 1 in Fig. 5b) or (2) as islands included in larger elongated grains with the same orientation (arrow 2 in Fig. 5b). On the scale of a single olivine grain internal distortions are minimal (0°–8°; Fig. 5c), and only free dislocations, without the occurrence of dislocation walls, can be observed (Fig. 6a). However, small misorientations of ~1–2° arise where fractures cut across single grains (Fig. 5c). In addition, examination of dislocation substructures indicates lower dislocation densities of DPO olivine relative to mesh-textured olivine grains (Fig. 6). µ-CT of a centimeter-sized rock cylinder reveals that the parallelism of the olivine grains, as well as the grains themselves, remains continuous in three dimensions over several hundred micrometers. As serpentine veins separate nearly every elongated olivine grain, we have used these veins to highlight the 3-D parallelism in Fig. 7. An animation of a projection series and the 3-D visualization of Fig. 7 is available online (Movie 1, online supplementary material, available from http://www.petrology.oxfordjournals.org).

Compositionally and spatially different lizardite and chrysotile have also been identified in addition to the minor antigorite rosettes and needles that overprint the DPO microstructures (Fig. 8a and c), using Raman spectroscopy (Fig. 9). Lizardite is found homogeneously distributed between the elongated olivine grains (Fig. 8c and d) or makes up transgranular serpentine veins crosscutting the DPOs (Fig. 8b and c). In contrast, chrysotile occurs as...
micrometer-sized patches within the aforementioned lizardite or as inclusions, fully enclosed within the elongated olivine grains (Fig. 10).

Thin clinopyroxene lamellae, measuring 1–3 μm in thickness and sandwiched between lizardite, were observed in all investigated DPOs (Fig. 8d and e). However, clinopyroxene lamellae are also commonly found completely enclosed within olivine grains without microscopically visible lizardite at the clinopyroxene–olivine contacts (Fig. 8f). All the lamellae have a discontinuous lens-shape and vary in length from 10 to 500 μm. The crystallographic plane of the clinopyroxene lamellae that is parallel to the elongated olivine–serpentine interphase boundary was found to be consistently [100] using EBSD analysis (Fig. 8e). Crystallographic analysis of a representative clinopyroxene lamella reveals a significant orientation spread in both [100] and [001] axes following a circle around the [010] axis, whereas the latter displays only minor dispersion (Fig. 11). Some DPOs exhibit an apparent bending but in a discontinuous manner and are separated by fractures. In contrast to the clinopyroxene lamellae, mosaic-like, randomly oriented aggregates of diopside grains (Fig. 8c and d) were observed intergrown with elongated olivine grains (Fig. 8e). The occurrence of these diopside grains varies in quantity from a sporadic minor dispersion (Fig. 11) to massive replacement of the DPOs (Fig. 12). Concomitantly, the abundance of magnetite increases with increasing diopside occurrence (compare Figs 8b and 12).

Magnetite grains display an elongated habit following the parallelism within the DPOs, both in two (Figs 4d and 8) and three dimensions (Fig. 7, Supplementary Data...
Table 3: Mineral compositions of serpentine varieties and Fe-oxides

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<tr>
<th>Mineral:</th>
<th>Serpentine</th>
<th>Lizardite (mesh)</th>
<th>Lizardite (DPO)</th>
<th>Chrysotile inclusions</th>
<th>Antigorite</th>
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<tr>
<td>SiO₂</td>
<td>wt %</td>
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<td>43.65 (2.77)</td>
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<td>TiO₂</td>
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<tr>
<td>Al₂O₃</td>
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<td>Cr₂O₃</td>
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<td>0.05 (0.08)</td>
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<td>FeO(tot)</td>
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<td>NiO</td>
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<td>MnO</td>
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<td>0.08 (0.10)</td>
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<tr>
<td>CaO</td>
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</tr>
<tr>
<td>Na₂O</td>
<td>b.d.l.</td>
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<td>Na₂O</td>
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<tr>
<td>Total</td>
<td>84.84 (7.68)</td>
<td>85.14 (2.61)</td>
<td>85.73 (3.93)</td>
<td>86.90 (2.03)</td>
<td>97.03 (1.47)</td>
</tr>
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</table>

Structural formula based on 7 oxygen for lizardite, chrysotile and antigorite and 4 oxygen for magnetite

- Si: 1.747 (0.139)
- Ti: b.d.l.
- Al: 0.001 (0.005)
- Cr: 0.001 (0.003)
- Fe²⁺: n.c.
- Fe³⁺: 0.246 (0.081)
- Ni: 0.007 (0.012)
- Mg: 2.983 (0.095)
- Mn: 0.008 (0.005)
- Ca: 0.007 (0.009)
- Na: b.d.l.
- X_Mg: 0.92 (0.02)

Values are average and 2σ, n, number of analyses; b.d.l., below detection limit; tot, total; rec, recalculated; n.c., not calculated; X_Mg = Mg/(Mg + Fe)

Movie 1), and are closely associated with the clinopyroxene lamellae (Fig. 8). Rarely, spherical magnetite is observed. Comparison of DPO and magnetic grain orientations in Fig. 13 for the area shown in Fig. 5b reveals that, although olivine orientations vary, magnetite grains consistently exhibit two specific orientations across the entire area.

Mineral chemistry

Olivine grains within DPO centers have an average X_Mg of 0.900 ± 0.002 and show a strong correlation with MnO content, with decreasing X_Mg as MnO concentrations increase (Fig. 14a). In contrast, NiO concentration decreases sharply from 0.5 to 0 wt % (average NiO = 0.21 ± 0.24 wt %) within a relatively small X_Mg range (Fig. 14b). Surrounding these centers Mn + Fe-rich, Ni-poor haloes of olivine grains (X_Mg = 0.850 ± 0.026) that have increased electron backscattering intensity develop (Fig. 8a and b). Within these olivine grain haloes MnO remains negatively correlated with X_Mg whereas NiO is independent of X_Mg (Fig. 14a and b).

