Nanostructure of serpentinisation products: importance for water transport and low-temperature alteration

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Abstract

The hydration of mantle rocks occurs at mid-ocean ridges, in subduction zones and in ophiolites where it strongly modifies the properties of the oceanic lithosphere. The nanostructure of the reaction products is poorly constrained, but it is very important, as it controls fluid transport during solid volume increase, and it influences phase reactivity during further fluid/rock interaction at low temperature. We image contacts between olivine and its hydration products at the nanoscale, in a dunite collected during the Oman Drilling Project that underwent nearly isochemical serpentinisation and solid volume increase. Olivine first reacts to form a ~ 100 nm thick coating composed of a brucite/serpentine mixture, suggesting isochemical serpentinisation at this scale too. Lizardite columns ~ 1 μm wide replace this mixture at its margin. The columns are embedded in a brucite-rich assemblage containing a

high density of nanopores that may favor fluid transport during reaction. We interpret these observations as a nanometre-scale, two-step process. Fluid pathways are formed rather than clogged by reaction products thanks to mass transfer at a scale limited to less than 100 nm. The preservation of the fluid pathways during solid volume increase explains the observed high extents of reaction. The presence of brucite in high porosity regions may explain its preferential reaction during low temperature fluid/rock interaction.

1. Introduction

Hydration of mantle rocks below $\sim 500^{\circ}\text{C}$ (i.e. serpentinisation) is of current scientific interest because it substantially modifies the physical properties, the composition and the RedOx conditions in the oceanic lithosphere (Escartín et al., 1997, 2001; Oufi, 2002; Charlou et al., 2002; Malvoisin, 2015), and it provides an energy source for biological organisms (Schulte et al., 2006; Templeton and Ellison, 2020; Kraus et al., 2021). This reaction often reaches completion while the solid volume increases by approximately 50 % during the replacement of primary olivine and pyroxene by serpentine (Macdonald and Fyfe, 1985). This is puzzling because reaction products are expected to precipitate in the pores leading to the clogging of the fluid pathways, consumption of fluid that forms a fast diffusion path, and armouring of reactive surfaces, all of which are negative feedbacks that might limit the extent of reaction (Kelemen and Hirth, 2012; Evans et al., 2020). This process is probably responsible for a decrease in permeability over several orders of magnitude that has been measured in flow-through serpentinisation experiments (Godard et al., 2013; Farough et al., 2015). However, the hypothesis that these negative feedbacks are self-limiting is inconsistent with the high

46 extents of reaction generally observed in naturally serpentinised peridotites (Macdonald and
47 Fyfe, 1985; Oufi, 2002), suggesting that additional processes are at play to allow for complete
48 serpentinisation.

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50 It has been proposed that serpentinisation could occur at constant volume through the export
51 of matter as aqueous species in the fluid (Thayer, 1966; Carmichael, 1987; Fletcher and
52 Merino, 2001). However, some natural samples have recorded nearly no change in ratios of
53 major elements during alteration (Mg/Si/Fe, e.g. Coleman and Keith, 1971) suggesting that
54 either hydration occurred with very little export of dissolved components with different
55 solubilities, or that there was large-scale, congruent dissolution of silicate minerals. Recent
56 work on microstructures indicates that serpentinisation in experiments (Klein and Le Roux,
57 2020) and in natural rocks (Malvoisin et al., 2020) is accompanied by large increases in solid
58 volume (30 to 110 percent). Because serpentinisation and carbonation rapidly add mass to
59 altered peridotite as a result of limited solubility of Mg, Si, Fe and Ca in aqueous fluids,
60 thermodynamic models indicate that hydration and carbonation produce increases of 40 to
61 60% in solid mass and volume (Malvoisin, 2015; de Obeso and Kelemen, 2018, 2020;
62 Kelemen, 2021a, 2021b). Because pore space in fresh and altered peridotites is limited
63 (commonly less than 5%, mainly in fractures), these increases in solid volume must occur in
64 an open system, and result in an increase in the total volume of serpentinised peridotites.

