Reaction-induced porosity and onset of low-temperature carbonation in abyssal peridotites: insights from 3D high-resolution microtomography

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ABSTRACT

In a drillcore sample of serpentinitized harzburgite from the uppermost oceanic crust (Mid-Atlantic Ridge, ODP Leg 209, Site 1270), we demonstrate using high-resolution 3D-microtomography that micron-sized open cavities are present. The development of porosity is interpreted to result from dissolution of brucite and/or olivine. Petrographic observations indicate that voids are integrated in a network of carbonate veins, the formation of which is linked to changing alkalinity in conjunction with dissolution reactions. Partial carbonate filling of pore spaces indicates that under static conditions low-temperature carbonation leads to clogging of fluid pathways and thus to a reduction in permeability. Electron microprobe analyses show that the inner walls of open voids are lined with Fe-rich precipitates. We propose that the iron in those phases was released by brucite or olivine dissolution and was subsequently oxidized and precipitated as ferric hydroxide. Thermodynamic computations show that this process may be a potential source of catabolic energy for microorganisms inhabiting serpentinites. The proposed carbonation mechanism implies that carbonate

precipitation may start soon after exposure of the abyssal peridotites, when dissolution of brucite and weathering of olivine begin, and continue until the phases become inaccessible to seawater. Predicting carbonation rates of abyssal peridotites will hence require understanding of permeability reactions.

Keywords: abyssal peridotite, carbonation, microtomography, serpentinization

INTRODUCTION AND GEOLOGICAL SETTING

Ultramafic rocks cropping out at the seafloor are a common constituent of slow- to ultraslow-spreading oceanic crust. Interaction of these rocks with seawater leads to formation of serpentinites, which is accompanied by dramatic changes of the physical and chemical properties of the oceanic lithosphere. Peridotites are prone to alteration under subaerial and submarine conditions, and pronounced alteration is observed to take place over a wide temperature range, from more than 400°C to ambient conditions. In recent years, there has been an increased interest in peridotite alteration, because ultramafic rocks bear the potential to be used as natural reservoirs for CO₂ due to mineral carbonation. The underlying process, referred to as listvenitization, is most effective in a temperature range from 150 to 250°C (Kelemen and Matter, 2008) and can ultimately lead to large volume carbonation (Rose, 1837; Naldrett, 1966; Halls and Zhao, 1995; Akbulut et al., 2006; Iyer et al., 2008; Beinlich and Austrheim, 2012). However, in the oceanic lithosphere calcium carbonate veins and not listvenites are common. These veins form in a temperature range from ca. 200°C down to ambient conditions (e.g., Bach et al., 2011) and contribute to a long-term storage of significant amounts of carbon dioxide within the oceanic crust, which likely has a moderating effect on the amount of atmospheric CO₂ (e.g., Staudigel et al., 1989; Alt and Teagle, 1999; Coogan and Gillis, 2013). The input of carbonate-bearing oceanic crust into subduction zones can later bring carbon to the Earth's mantle or lead to CO₂ release to the atmosphere through volcanic activity at convergent plate boundaries. The carbonate veins found are typically fillings of tectonically opened spaces and often lack evidence for direct carbonation of the ultramafic host rock. Whether pervasive carbonation of ultramafic rocks can take place is – among other factors – strongly dependent on the temperature. Although the thermodynamic driving force (i.e. negative ΔG_r) would in principle promote carbonation reactions, formation of carbonate at ambient temperature conditions is sluggish compared to high-T carbonate precipitation (Lackner et al., 1995; Kelemen and Matter, 2008; Matter and Kelemen, 2009).

Besides the temperature conditions, another requirement is the presence of pathways that allow for the element transport of chemical components such as dissolved inorganic carbon (DIC) and silica. In this context a major point of discussion regarding carbonation of peridotites is the volume change, which might either induce cracking and hence increase the permeability (e.g., Rudge et al., 2010), or lead to clogging of permeability and porosity (e.g., Jamtveit and Austrheim, 2010; Hövelmann et al., 2012).

At temperatures conducive to life, the water-rock reactions that may lead to carbonate formation may also provide energy for chemolithoautotrophic microorganisms in the ocean floor. Ultramafic host rocks are particularly important in this regard, because oxidation of hydrogen and methane originating from deep serpentinization reactions provides energy that is easily available to chemolithoautotrophic organisms (e.g., Amend et al., 2011). Iron oxidation in ultramafic rocks constitutes an additional potential energy source, and water-rock reactions between serpentinized peridotite and water may release hydrogen that can fuel microbial life (e.g., Okland et al., 2012; Bach, 2016). Although it has been questioned that low-temperature serpentinization reactions are able to produce significant amounts of hydrogen (McCollom and Donaldson, 2016), it might still be available due to reactions occurring at greater depth and higher temperatures. Other studies have identified organic compounds within pores of serpentinites exposed to the seafloor and have suggested a relation between hydrogen release and CO₂ reduction (Menez et al., 2012). DIC is highly depleted in alkaline waters associated with low-temperature serpentinization environments; e.g., Schwarzenbach et al. (2013) report DIC concentrations <16 µmol/l in low-temperature alkaline springs from northern Italy. Carbonate precipitation removes DIC from water residing in serpentinite void space and hence removes DIC from being turned into biomass by chemolithoautotrophs. Also, carbonate precipitation will change the rock permeability and hence affect water flow essential for life.