The serpentine varieties show a distinct difference in Al and Cr concentrations (Fig. 14c and d). Lizardite grains (X_Mg = 0.92 ± 0.02) and antigorite (X_Mg = 0.96 ± 0.02) are low in Al₂O₃ as well as Cr₂O₃. However, chrysotile grains enclosed in the DPO olivine (X_Mg = 0.95 ± 0.02) display elevated Al₂O₃ and Cr₂O₃ concentrations.
Fig. 4. (a, b) Optical photomicrographs under crossed polars (variable polarizer and analyzer positions) giving an overview of two DPOs (within dashed borderline). (c) Close-up of the DPO in (b) highlighting the parallelism of the olivine (Ol) grains with varying second-order interference colors and undulose extinction. (d) Photomicrograph in plane-polarized light showing magnetite (Mag) grains following the parallel north–south elongation trend of the olivine grains. (e) Photomicrograph under crossed polars of olivine grains within the vicinity of a DPO (upper left side within dashed borderline) that are partially replaced by lizardite (Lz) to form a mesh texture. Because of the retention of crystallographic continuity during serpentinization the approximate grain size of primary mantle olivine grains, measuring ~6–7 mm, is still visible. (f) Magnified photomicrograph under crossed polars of an area in (e), highlighting the relationships between lizardite and antigorite (Atg), where the latter overprints the former.
Comparison of SiO\textsubscript{2} wt % with X\textsubscript{Mg} of lizardite grains also implies the cryptic presence of brucite. All clinopyroxene lamellae display elevated Al\textsubscript{2}O\textsubscript{3} (2.09±0.90 wt %) and Cr\textsubscript{2}O\textsubscript{3} (0.79±0.30 wt %) contents, which is highlighted in the element distribution maps in Fig. 10. Mosaic-like diopside aggregates are nearly pure diopside, with only minor concentrations of Al\textsubscript{2}O\textsubscript{3} (0±10±0.16 wt %) and Cr\textsubscript{2}O\textsubscript{3} (0±14±0.16 wt %). A comparison between the clinopyroxene varieties can be found in Fig. 10 and f. Associated magnetite grains have Cr\textsubscript{2}O\textsubscript{3} concentrations of up to 25 wt %; however, small magnetite grains (>5 \textmu m) in this area are commonly low in Cr.

**Domain II: detailed characterization**

**Microstructures**

Lizardite±brucite (verified using Raman spectroscopy) replaces olivine grains, measuring ~5–7 mm diameter, forming a typical mesh texture in two (Fig. 4e and f) and three dimensions (Fig. 7). Lizardite-serpentinitization varies locally on the centimeter scale from >10 to ~50%. In addition, olivine grains are penetrated by crosscutting antigorite blades, further separating the olivine grains into smaller grain domains. In both textures, currently separated grains can be assigned to an originally single grain owing to their retention of optical continuity (Fig. 4e). Single olivine grain relicts commonly display intragranular kink bands and undulose optical extinction. Throughout Domain II several inclusion trails of serpentinite and locally chlorite, with a trail width of 5–20 \textmu m, are found to transsect olivine domains (Fig. 15). Dislocation microstructure analysis of mesh-textured olivine grains reveals organized dislocation walls, with areas of high free dislocation densities between them (Fig. 6b). The dislocation wall spacing is 5 \textmu m on average.
but can vary between 2 and 10 μm. Straight dislocations are also observed at the rims of the mesh-textured olivine grains that are nearly perpendicular to the grain margins. Crystallographic orientation mapping shows that areas between dislocation walls have intragranular misorientations of several degrees (Fig. 5d). Pole figure representation of crystal orientations across dislocation walls shows systematic dispersions of the two main olivine crystallographic axes following a half-circle around the third main axis, which itself does not display any significant dispersion (Fig. 5e).

Magnetite grains in Domain II are dispersed and follow the mesh texture in two (Fig. 8a, lower left) and three dimensions (Fig. 7; Supplementary Data Movie 1). Comparison of crystallographic orientations between magnetite grains and associated mesh-textured olivine shows that single magnetite grain orientations display a topotactic relationship in two different orientations, which is dependent on the host olivine orientation (Fig. 13b). Single clinopyroxene grains (Fig. 8a and b), measuring ~0.6–1 mm diameter, occur within Domain II and are generally located in the vicinity of DPOs (Domain I). All large clinopyroxene grains are partially pseudomorphically serpentinized along fractures and cleavage planes and are occasionally replaced by pure diopside.