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66 The preservation of fluid pathways during serpentinisation is essential to sustain reaction as
67 the solid volume increases. Tectonic deformation and thermal cracking can generate fracture
68 networks in peridotites (Demartin et al., 2004; Rouméjon et al., 2014). Fractures can also be

formed by the reaction itself. Macdonald and Fyfe (1985) and O'Hanley (1992) proposed that volume increase at the serpentine/olivine interface is accommodated through formation of expansion fractures, allowing for efficient fluid transport. The increase in volume during serpentinisation can increase differential stress to a level sufficient to generate fractures in the primary minerals, potentially maintaining or enhancing permeability, and increasing reactive surface area and reaction rates in a positive feedback mechanism (Macdonald and Fyfe, 1985; O'Hanley, 1992; Jamtveit et al., 2009; Rudge et al., 2010; Plümper et al., 2012; Malvoisin et al., 2012, 2017; Kelemen and Hirth, 2012; Evans et al., 2020; Yoshida et al., 2020). However, this process alone may not be sufficient to prevent clogging of porosity. A recent numerical study has shown that the scale of mass transfer during reaction plays a key role for fluid pathway preservation (Malvoisin et al., 2021). If element transport occurs between the reaction front and the pores, porosity clogging leads to reaction shutdown. However, if the reaction products precipitate at the reaction front, pre-existing pores can be preserved allowing continuous fluid transport through time. This latter model assumes that fluid can be transported through the reaction products.

Tutolo et al. (2016) measured a nanoscale porosity of several percent in serpentinised peridotites, probably associated with diffusive water transport in the serpentinisation products. However, even if this nanoscale porosity plays a key role for reaction, its distribution and its relationship with the reaction products are still not known. The porous network formed during serpentinisation is also probably re-used during post-serpentinisation alteration at high water to rock ratio and low temperature ($< 150^{\circ}\text{C}$). As for serpentinisation at higher temperature, this further alteration is thought to induce ferrous iron oxidation associated with water

dissociation and molecular hydrogen generation (Sleep et al., 2004; Seyfried et al., 2007; Klein et al., 2009; McCollom and Seewald, 2013; Miller et al., 2016, 2017; Ellison et al., 2021). Hydrogen production at low temperature probably supports microbial activity (Templeton and Ellison, 2020). Among the serpentinisation products, ferroan brucite ((Mg,Fe)(OH)₂) appears to preferentially react by being extensively dissolved, by forming (hydro-)oxides (Jöns et al., 2017; Klein et al., 2020) or by reacting with SiO_{2,aq} to form serpentine (Tutolo et al., 2018). This difference in reactivity among the serpentinisation products may originate from their nanostructure.

Here we use high resolution imaging at the nanoscale to constrain the structure and the composition of the hydration products of olivine in an extensively serpentinised dunite collected during the Oman Drilling Project (Kelemen, 2021b). The observations suggest a mechanism for reaction product formation, and an explanation for brucite high reactivity during post-serpentinisation alteration.

2. Material and methods

2.1. Serpentinised dunite sample

The studied sample was collected in the “Multi-Borehole Observatory” (Kelemen, 2021b) during the Oman Drilling Project in the Wadi Tayi massif of the Samail Ophiolite (Kelemen et al., 2020). It comes from 215 m depth in Hole BA4A (sample BA4A-81-1-1-17, Kelemen et al., 2020). Hole BA4A is composed of an alternation of dunite (64 %) and minor harzburgite (26 %) with no systematic lithologic trends. We collected one of the freshest dunite in the middle of a 26 m thick body bound by 3 m and 0.4 m thick harzburgites at its top

and bottom, respectively (see details in the visual core description in Kelemen et al., 2020).

Dunite is crosscut by ~ 30 gabbro and pyroxene dykes ranging in thickness from 0.05 to 1.5 m (Kelemen et al., 2020). The studied sample is dyke free. Malvoisin et al. (2020) provide a full mineralogical and chemical description of the sample; a brief summary is given below.

The sample is cross-cut by a 100 μ m-wide serpentine vein surrounded by a homogeneous mesh texture with olivine relicts in the centre of the meshes. X-ray microtomography reveals that it has been more than 80 % serpentinised. The reaction products form a submicron scale mixture of iron-rich brucite and serpentine. Olivine contains parallel inclusions of clinopyroxene + magnetite intergrowths which do not contain other serpentinization reaction products. This indicates that these inclusions have an orientation relationship with olivine acquired during a pre-serpentinization event, probably during symplectic exsolution in olivine at high temperature (Moseley, 1984). Malvoisin et al. (2020) measured the deformation of these inclusions during serpentinisation to estimate a change in volume during reaction close to 50 %. The major element composition indicates that there has not been significant mass transfer during reaction, except for the addition of H₂O. This is confirmed by profiles in trace elements, showing that the pre-serpentinization zoning in Al, Ti, V, Sc and Cr of olivine is preserved during the reaction (Malvoisin et al., 2020). The sample thus recorded isochemical serpentinisation with an associated solid volume increase corresponding to the value expected for reaction in a closed system. This mass transfer limited to the subgrain scale is characteristic of the incipient stage of serpentinization (Evans et al., 2013). The observations performed here are thus relevant for this stage, and mineral-specific rather than rock-specific. They are thus expected to apply to both dunite and harzburgite. We study here the contact between olivine and the serpentine/brucite mixture.

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139 2.2. *Methods*

140 We first determined the composition and the texture of the sample at the micrometre scale
141 with a field-emission scanning electron microscope (Tescan Mira II LMU) at the University
142 of Lausanne. It was operated at 10 kV and 8 mm working distance. We then used imaging at
143 the nanoscale to characterize the contacts.

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145 2.2.1. *Focused ion beam nanotomography*

146 The 3-D nanostructure of the contact between olivine relics and its reaction products was
147 determined with focused ion beam (FIB) tomography. A Zeiss Crossbeam 540 apparatus
148 equipped with a field emission Scanning Electron Microscope (SEM) was used at the CIME-
149 EPFL Laboratory (Lausanne) to sequentially mill 10 nm thick layers of a cuboid of size
150 10x20x13 μm . Inbetween milling stages, SEM images were acquired at 1.7 kV and 2.5 nA
151 with a dwell time of 15 μs . The pixel size is of 10x10 nm. We used the MultiStackReg plug-in
152 (Thévenaz et al., 1998) of the FIJI software to align the stack of images. We developed a
153 Matlab code based on a median filter and on dilatation/erosion techniques to segment the
154 images based on their back-scattered electron (BSE) intensity.

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156 2.2.2. *Transmission electron microscopy*

157 We extracted disks from a 30 μm -thick petrographic thin section glued with CrystalBond
158 epoxy for Transmission Electron Microscopy (TEM) analyses. The disks were then milled
159 with an Ar⁺ ion polisher (PIPS II - Gatan, CMTC, Grenoble) operating at low incidence.
160 Then, the electron transparent bevels were coated with a 10 nm thick carbon film. We

acquired high resolution images (HRTEM) with a JEOL JEM-2010 operated at 200 keV and having a 0.23 nm point to point resolution (CINaM, Marseille, France). We also obtained chemical maps at the nanoscale using a Field Electron Gun JEOL 2100F TEM operated at 200 keV and equipped with an EDX JEOL Centurio 1 detector (CMTC, Grenoble, France) in Scanning Transmission Electron mode (STEM) combined with Energy Dispersive Spectrometry (EDS) mapping.

In addition, an automated crystal orientation mapping tool (ASTAR[®]; NanoMEGAS) was used to map phase distribution and crystal orientation in the samples (Rauch and Véron, 2014). 500x500 pixel maps were acquired at 200 keV with a probe size of 1.5 nm and by precessing the incident beam with an angle of 0.5°. Step sizes of 3 and 4 nm were used, leading to map sizes of 1.5x1.5 µm and 2x2 µm, respectively. The electron diffraction patterns acquired at each pixel were compared with template matching to a bank of patterns pre-computed for the crystallographic structures of lizardite (Mellini and Viti, 1994), brucite (Chakoumakos et al., 2013) and olivine (Angel and Nestola, 2016). The reliability parameter defined in Rauch and Véron (2014) was used to generate a transparency mask which was superimposed on the phase and orientation maps to darken the pixels with a low reliability.

3. Results

The sample is highly homogeneous in microtexture. The reaction products around relict olivine grains are dominated by a mixture of serpentine and brucite with minor magnetite grains (Figure 1). At several micrometres to several tens of micrometres from the olivine surface, bright Fe-rich brucite appears to segregate in several micrometre wide zones with

diffuse margins and in association with magnetite (Figures 1 A and C). Electron microprobe analyses always correspond to a mixture of serpentine and brucite, revealing that brucite segregation is never complete at the micrometre scale (Malvoisin et al., 2020). Near the olivine surface, the serpentine/brucite mixture is more homogeneous in colour suggesting a more intimate mixing. Nevertheless, linear and parallel brighter zones reveal an organized structure at the submicrometre scale (Figures 1 B and D – black arrows). We investigated this structure at the nanoscale by focusing on the olivine/serpentine + brucite contact.