Mineral chemistry

Olivine grain relicts within Domain II are compositionally homogeneous with average $X_{\text{Mg}}$ NiO and MnO concentrations of 0.90 ± 0.02, 0.38 ± 0.20 wt% and 0.29 ± 0.14 wt%, respectively. The large clinopyroxene grains in this area are Al- and Cr-bearing with a similar composition to the DPO clinopyroxene lamellae (Fig. 14e and f). Dispersed magnetite grains are typically low in Cr, although grains with elevated Cr content can also be found. Cores of hystodiomorphic Cr-spinel grains display...
Fig. 8. (a, b) BSE images of DPOs encompassed by mesh-textured olivine (Ol) grains that are partly serpentinized and large, partly altered, primary clinopyroxene (Cpx) grains. A universal feature of the DPOs is the occurrence of an Mn-rich olivine halo encompassing the central parallel area (within dashed borderline). The apparent bending of the entire DPO in (a) should be noted (bending is traced with dashed lines). (c–e) BSE images of the central DPO areas displaying the occurrence of diopside aggregates (Di agg.), clinopyroxene lamellae (lam.) between every single parallel olivine ‘pseudo-cleavage’ [arrows without an adjoining label in (d)], and lizardite ± brucite (Lz ± Brc) either within the ‘pseudo-cleavage’ or as crosscutting fractures. Clinopyroxene lamellae consistently have their (100) plane parallel to one another as shown in (e). Magnetite (Mag) grains frequently follow the olivine grain parallelism and are closely associated with the clinopyroxene lamellae. Diopside aggregates occur primarily within the olivine or at olivine–lizardite grain boundaries. (f) High-resolution BSE image of the central area in (d), illustrating the frequent appearance of fully enclosed clinopyroxene lamellae within olivine. Atg, antigorite.
negatively correlated Cr\textsubscript{2}O\textsubscript{3} (40–55 wt %) and Al\textsubscript{2}O\textsubscript{3} (8–30 wt %) concentrations (Cr\# = 0.5–0.8). MnO contents of Cr-spinel grains range from 0.2 to 10 wt %. However, most Cr-spinel grains are altered to ferrichromite and display chlorite alteration corona.

**DISCUSSION**

**Microstructure origin**

Perfectly cleaved olivine, magmatic replacement or fluid-mediated, multi-stage pseudomorphism?

At first sight the DPO microstructures resemble ‘perfectly cleaved’ olivine grains that are thought to be the result of a deformation-induced, crystallographically controlled parting, which typically occurs along the (100) and (010) planes with no significant misorientation between olivine segments (Hawkes, 1946; Kuoëda & Shimoda, 1967; Kutty et al., 1983; Aikawa & Tokonami, 1987; Obara & Ishii, 1998; Murata et al., 2009; Nozaka & Ito, 2011). However, there are several microstructural characteristics of the DPOs that cannot be explained by this simple crystallographically controlled parting model. First, the DPOs occur in isolation, encompassed by mesh-textured olivine grains (Fig. 4). Second, although some elongated olivine grains form single domains with minimal misorientation within the DPOs (blue area in Fig. 5b), others lack any crystal-preferred orientation associated with the parting and are highly misoriented with respect to one another. Third, the µCT visualization of magnetite and serpentine reveals that the DPO olivine grains are parallel in three dimensions and are completely surrounded by the mesh-textured olivine (Fig. 7).

In contrast, olivine grains in a shear zone that display ‘perfect cleavage’ are not found in isolation, but as many grains that have been aligned during deformation. Nozaka & Ito (2011) interpreted the ‘perfect cleavage’ of these olivine grains to be the consequence of brittle failure along dislocation walls with contemporaneous antigorite penetration. This scenario would produce a more systematic rock fabric where multiple neighboring grains are rotated towards the stable shear plane and develop a parting (e.g. Lister & Snoke, 1984), rather than the observed isolated DPOs. Moreover, the parted segments of these grains would have a low degree of misorientation between each other or systematic crystallographic deviations. Similarly, parting as a result of shock-induced deformation would also lead to planar fracturing along specific planes without the induction of single domain rotational deformation, and thus cannot explain the observed DPO structures either (e.g. Muller & Horneman, 1969). In fact, none of the deformation processes that produce parting in olivine can account for the progressive rotation of single elongated olivine grains in the DPOs with retention of a parallel habit in the third dimension (Fig. 7), because discontinuous olivine rods within a heterogeneous stress field would be necessary to produce this structure. Furthermore, the development of a hierarchical mesh-texture network surrounding the DPOs indicates that serpentinization was independent of far-field (tectonic) stresses on a grain-scale (e.g. Iyer et al., 2008b). During syn-metamorphic deformation, a preferentially oriented fracture network would probably develop, affecting both the DPOs and the encompassing mesh-textured olivine grains. Furthermore, dislocation density and low-angle subgrain boundaries indicative of high-temperature crystal-plastic deformation are found only within olivine of Domain II (compare with Arndt et al., 2010; Soustelle et al., 2010) and do not occur in DPO olivine grains (Figs 5c and 6a). A similar absence of microstructural markers for dislocation creep has recently been observed in metamorphic olivine after antigorite (Padron-Navarta et al., 2010) and has been interpreted to be indicative of secondary olivine formation. In addition, crystallographic relationships of magnetite and olivine throughout the samples indicate that the DPOs are significantly different from the surrounding...
mesh-textured olivine grain matrix (Fig. 13). Consequently, we propose that the DPOs are of metamorphic and secondary origin in comparison with surrounding relicts of predominantly primary mantle olivine. Comparisons of MnO and NiO concentrations within the mesh-textured olivine and DPO olivine grains (Fig. 14a and b) with those from previous investigations of well-documented secondary olivine after serpentine support the secondary nature of the DPO olivine grains (e.g. Pinsent & Hirst, 1977; Vance & Dungan, 1977; O’Hanley, 1996).

Al- and Cr-rich chrysotile found exclusively as heterogeneously distributed inclusions within the DPOs (Fig. 10) can help to constrain the protolith mineral. If these serpentine inclusions formed after DPO olivine via the infiltration of Al- and Cr-bearing fluids they would be widespread in occurrence. However, we did not observe any serpentine with similar Al and Cr concentrations, or microstructural associations, outside the DPOs; thus they are directly related to the protolith mineral. As Al is found neither as a major nor trace component within olivine, whereas serpentine after orthopyroxene is known to incorporate considerable amounts of Al and Cr (e.g. Dungan, 1979; Wicks & Plant, 1979; Viti & Mellini, 1998), we propose that the protolith mineral was an orthopyroxene grain.