3.1. Morphology in three dimensions

We used FIB nanotomography to reveal the 3D structure at the nanoscale of the reaction products. We identified three reaction products of the serpentinisation reaction. The brightest regions have a platy habit, reaching a maximum size of 10 μm long and 400 nm wide (Figure 2). They correspond to the parallel and bright zones observed on SEM images. They are also regularly distributed in the reaction products, and have a preferential orientation with their longest axis roughly normal to the olivine surface, as shown on the three dimensional reconstructions on Figure 3. Sections parallel to the olivine surface show 1-2 μm wide polygons delimited by the brightest regions which form a honeycomb microstructure in 3D (Figures 2 and 3). The columns filling this microstructure are composed of the darkest phase. The third phase of intermediate grey tint in BSE images forms a ~ 200 nm thick continuous coating at the olivine surface (Figure 3 – orange region). We also observed connected pores forming up to 100 nm thick planes parallel to the olivine surface (Figure 2).

3.2. Structure at the nanoscale

EDS mapping in STEM mode confirmed the presence of three types of reaction products with different compositions (Figure 4). The reaction products are volumetrically dominated by the darkest phase on SEM images perpendicular to the olivine surface, with a homogeneous composition. The molar $\text{Mg}/(\text{Mg}+\text{Fe})$ and $(\text{Mg} + \text{Fe})/\text{Si}$ ratios measured in this phase are close to those measured at larger scale in lizardite (0.96 and 1.5, respectively; Malvoisin et al., 2020). This phase is hereafter referred as columnar lizardite. The brightest zones on SEM images appear as discontinuous domains with a low $\text{Mg}/(\text{Mg} + \text{Fe})$ ratio and a $(\text{Mg} + \text{Fe})/\text{Si}$ ratio higher than in olivine. This suggests that these interstitial zones are composed of a mixture of brucite and serpentine (hereafter interstitial mixture). The region coating the olivine surface has a rather homogeneous composition with $\text{Mg}/(\text{Mg} + \text{Fe})$ and $(\text{Mg} + \text{Fe})/\text{Si}$ ratios close to those of olivine. Such a composition again indicates a serpentine/brucite mixture (hereafter coating mixture) but richer in serpentine than the interstitial mixture (Figure 4 B and C). Graduations in chemical composition from the coating to the interstitial mixtures were observed at the base of the interstitial mixture, especially when the interstitial mixture is slightly oblique to the olivine surface (Figure 4 D and E). This change in composition probably corresponds to an increase in the brucite fraction in the brucite/serpentine mixture.

The automated crystal orientation maps confirmed the presence of lizardite in the columns occurring as $\sim 1 \mu\text{m}$ wide and $> 3 \mu\text{m}$ long grains with minor intercalated brucite lamellae (Figure 5). The orientations of lizardite and brucite lamellae in the columns are identical with their [001] axis radiating out from the olivine surface (Figure 5 B and D). Grains in the brucite/serpentine mixtures have a size below 100 nm and a random orientation.

Ordered (columnar lizardite) and disordered (coating and interstitial mixtures) domains were also observed on HRTEM images (Figure 6). The (001) basal planes of columnar lizardite are parallel to the contact between olivine and reaction products. The columnar lizardite displays sharp contacts with disordered brucite/serpentine mixtures (Figure 6 A and D). The coating mixture is continuous between olivine surface and lizardite columns, even though it varies in thickness from less than 50 nm to ~ 200 nm (Figure 6 D). Electron diffraction confirms that the disordered domains are composed of brucite and lizardite intermixed at a scale less than 100 nm (Figure 6B). The stack of differently oriented lizardite and brucite grains leads to extensive distortion and nanoscale pore formation along the (001) basal plane of both sheet-like minerals. The pores are approximately 10 nm wide and 1 nm high. Image analysis of Figure 6 A allowed a rough estimate of ~ 3 % porosity in the interstitial mixture. (Mg+Fe)/Si molar ratios measured with EDS point analyses are of ~ 2.0, 1.9, 1.6 and 2.4 in olivine, coating mixture, columnar lizardite and interstitial mixture, respectively (the locations of the analysed points are given in Figures 4 A and 6 A). The higher (Mg+Fe)/Si ratios in the disordered domains compared to the ordered domains are in agreement with the EDS mapping and the automated crystal orientation maps. The higher (Mg+Fe)/Si ratio ratio in the interstitial mixture compared to the coating mixture also suggests a higher proportion of brucite inbetween the lizardite columns.