Mantle orthopyroxene grains commonly exhibit microscopic and submicroscopic solid-state diffusion-driven exsolution features, originating from cooling or decompression of the originally high-temperature and -pressure orthopyroxene (e.g. Buseck et al., 1980). Of these features, exsolution of (100) clinopyroxene lamellae is a common subsolidus feature in orthopyroxene grains, which often remain nearly undisturbed during serpentinization (Viti et al., 2005). In contrast, if the DPO clinopyroxene lamellae were exsolved directly from the DPO olivine, as observed in some natural occurrences (e.g. Markl et al., 2001), the intensive brittle deformation described earlier that is needed to explain the observed DPO misorientations should affect both the exsolution lamellae and the host mineral. However, within the DPOs, clinopyroxene lamellae display systematic lattice distortions indicative of
high-temperature crystal-plastic deformation (Fig. 11), which are absent within the surrounding DPO olivine (Figs 5c and 6a). Furthermore, the DPO clinopyroxene lamellae are consistently aligned in the (100) orientation (Fig. 8e), without any relationship to the varying orientations of the DPO olivine grains. If the lamellae were hydrothermal in origin their Al$_2$O$_3$ and Cr$_2$O$_3$ concentrations should be comparable with those of the pure diopside aggregates that also occur within the DPOs, which have the characteristic clinopyroxene composition of hydrothermal secondary origin within meta-peridotites (e.g. Frost, 1975; Evans, 1977; Peretti et al., 1992; Li et al., 2004; McCollom & Bach, 2009). However, the lamellae have Al$_2$O$_3$ and Cr$_2$O$_3$ concentrations comparable with those of published clinopyroxene exsolution lamellae within orthopyroxene grains (Al$_2$O$_3$ ≈ 2.5–7.5 wt %, Cr$_2$O$_3$ ≈ 1–2 wt %; Cannat et al., 1992; Viti et al., 2005; Dijkstra et al., 2010) and those of primary single clinopyroxene grains from the investigated samples, which are higher than the hydrothermal diopside, supporting the origin of the lamellae as a ‘primary’ solid-state exsolution from a now extinct orthopyroxene grain (Fig. 14e and f).

Although the whole-rock geochemistry implies the former presence of orthopyroxene (Fig. 2a) we did not observe any primary orthopyroxene grains or bastite after orthopyroxene within the LOC meta-peridotite. The only
bastite identified in the LOC is restricted to meta-orthopyroxenite dykes within the layered cumulate section of the ophiolite (Iyer et al., 2008a). Orthopyroxene can be directly replaced by olivine during ‘dunitization’, either through partial melting and basaltic melt extraction (e.g. Kelemen, 1990), or the infiltration of a silica-undersaturated, carbonatite melt (e.g. Yaxley et al., 1991). The former is unlikely, as partial melting would shift the whole-rock composition to dunite (Fig. 16) and the latter should leave substantial traces of accessory minerals such as apatite and titanite, which are absent in the LOC meta-peridotite. Reactions indicative of these processes would also affect the clinopyroxene lamellae and the primary clinopyroxene grains; however, they remain predominantly unaltered. Moreover, both aforementioned scenarios would lead to a systematic ‘replacement’ without the observed misorientations (Fig. 5b) or Al- and Cr-rich serpentine inclusions that are exclusively found within the DPO olivine grains (Fig. 10).

Therefore, we suggest that the precursor silicate of each DPO was a single orthopyroxene grain with clinopyroxene exsolution lamellae that was initially pseudomorphically serpentinized to form a so-called bastite (Dungan, 1979) and later completely dehydrated to result in the secondary olivine that dominates the present microstructure.

**Pseudomorphism during orthopyroxene hydration and bastite dehydration**

Preservation of protolithic orthopyroxene features in the DPOs, such as the bent clinopyroxene lamellae visible over several hundred micrometers, indicates that both hydration and dehydration proceeded to a great extent pseudomorphically (Fig. 8). This is also indicated by the retention of morphological outlines. Indeed, average DPO sizes, measuring ~1–5 mm diameter, are in agreement with typical mantle orthopyroxene grain sizes (e.g. Mercier & Nicolas, 1973; Ceuleneer et al., 1988; Soustelle et al., 2010). Mesh-textured olivine grains (~6 mm diameter; Fig. 5c) from less intensively antigorite-serpentinized areas, are also in agreement with primary mantle grain sizes. Moreover, Mn-rich olivine haloes observed at the DPO margins probably represent an area of disequilibrium at former olivine–orthopyroxene interphase boundaries (Fig. 5a and b); however, their timing within the alteration sequence is not resolvable.

The presence of mineral pseudomorphs in retrograde metamorphic rocks but their absence in prograde rocks led Carmichael (1969) to argue that prograde transformation mechanisms, generally involving dehydration, do not involve simple replacement. From this observation Ferry (2000) concluded that the force of crystallization plays a crucial role during pseudomorphic mineral replacement. Force of crystallization is the mechanical work exerted from a growing crystal onto its surroundings if the surrounding has a finite yield strength. Ferry (2000) inferred that a negative total reaction molar volume change, taking the large molar volume of free H₂O into account (e.g. $V_{\text{mic,calc}}$ H₂O = 20 cm³ mol⁻¹ at 350°C and 2 kbar; Duan et al., 2008), will result in a negative strain free energy promoting pseudomorphism. In contrast, during dehydration reactions the total molar volume change is positive and force of crystallization prohibits pseudomorphic replacement. This approach, however, considers only a closed system, neglecting the preservation of the solid component’s volume. Particularly in the case of mineral dehydration (assuming solely thermal dehydration), water needs to be removed to drive the reaction away from equilibrium (e.g. Ague et al., 1998). Thus, our observations of pseudomorph retention during...
Fig. 14. Compositional comparison of mesh-textured olivine vs DPO olivine in (a) and (b), the three identified serpentine varieties in (c) and (d), and large clinopyroxene grains, clinopyroxene lamellae as well as diopside aggregates in (e) and (f). With respect to (a) and (b), DPOs are subdivided into central areas (DPO center) and the Mn$^+$-Fe-rich, Ni-poor olivine halo (DPO halo) at the margin of the domains (see Fig. 8a and b). In (c) and (d) analyses of lizardite from both the mesh-textured olivine grains and between the parallel olivine grains within the DPOs have the same compositional characteristics. In (e) and (f) large clinopyroxene grains outside the DPOs and clinopyroxene lamellae within the DPOs overlap in composition (gray area), whereas diopside aggregate compositions do not. Dashed lines indicate 0 wt%.

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orthopyroxene–bastite dehydration indicate that the molar volume of water would have only a minor influence on the force of crystallization and pseudomorphs may well develop during prograde metamorphism.

Although orthopyroxene has been observed to hydrate directly to form talc and secondary olivine at temperatures well within the stability field of olivine (≥600°C) via a reaction such as (Kimball et al., 1985)

\[
5\text{MgSiO}_3 + \text{H}_2\text{O} \rightarrow \text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4 + \text{Mg}_2\text{SiO}_4
\]

(En) (Tlc) (Ol)

(1)

it is unlikely that this occurred in our samples, as we do not find evidence for concomitant talc co-evolution with the secondary olivine. Even if talc was present and subsequently overprinted, reaction (1) would produce ~40% olivine, whereas in our samples the observable area per cent of olivine in the DPOs is 65–70%. Fully enclosed clinopyroxene lamellae within olivine, in conjunction with the compositional characteristics of the DPO lizardite (Fig. 14c and d), imply that prior to lizardite formation the amount of olivine was 10–20% more than what is observable today.

A variety of studies have shown that lizardite forms as the major bastite component with minor chrysotile, although the MgO–SiO₂–H₂O (MSH) phase diagram predicts that orthopyroxene should form antigorite + talc at high temperatures if water is present. However, water infiltration into unserpentinized peridotite will be at low flow rates owing to their low permeability and porosity, hindering the hydration of orthopyroxene to antigorite + talc. Nevertheless, even if water is able to penetrate to the reaction site, lizardite may form owing to the stabilizing effect of trivalent cations (Al³⁺, Cr³⁺, Fe³⁺) present in lizardite after orthopyroxene (e.g. Wicks & Whittaker, 1977; Dungan, 1979; Viti & Mellini, 1998). Although the only bastite–serpentine relicts identified in our samples are Al- and Cr-rich chrysotile inclusions (Figs 9 and 10), we cannot rule out the presence of lizardite with similar Al and Cr concentrations within the DPOs, which may simply be a result of the amount of Raman spectroscopic analyses executed. Nevertheless, the absence of antigorite and talc, as well as the survival of some Al- and Cr-rich chrysotile (and lizardite?) as inclusions within the DPO olivine, suggests that in the investigated samples orthopyroxene serpentinization proceeded as described in previous studies (e.g. Dungan, 1979). Balancing the reaction on volume results in the pseudomorphic replacement (approximate \( V_m \) of enstatite and lizardite are 23 and 100 mol cm⁻³, respectively)

\[
4\text{MgSiO}_3 + 2\text{H}^+_{(aq)} + \text{H}_2\text{O} \rightarrow \text{Mg}_8\text{Si}_4\text{O}_{12}(\text{OH})_5 + \text{SiO}_2(\text{aq})
\]

(En) (Lz/Ol)

(2)
indicating that Mg and Si are lost to the fluid during orthopyroxene serpentinization. In turn, on the basis of the observations above, orthopyroxene–bastite dehydration also proceeds primarily via an isovolumetric reaction such as (approximate $V_m$ of lizardite and olivine are 100 cm$^3$ mol$^{-1}$ and 30 cm$^3$ mol$^{-1}$, respectively)

$$\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4 + \text{Mg}^{2+}_{(aq)} \rightarrow 2\text{Mg}_2\text{SiO}_4 + 2\text{H}^+_{(aq)} + \text{H}_2\text{O}.$$  

(1

Reactions (2) and (3) are a rough estimate, as we do not know the composition of the fluid, the amount of transiently generated porosity during replacement and whether talc formed. However, comparison of both reactions highlights that overall only SiO$_2$$_{(aq)}$ would need to be removed to maintain constant volume during a sequential alteration scenario of orthopyroxene hydration and bastite dehydration. Comparison of calculated model harzburgite with a whole-rock composition of DPO-containing meta-peridotite indicates that the released SiO$_2$$_{(aq)}$ was mobile on only a micrometer to centimeter scale, because large-scale desilification with migration of SiO$_2$$_{(aq)}$ out of the system would shift the whole-rock composition considerably towards a dunite composition (Fig. 16). Strong gradients in silica activity ($a$SiO$_2$$_{(aq)}$) are known to develop between orthopyroxene and olivine during serpentinization (Frost & Beard, 2007; Klein et al., 2009; therefore, it is likely that the released SiO$_2$$_{(aq)}$ reacted with surrounding olivine to form serpentine without brucite via a reaction such as

$$3\text{Mg}_2\text{SiO}_4 + \text{SiO}_2_{(aq)} + 4\text{H}_2\text{O} \rightarrow 2\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4.$$  

(4

This reaction is possible above 400°C; thus, if water is able to penetrate to the orthopyroxene grains the released SiO$_2$$_{(aq)}$ would aid olivine serpentinization, even within the olivine stability field (e.g. Frost & Beard, 2007; Evans, 2010). A ‘back-of-the-envelope’ calculation, assuming a peridotite composition of 80% olivine and 20% orthopyroxene, where all orthopyroxene has been serpentinized following reaction (2), indicates that the released SiO$_2$$_{(aq)}$ could aid in the hydration of ~40% olivine directly to serpentine without the production of brucite.