4. Discussion

4.1. Mechanism of fluid pathway preservation

The observation of a continuous disordered domain composed of a brucite/lizardite mixture is, to our knowledge, the first documentation of such a coating at the olivine surface. However, amorphous or poorly crystalline material (often called proto-serpentine) has been produced during olivine hydration in experiments (Daval et al., 2011; Godard et al., 2013; Lafay et al., 2016) and observed in natural samples (Cressey, 1979; Andreani et al., 2004; Rumori et al., 2004; Boudier et al., 2010; de Obeso and Kelemen, 2018). The location of the coating mixture at the olivine contact, and its continuity, suggest that it is the first product of olivine hydration (Figure 7). This first step involves local dissolution and precipitation as proposed for replacement reactions (Putnis, 2009). In such a process, the aqueous species formed during olivine dissolution precipitate locally at the olivine/coating mixture contact. The composition of the mixture with a (Mg+Fe)/Si ratio similar to olivine suggests that this first step is isochemical, with limited mass transfer and porosity clogging at a scale > 100 nm. Transport through the thin coating layer may occur by diffusion (Figure 7 B). In contrast to the thin coating layer, the reaction products are volumetrically dominated by the adjoining lizardite columns with a honeycomb microstructure. The pattern described here is similar to those formed by desiccation or magma cooling (i.e. columnar joints). The columns forming such patterns are oriented in parallel to the main gradient in temperature or concentration. Here, olivine dissolution controls the main gradient in aqueous species concentration. As a result, the columns are oriented perpendicularly to the olivine surface. Goehring et al. (2009) proposed the following scaling law for columnar pattern formation:

$$Pe = (v L_c)/D \quad (1)$$

where Pe is the dimensionless Péclet number comparing advection and diffusion, v is the speed of pattern development, L_c is the characteristic size of the pattern, and D is the

diffusivity. Goehring et al. (2009) have shown that formation of patterns similar to the one described here requires $Pe \sim 0.1$. Using experimentally-determined serpentinisation rates (Lafay et al., 2012; Malvoisin et al., 2012; McCollom et al., 2016) and a characteristic pattern size of $\sim 1 \mu\text{m}$ (lizardite column width), equation (1) provides a rough estimate for diffusivity through the coating mixture between 10^{-17} and $10^{-20} \text{ m}^2/\text{s}$. These values are consistent with the values estimated experimentally for intergranular diffusivity during serpentinization (Malvoisin and Brunet, 2014) and approximately 10 orders of magnitude smaller than diffusivity in a free fluid ($10^{-9} \text{ m}^2/\text{s}$; Oelkers and Helgeson, 1988). This may explain why the mineralogical processes described here occur at a scale below 100 nm, without mass transfer into the nanopores and porosity clogging.

Lizardite columns similar to the ones described here have also been identified by Boudier et al. (2010) in a harzburgite from Oman, where they were interpreted as evidence for a non-topotaxial relationship between olivine and lizardite. Rumori et al. (2004) and Rouméjon et al. (2015) also reported the presence of columnar lizardite in mesh textures found in harzburgites from the Alps and the Southwest Indian Ridge. Cressey (1979) observed the presence of lizardite plates formed after olivine. This suggests that the formation of lizardite columns is a common process during mesh texture formation in both dunite and harzburgite.

The lizardite columns are separated by a 100-400 nm wide brucite/lizardite mixture with crystallographic characteristics similar to the coating mixture but with a higher proportion of brucite. To our knowledge, the fact that the lizardite columns is embedded in a brucite-rich mineralogical assemblage has not been previously reported. The composition of the interstitial

mixture and the lizardite columns and their location at the contact with the coating mixture, suggest that their formation constitutes a second step in the serpentinisation process (Figure 7 B). The volumetric proportion of brucite estimated with image analysis in the reaction products is of 10 % and 22% in the phase maps of Figure 5A and 5C, respectively. These proportions are consistent with the proportion of 19 % expected for the isochemical serpentinisation of olivine, which was documented at larger scale in the same sample (Malvoisin et al., 2020), suggesting again that reaction occurs with mass transfer limited to a scale < 100 nm. The brucite grain size does not seem to evolve significantly during the second step of the reaction while lizardite forms micrometer-wide and well-ordered columns at the expense of nanometer-sized grains in the coating mixture. This difference in grain size evolution probably reflects a difference in solubility of the lizardite and brucite grains in the coating mixture at ~ 200 nm from the olivine surface where lizardite columns are formed. Small grains are less stable than large grains due to their greater surface area. This is the driving force for Ostwald ripening during which small grains dissolve while large grains grow. The grain size at which the transition from dissolution to growth occurs (saturation grain size; d) can be defined as (Steefel and Van Cappellen, 1990):