Although it is possible to define a narrow temperature field (~350–400°C) in which lizardite/Chrysotile (Mg-end-member) dehydration occurs contemporaneously with olivine hydration to antigorite, the presence of Al in lizardite/chrysotile after orthopyroxene, which is inferred to be several weight per cent (Fig. 10), stabilizes lizardite/chrysotile to temperatures above 500°C (Caruso & Chernosky, 1979). Both the Al and Cr must have been mobile during orthopyroxene–bastite dehydration as neither is incorporated into the resulting olivine. Whereas Cr was probably incorporated into the abundant Cr-magnetite grains, Al shows no evidence of being assimilated into new mineral phases, neither in interfacial areas in the DPOs nor in their surroundings. Thus, we have to assume that Al was mobile on at least the thin section-scale and was either transported away or diluted in subsequent hydration events to be incorporated into, for example, newly forming serpentine minerals. Although Al has long been regarded as an inert element in geological processes (e.g. Carmichael, 1969; Ragnarsdóttir & Walther, 1985; Walther, 1997), more recent natural and experimental investigations have indicated that it can be mobile during fluid–rock interaction in the deep crust and mantle (e.g. Tagirov & Schott, 2001; Newton & Manning, 2008).

### Placing DPO formation within the alteration sequence

Within the investigated samples there are three distinguishable sets of microstructures that can be assigned to different stages in the metamorphic evolution of the investigated meta-peridotite. Although the characteristics of the first, high-temperature stage do not have to be simultaneous, it led to the exsolution of clinopyroxene lamellae, the formation of crystal-plastic deformation structures that remain visible owing to the bending of some DPOs (Fig. 8a; Domain 1), and the formation of subgrain boundaries within some of the new mesh-textured olivine.
(Domain II). The second and third stages can be deduced from examination of reaction microstructures and cross-cutting relationships of serpentine varieties within Domain II, which imply that two extensive serpentinization stages occurred that can be traced throughout the entire mantle section: (1) partial lizardite-serpentinization of olivine resulting in mesh-texture formation followed by (2) a later antigorite-serpentinization of olivine relics and massive antigorite-overprinting of all previous microstructures (Figs 4 and 8). At first glance it appears that the orthopyroxene hydration could be assigned to the lizardite-serpentinization stage and the dehydration to the antigorite-serpentinization stage. However, there are several observations that indicate that DPO formation occurred prior to the aforementioned serpentinization stages.

In the most recent stage, antigorite randomly overprints the secondary olivine within the DPOs (Fig. 8), therefore postdating the DPO formation. Furthermore, the temperature range of the antigorite-serpentinization stage (~300–450°C) is estimated to be below the expected stability range of Al-rich serpentine (~500°C; Caruso & Chernosky, 1979) observed as inclusions within the DPO olivine (Fig. 10). We do not observe any talc + olivine in the investigated samples, which can be formed through lizardite/chrysotile or antigorite breakdown. According to Gibbs’ free energy considerations, the lack of such a transformation suggests that the antigorite-serpentinization stage probably did not exceed 450–500°C (Evans, 2004, Fig. 6). This is supported by the absence of tremolite formation after primary or secondary clinopyroxene (Fig. 17b). There is also compelling evidence that antigorite ± brucite was formed directly from primary mantle olivine grains during fluid infiltration (Plummer et al., 2012), rather than solely as a result of thermal, H₂O-conserving lizardite/chrysotile recrystallization. This suggests that the antigorite-serpentinization temperature may not have exceeded even ~400°C because olivine (pure forsterite) is stable above this temperature when excess H₂O is present (Evans, 2004). Therefore, the stability of Al-rich lizardite/chrysotile, originating from orthopyroxene serpentinization, exceeds the upper temperature limit for the antigorite-serpentinization stage and thus would not be expected to dehydrate. This is in agreement with observed lizardite (~1–5 wt % Al₂O₃) survival well beyond the antigorite-out reaction (Frost, 1975).

Lizardite ± brucite veins crosscut the DPO microstructures, indicating that DPO olivine formation also pre-dates the lizardite-serpentinization event. Lizardite replacement of the DPO olivine is also evident along the DPO ‘pseudo-cleavage’, because the Al-free lizardite found between the parallel olivine domains (Domain I) shows a compositional overlap with lizardite that forms the mesh texture in olivine grains in Domain II (Fig. 14c and d). Moreover, the cryptic presence of brucite in the Al-free lizardite in Domain I implies that it formed after the DPO olivine and not during primary orthopyroxene hydration, as brucite formation during orthopyroxene serpentinization is unfavorable owing to an increased $\delta\text{SiO}_2$ hydration environment (e.g. Frost & Beard, 2007). In this case the interphase boundary between the metamorphic olivine and clinopyroxene exsolution lamellae was a preferred site for fluid infiltration and serpentinization initiation, creating the observed ‘pseudo-cleavage’ appearance with the sequence olivine–lizardite–clinopyroxene–lizardite–olivine. As lizardite-serpentinization temperatures (~50–300°C, Fig. 14) can be expected to have been lower than those of the antigorite-serpentinization event, orthopyroxene–bastite dehydration could have not occurred during this stage either.

On the basis of the microstructural and microchemical investigations, as well as phase stability considerations, we suggest that two metamorphic events occurred in addition to the observed lizardite- and antigorite-serpentinization episodes: (1) a hydration stage that led to the orthopyroxene serpentinization and serpentinization of the surrounding olivine grains aided by the released $\delta\text{SiO}_2$ upon orthopyroxene serpentinization and (2) a transient dehydration stage that dehydrated orthopyroxene–bastites and ‘healed’ any mesh textures after olivine (Fig. 15). Although direct indications for the latter are scare, re-hydration and subsequent serpentinization probably reused previous, pre-existing fluid pathways to obliterate the microstructural evidence. None the less, both metamorphic stages that pre-date the evident lizardite- and antigorite-serpentinization stages are recorded by the DPO microstructure (Fig. 17).

**Searching for the dehydration event**

Deserpentinization has been suggested to be either the result of contact metamorphic events, such as magma infiltration into meta-peridotites or serpentinites (Trommsdorff & Evans, 1972; Vance & Dungan, 1977), as a consequence of hydrated oceanic lithosphere subduction (e.g. Hacker et al., 2003; Padron-Navarta et al., 2011), or due to Barrovan-type metamorphism during mountain building (e.g. Evans, 1977). However, in the LOC large-scale magmatic intrusions that could induce dehydration are absent. Similarly, an entire ophiolite sequence that has undergone subduction and later exhumation would be expected to be at least partially dismembered and should show blueschist- and/or eclogite-facies associations within the crustal section (e.g. Angiboust et al., 2011), but neither are observed on Leka (Fig. 1). It has been suggested that the antigorite-serpentinization overprint is a consequence of Caledonian regional metamorphism that produced a regular Barrovan-type metamorphic pattern throughout the mantle fragments in the Scandinavian Caledonides, with an increase of
Fig. 17. (a) Relative chronology of the microstructure evolution summarizing the observed transient dehydration within the mantle meta-peridotite of the Leka Ophiolite Complex. The evolution is illustrated using the three main rock-forming minerals orthopyroxene (Opx), olivine (Ol) and clinopyroxene (Cpx); spinel is excluded because of a negligible contribution to the DPO evolution. (b) Phase diagram in the system MgO-SiO$_2$-H$_2$O (MSH) displaying the stability of antigorite (Atg), lizardite (Lz) and chrysotile (Ctl) with varying temperature and pressure, using a compilation of available data from experimental, theoretical and naturally constrained data sources (Andreani et al., 2007, and references therein). White curve above 400°C is added from the system CaO-MgO-SiO$_2$-H$_2$O (CMSH) and dashed curves from MgO-Al$_2$O$_3$-SiO$_2$-H$_2$O (MASH) to illustrate the breakdown of diopside + antigorite (Di + Atg) to tremolite (Tr-in) and the enlarged stability field of lizardite (and possibly chrysotile) as a function of its Al content ($X_{\text{Al}}=0.2$ is 3.7 wt % Al$_2$O$_3$ and $X_{\text{Al}}=0.5$ is 9.2 wt % Al$_2$O$_3$), respectively. Temperature ranges for the different evolutionary stages of the DPO microstructure are indicated above the phase diagram. MS$_1$ is not shown in (b) as this microstructure is the result of a decompression event occurring at higher temperatures. Brc, brucite; Chl, chlorite; En, enstatite; Fo, forsterite; Tlc, talc.
metamorphic grade from SE to NW (Bucher-Nurminen, 1991). Thus, if the observed dehydration was a consequence of Barrovian-type metamorphism, its transient nature and the subsequent lower temperature rehydration to lizardite prior to antigorite-serpentinization (Fig. 17a) need to be accounted for. Alternatively, both the lizardite- and antigorite-serpentinization could be synchronous or post-date Caledonian metamorphism, although this is unlikely as the LOC is situated in the Upper or Uppermost Allochthon and hence, on the basis of the Norwegian tectonostratigraphy, the antigorite-serpentinization should represent the lowest grade (<400°C) of Caledonian metamorphism (Bucher-Nurminen, 1991).

Deserpentization can also occur in lower pressure settings; for example, where fault movements displace serpentinitized mantle to come in contact with the hotter end of an adjacent ridge segment (Rutter & Brodie, 1987). In situ, low-pressure transient dehydration has been proposed to occur owing to the feedback between mantle hydration and hydrothermal convection at oceanic spreading centers. Simulations of such feedback, which take into account evolving permeability, indicate that in situ serpentine hydration–dehydration–rehydration can be active in transient phases as convective cells are formed and merge together (Iyer et al., 2010). Subsequently the deserpentized mantle can once again be re-hydrated when a quasi-steady-state regime is established and temperatures favor serpentinitization, overprinting initial deserpentization episodes. Alternatively, influx of new hot asthenosphere or fluid flux contributions from a subducting slab may also be common in the supra-subduction zone settings of evolving ophiolites (Shervais, 2001; Hyndman & Peacock, 2003), contributing to the thermal fluctuations required.

At present, we are unable to unequivocally answer what initiated the dehydration event. Further isotope and trace element data analyses are required to elucidate the origin of the fluid(s) that induced serpentinitization and thus identify the metamorphic event that caused dehydration of the meta-peridotite. During ‘conventional’ serpentinitization, fully serpentinitized orthopyroxene grains are typically surrounded by considerably serpentinitized olivine grains; hence, detailed analysis of the olivine serpentinitization prior to dehydration is also required to determine the extent of the first hydration stage. With respect to the latter, it is interesting to note that examinations of serpentinitized meta-dunite within the ultramafic cumulate section (Fig. 1) do not exhibit microstructures that indicate extensive serpentine dehydration.