$$d = \frac{2 \sigma V_m}{R T \ln \Omega} \quad (2)$$

where σ is the surface free energy, V_m is the molar volume, R is the gas constant, Ω is the supersaturation defined as the ratio between the activity product for the dissolution reaction and the equilibrium constant. Ω is not expected to be significantly different for brucite and lizardite in the coating mixture (Malvoisin and Brunet, 2014). However, σ is 1.5 J/m² for the (111) SiO₂ surface and 0.05 J/m² for the (001) Mg(OH)₂ surface (Churakov et al., 2004;

Krasilin, 2020). These data indicates that the surface energy of lizardite could be approximately one order of magnitude higher than for brucite. For Ω values calculated with SUPCRT92 (Johnson et al., 1992) by assuming thermodynamic equilibrium between lizardite and brucite and the same rate of Mg^{2+} and $\text{SiO}_{2,\text{aq}}$ diffusion, the calculated d values are one to two orders of magnitude higher for chrysotile than for brucite (Figure 8). For a given supersaturation, lizardite grains have thus to be significantly larger than brucite grains to be preserved. Supersaturation is expected to decrease with distance from the olivine surface due to diffusion. At a distance of ~ 200 nm from the olivine surface, nanometre-sized lizardite grains are thus probably no more stable in the coating mixture where they dissolve to recrystallize in lizardite columns, as already suggested by Cressey (1979) and Rumori et al. (2004). The brucite nanograins are thermodynamically stable at this distance from olivine, and mechanically segregate at the column margins to form the interstitial mixture. This may not be always true, especially further away from the olivine surface where brucite layers are sometimes observed to be intercalated inbetween lizardite layers in the columns (Figure 5). Brucite mechanical segregation in the interstitial mixture probably leads to significant viscous deformation and rotation that might contribute to formation of the nanoscale porosity observed at the column margins. Fully crystalline lizardite probably occupies a smaller volume in the well-ordered columns than in the polycrystalline coating mixture. Solid volume may thus decrease during the coating mixture $\rightarrow$ columnar lizardite + interstitial mixture reaction, also contributing to porosity formation. Tutolo et al. (2016) measured a porosity of several percent at the nanoscale in drill core samples from mid-ocean ridges. We probably image this same kind of porosity in our samples, ~ 3 % in interstitial mixture, and ~ 0.5 % when averaged over the entire alteration assemblage. In addition, the orientation of the

interstitial mixture perpendicular to the olivine surface suggests that these domains can act as preferential fluid pathways at a scale of tens of microns (Figure 7). The size of the pores in the interstitial mixture and their low connectivity may not favor fluid transport driven by fluid pressure gradients but rather by diffusion under gradients in dissolved ions, electric potential (Plümper et al., 2017) or surface energy (Evans et al., 2018).

Our observations and interpretations regarding mass transfer limited to a scale of less than 100 nm are essential to constrain previously proposed reaction mechanisms. Numerical simulations have shown that limited mass transfer during reaction plays a key role for fluid pathway preservation and high extent of reaction to be achieved (Malvoisin et al., 2021). The solid volume increase is not accommodated by porosity clogging, but rather by deformation associated with tectonics or the reaction itself. Limited mass transfer during reaction favors stress-build up (Malvoisin et al., 2021), which may lead to expansion or cracking (Macdonald and Fyfe, 1985; O'Hanley, 1992; Jamtveit et al., 2009; Rudge et al., 2010; Malvoisin et al., 2012, 2017; Kelemen and Hirth, 2012; Evans et al., 2020; Yoshida et al., 2020).

Previous petrological observations also provide evidence for limited mass transfer during serpentinisation. Beard et al. (2009) identified a first isochemical stage of serpentine + brucite formation at the expense of olivine at low water to rock ratio. Evans et al. (2013) interpreted the presence of serpentine + brucite in harzburgite as evidence for limited silica transfer during the incipient stage of the reaction. The nanostructure described here could thus also be formed in harzburgite at this stage. As the reaction continues, the fluid flux can increase leading to mass transfer at larger scale with possible modification of the initially formed

mineralogical assemblages. Frost et al. (2013) suggest that the initially formed brucite can react to form serpentine and magnetite. Such a reaction is not observed in the sample studied here but the observed nanostructure can give insights on serpentinisation product reactivity during further fluid/rock interaction.

4.2. Implication for post-serpentinisation alteration

As discussed above, the incipient stage of serpentinisation at low water to rock ratio is generally isochemical, aside from addition of H₂O accompanied by very limited dissolution. However, fluid influx can continue in serpentinised peridotites, favoring mass transfer at large scale. The switch from isochemical reaction (except for the addition of water) to open system conditions generally induces a decrease in the MgO/SiO₂ ratio of the serpentinised peridotites by several percents (Snow and Dick, 1995; Niu, 2004; Malvoisin, 2015). This decrease could be associated with Si gain (Malvoisin, 2015; de Obeso and Kelemen, 2018; Templeton and Ellison, 2020) and/or Mg loss (Snow and Dick, 1995; de Obeso and Kelemen, 2020; de Obeso et al., 2021). Si-rich fluids can be formed during orthopyroxene serpentinisation (Beard et al., 2009; Frost et al., 2013) or mafic rock alteration (Bach et al., 2004; Paulick et al., 2006). Mg loss is probably associated with brucite dissolution leading to the formation of voids in serpentinised peridotites (Jöns et al., 2017), and magnesite precipitation in veins (Kelemen and Matter, 2008; Kelemen et al., 2011; García del Real et al., 2016).

Whether due to Mg-loss or Si-addition, it is apparent that brucite reacts rapidly during peridotite weathering. Comparing oceanic serpentinised peridotites collected by dredging versus drilling, Klein et al. (2020) demonstrated that there is a systematically lower brucite

content in the dredged samples suggesting brucite alteration during low temperature alteration with seawater on the seafloor. Kelemen et al. (2020) and Ellison et al. (2021) reported that brucite is detectable via X-Ray diffraction only below 100 m depth in drill core from Oman Drilling Project Hole BA3A, despite the fact that the protolith was an Si-poor dunite, suggesting brucite was dissolved or reacted to form other minerals near the surface. Kelemen et al. (2020) also observed brucite absence in dunites from Oman Drilling Project Hole BA4A but in a more limited section of the core ranging from the surface to 18 m depth. Compilation of MgO/SiO₂ data does not show a significant shift to low values compared to the terrestrial array in the peridotites from the Holes BA1B, BA3A and BA4A (Kelemen, 2021b). This probably indicates that brucite dissolution or silicification is spatially limited near the surface and thus only concerns a limited number of collected samples. An alternative explanation would be that brucite reaction near the surface does not involve mass transfer. Brucite could indeed react with serpentine according to the following reaction of iron oxidation:

Brucite + Amakinite + Mg-lizardite = Mg-cronstedtite + Water + Molecular Hydrogen

Determining if mass transfer is involved in brucite removal in Oman will require further investigations of the rock microtexture and composition.

In the present study, brucite is found to occur as < 100 nm grains with a high surface area (Figure 5). Moreover, brucite occurs in regions rich in nanopores (Figure 6) where fluids may be preferentially transported (Figure 7). As a result, the reactive surface area and porosity are larger in brucite-rich than in lizardite-rich domains, which may help to explain the relatively high reactivity of brucite at low temperature.

5. Conclusion

We studied the nanostructure of the products of serpentinisation in a sample from the Oman Drilling Project. The observations suggest a reaction in two steps. A brucite + serpentine mixture first precipitates at the olivine surface. The mixture then partly dissolves to form lizardite columns separated by a brucite-rich assemblage of brucite + serpentine grains containing a high density of nanopores. These observations indicate mass transfer limited to a scale below 100 nm during serpentinisation, preventing clogging of porosity and allowing for complete reaction to be achieved. Brucite occurs as nanograins in the fluid pathways, which favors its alteration at low temperature during further post-serpentinisation fluid/rock interaction.

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Figure captions

Figure 1: Back-scattered electron images of the reaction products around relicts of olivine.

The reaction products are composed of a serpentine + brucite mixture (Srp + Brc). Magnetite
(Mag) is formed during pre-serpentinization exsolution in olivine. The red arrows point
towards brucite-rich regions. The black arrows point towards bright and parallel phases in the
serpentine + brucite mixture near the contact with olivine grain.