**Recognition and survival of microstructures during multi-stage, fluid-mediated pseudomorphism**

Metamorphic rocks can undergo a prolonged history, which can be partly or completely deciphered from the present-day microstructures, either as an evolution along a polyphase P–T path or simply because of multiple fluid infiltration events. For example, fluid-mediated mineral replacement reactions often retain the external form (habit) and crystallographic details of the parent. Although complete replacement reactions make it difficult to identify the metamorphic nature of the system, requirements for pseudomorphism can be used to help understand the reactions because of their ability to retain crucial information about the replaced mineral (e.g. the retention of micron-sized twinning; Putnis, 2009). As seen in Fig. 8, this information can also be the survival of a specific mineral phase, which may regulate the microstructure from an early stage in the rock’s history. In the DPOs, although the clinopyroxene lamellae originate from the subsolidus re-equilibration of the former orthopyroxene grain, they controlled the evolution of the microstructure by providing fluid pathways and defining the single elongated secondary olivine grains (Fig. 8). Misinterpretation of fully enclosed clinopyroxene lamellae within olivine (Fig. 8f) could lead to erroneous conclusions; for example, that the clinopyroxene lamellae were the result of solid-state exsolution from olivine, implying incorrect formation conditions and thus metamorphic history (see Ren et al., 2008). Even when these mineral relics are obscured by the hydrothermal equivalent of the relict phase (diopside aggregates), certain characteristics such as the chemistry and crystallographic orientation can still be identified (Fig. 12). Detailed investigations, coupling crystallographic and chemical data, may lead to more widespread recognition of such ‘ghost’ mineral microstructures. For example, the occurrence of oriented lamellae in minerals, especially those that cannot be explained by classical closed-system solid-state diffusion-driven unmixing, may represent such ‘ghost’ microstructure and not, as suggested, solid-state exsolution of either an exotic precursor phase, occurring at ultrahigh-pressure conditions (Dobrzhinetskaya et al., 2009), or a precipitate caused by diffusional exchange with the matrix through an intact host crystal lattice (open-system precipitation; Proyer et al., 2009). In a fluid-driven reaction environment the mechanism of textural re-equilibration will also be through dissolution and reprecipitation, thus ‘closure temperatures’ at which microstructures cease to evolve will be much lower than during solid-state diffusion (Putnis, 2009; Putnis & Austrheim, 2010). Hence, evidence for microstructures as a result of an interface-coupled dissolution–reprecipitation mechanism may be only cryptically preserved or not at all. However, careful investigations of mineral replacement reactions by applying a multi-method approach that encompasses a combination of microstructural, crystallographic and microchemical analytical methods may enable us to see through multiple sequential events.
SUMMARY AND CONCLUSIONS

We have examined the pseudomorphism of single orthopyroxene grains via serpentine–bastites to secondary olivine, recording a transient dehydration stage within the oceanic lithospheric mantle section of the Leka Ophiolite Complex (Norway). On the basis of observed 2-D and 3-D mineral replacement microstructures, their consecutive relationships, crystallography, mineral chemistry and phase stabilities, we can summarize the observed hydration–dehydration–rehydration sequence in terms of the following proposed evolutionary sequence (Fig. 17).

1. During subsolidus solid-state re-equilibration at high temperature orthopyroxene grains exsolve clinopyroxene lamellae (MS$_1$). The clinopyroxene lamellae exhibit crystal-plastic deformation-induced bending, indicating that the rock was subject to asthenospheric mantle flow during or after orthopyroxene exsolution.

2. Orthopyroxene hydrates to form serpentine (bastite; MS$_2$) with partial serpentinization of surrounding olivine grains [200–400°C(?)], probably aided by the SiO$_2(aq)$ released during pseudomorphic orthopyroxene serpentinization. Clinopyroxene exsolution lamellae survive.

3. Dehydration of orthopyroxene–bastites (MS$_2$) causes serpentine breakdown to secondary olivine enclosing Al- and Cr-rich bastite–serpentine relics (>500°C). Clinopyroxene exsolution lamellae prevail and control the parallelism of the secondary olivine grains to result in the DPO microstructure. Dehydration ‘heals’ any mesh textures formed in the primary olivine grains.

4. Re-hydration at low temperatures (c. <300°C) initiates lizardite-serpentinization of the DPOs as well as the primary mantle olivine and clinopyroxene grains (MS$_3$). Lizardite-serpentinization probably re-uses previous, pre-existing fluid pathways to obliterate the microstructural evidence of ‘healed’ mesh textures.

5. Later higher temperature hydration (300–400°C) initiates antigorite-serpentinization replacing both relict mantle olivine and secondary DPO olivine, destroying all former underlying microstructures (MS$_3$).

We have shown that microstructures that have undergone multiple overprinting processes can still retain evidence of the earlier metamorphic stages during the history of a rock. Although some events are easily distinguishable, others are evident only because of their crystallographic and petrological relationships with respect to later events. Thus, a detailed examination of the mineral chemistry, reaction microstructures and crystallographic associations was required, utilizing a wide range of analytical techniques. The restriction of intensive deformation to shear zones during fluid–rock interaction preserves markers for pseudomorphism and the original spatial relationships between phases, aiding the determination of the different processes that took place. Mineral tracers, such as magnetite and serpentine in the DPOs, are critical when deciphering the 3-D parallelism of the DPO olivine structure and their isolation within the surrounding mesh texture. The determination of the dehydration event demonstrates that although the microstructures can provide clues to the rock history, further research with respect to isotope and trace element analysis is required. It is crucial to identify the origin of fluid(s) that induced serpentinization, to relate the different serpentinization episodes to possible infiltration of circulating seawater, released subduction zone fluids or fluids infiltrating during Caledonian regional metamorphism and thus further unravel the origin of the dehydration event.

Although our understanding of the mineralogical changes observed in this study is restricted to the investigated area, it is a logical progression that transient dehydration could be a much more widespread phenomenon within the oceanic lithospheric mantle than is currently acknowledged. Furthermore, the survival of microstructures and minerals during succeeding metamorphic events results in complex structures that are prone to misinterpretation. In particular, fluid-mediated (pseudomorphic) replacement reactions that have gone to completion will probably leave only cryptic traces of their possibly long and complex history.

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SUPPLEMENTARY DATA
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REFERENCES