Figure 2: Back-scattered electrons images reconstructed from Focused Ion Beam-Scanning
Electron Microscopy tomography. A, B and D correspond to three orthogonal sections across
the cuboid. The orientation of the planes is indicated on each panel. C: three-dimensional
representation of the spatial relationships between the sections. The white arrows point
towards thin continuous pores parallel to the olivine surface. CL: columnar lizardite. CM:
brucite/serpentine mixture coating the olivine surface. IM: brucite/serpentine mixture
inbetween the lizardite columns. Cpx/Mag: clinopyroxene/magnetite platelets initially
contained in olivine and chemically inert during reaction. The scale bar is 2 μm .

711

712 **Figure 3:** Contact between olivine and its reaction products segmented in 3D. Olivine in
713 green, brucite/serpentine mixture coating the olivine surface (coating mixture) in orange and
714 brucite/serpentine mixture separating lizardite columns (interstitial mixture) in red. Lizardite
715 columns are represented as voids between the other materials. A: Entire volume. B:
716 Subvolume located with a black box in A and viewed from the top of A (the red arrow in A
717 indicates the direction of view).

718

719 **Figure 4:** Semi-quantitative compositional maps obtained with TEM-EDS mapping. A:
720 Merged TEM images. A map of the (Mg + Fe)/Si ratio is superimposed on the images on the
721 left (B). The red and blue boxes locate the images displayed in Figure 6 A and D. The red dot
722 indicates the selected area for electron diffraction in Figure 6 B. The green and yellow dots
723 locate the EDS point analyses of the coating mixture and olivine, respectively. The yellow
724 box locates the automated crystal orientation maps displayed in Figure 5. B and D: (Mg +
725 Fe)/Si ratio map. C and E: Mg/(Mg+Fe) ratio maps. The arrows indicate the orientation of the
726 lizardite columns. CL: columnar lizardite; IM: lizardite/brucite mixture between lizardite
727 columns; CM: lizardite/brucite mixture coating the olivine surface.

728

729 **Figure 5:** Maps acquired with the automated crystal orientation tool at the olivine/serpentine
730 + brucite contact. A and C: phase maps. B and D: orientation maps (colour code is shown in
731 the bottom right panel). The yellow arrows point towards columnar lizardite and intercalated
732 brucite grains. Note the similar orientation of lizardite and brucite grains in columnar lizardite.

CL: columnar lizardite; IM: lizardite/brucite mixture between lizardite columns; CM: lizardite/brucite mixture coating the olivine surface.

Figure 6: TEM images of the reaction products (see location on Figure 4). A: Contact between columnar lizardite with a single orientation and the brucite-rich interstitial mixture (IM) composed of small lizardite and brucite grains of different orientations. The interstitial mixture contains nanometre-sized pores elongated in the (001) plane of the sheet minerals (red arrows). The dots locate the EDS point analyses. B: Selected, indexed area of electron diffraction acquired in the interstitial mixture. C: HRTEM image of the interstitial mixture composed of variably oriented lizardite and brucite grains. D: TEM image of the olivine/reaction products contact showing the presence of a brucite/serpentine mixture (CM) at the contact. Brc: brucite; Liz: Lizardite.

Figure 7: Sketch summarising the nanoscale observations. A: Olivine hydration forms three types of reaction products: a brucite/lizardite mixture coating the olivine surface (CM), lizardite columns (CL) and a brucite-rich porous mixture inbetween the lizardite columns (IM). B: Processes interpreted from the nanoscale observations. Alteration takes place through a two-step process: First, olivine and water react to form the coating mixture (1). This assemblage then evolves through dissolution of lizardite in the coating mixture and its reprecipitation in the lizardite columns (Ostwald ripening; 2), together with mechanical segregation of brucite in the interstitial mixture (3).

Figure 8: Saturation grain size (defined in equation (2)) as a function of saturation for brucite (dashed line) and lizardite (plain line). The grains are expected to dissolve and grow below and above these lines, respectively. The maximum and minimum saturations correspond to the equilibria of the aqueous solution with olivine and lizardite/brucite mineralogical assemblage, respectively. They are calculated with SUPCRT92 (Johnson et al., 1992) by assuming the same diffusivity for Mg^{2+} and $\text{SiO}_{2,\text{aq}}$. The dotted line indicates the measured width of the lizardite columns.

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