All these aspects come together at slow-spreading mid-oceanic ridges, which typically feature outcrops of abyssal peridotites, exposed to seawater due to extensional faulting. In such areas peridotite-seawater interaction is observed, which leads to serpentinization and abundant carbonate veining. Ocean Drilling Program (ODP) Expedition 209 was aimed at sampling mantle rocks and associated gabbros to better understand the interplay between deformation and melt migration in the 15°20'N area at the Mid-Atlantic ridge (Kelemen et al., 2004). In the present study we focus on Site 1270 (14°43.2702'N, 44°53.0839'W), which is located south of the prominent 15°20'N fracture zone and only a few kilometers east of the ultramafic-hosted Logatchev hydrothermal vent field. At Logatchev, venting of hydrothermal fluids with elevated hydrogen concentrations (Charlou et al., 2002; Schmidt et al., 2007) point to ongoing serpentinization below the seafloor. In drill cores from Site 1270, pervasively serpentinized harzburgites and dunites as well as chlorite-tremolite-altered gabbroic intrusion are found. Minor carbonate veins occur as well. The physico-chemical conditions of serpentinization and the interplay with deformation have already been studied using samples from Leg 209 (Jöns et al., 2009; Klein et al., 2009; Jöns et al., 2010). Here, we extend and link the previous studies to observations on the low-temperature seafloor alteration of serpentinized peridotites in the uppermost section of Hole 1270D, where the interplay between reaction-induced porosity and low-temperature carbonate formation can be examined. Furthermore, we highlight the influence of pre-existing serpentinization textures on the low-temperature alteration processes.

Methods

Optical microscopy and FE-scanning electron microscopy

A petrographic thin section was investigated in both transmitted and reflected light using a Leica DM RXP HC microscope to characterize rock microstructures. Subsequent scanning electron microscopy (Zeiss Supra 40 FE-SEM, University of Bremen) was applied

on gold-coated broken sample surfaces with an accelerating voltage in the range of 5 – 15 kV. The SEM was equipped with an EDX system (INCA PentaFETx3, Oxford Instruments), which allowed for approximation of the chemical composition of mineral phases.

X-ray diffraction and electron microprobe analyses

The mineralogical composition of the sample was determined by means of X-ray diffraction analysis using a Panalytical X'Pert PRO X-ray diffractometer (University of Bremen, Germany) with Cu K α radiation. A sample powder pellet was scanned from $2\Theta = 3^\circ$ to 85° (step size: $0.0170^\circ 2\Theta$) with a voltage of 45kV and a current of 40mA.

Chemical compositions of minerals in petrographic thin sections were determined with a JEOL Superprobe JXA 8900 R electron microprobe at the University of Kiel (Germany). The microprobe is equipped with five wavelength-dispersive spectrometers and an energy-dispersive X-ray spectrometer system. Minerals were typically measured with an accelerating voltage of 15kV for a beam current of 10-20 nA and a fully focused electron beam. Synthetic materials and natural minerals standards were used as standards; the raw data were corrected using the CITZAF method of Armstrong (1995). Back-scattered electron images as well as micro-scale element distribution maps were obtained to complement the petrographic observations. Additional X-ray element mapping was performed using a Cameca SXFiveFE electron microprobe at Ruhr-Universität Bochum (Germany).

X-ray microtomography

A tetragonal prism, 5 mm wide and 25 mm high, was cut from the sample and scanned with the SkyScan 1172 device of the Experimental and Theoretical Petrology group at Kiel University (Germany) with a beam energy of 100 kV, a flux of 100 μ A at a detector resolution of 2.54 μ m per pixel using a 360 degree rotation with a step size of 0.36 degrees and 0.5 mm Al foil. The SkyScan software NRecon was used for reconstruction from the

transmission images. Segmentation, and 3D image analysis on the stack of 1944 images (2044 x 2040 voxels) were done using the SkyScan software CT-Analyser. A plugin for the multi-platform free image processing package Fiji, 3D Viewer (see Schmid et al., 2010 for details), has been employed to visualise the 3D structural models of the porous structure and high density minerals. Avizo 9.0.1 (FEI) was used for filtering (3D Sigma followed by 2D non-local means), visualization and clipping of the volumetric reconstructions (Fig. 1a, 1b, 1d-f). A plugin for the multi-platform free image processing package Fiji, 3D Viewer (see Schmid et al., 2010 for details), has been employed to visualize the 3D structural models of the porous structure and high density minerals in Fig. 1c. The reconstruction of the rock fabric by μ -CT is basically a characterization of the material density arrangement within the samples. Each voxel represents the mean linear attenuation coefficient for X-rays of the corresponding volume of the sample and depends on the energy of the X-rays and on density and atomic number of the scanned material. In the reconstructed images, areas of high attenuation (e.g., accessory minerals, orthopyroxene) are encoded in light gray values, whereas areas of low X-ray absorption are color-coded in dark gray (serpentine minerals) or black (voids). Since each image consists of isometric voxels (volumetric pixels) and has a certain thickness depending on the detector resolution, a stack of images contains true volumetric information.

After segmentation (i.e., the recognition of different fabric compounds by assigning gray values) and binarization (allows processing exclusively those voxels that passed the segmentation step), quantitative 3D image analysis was done on a stack of 1944 images (2044 x 2040 voxels), using a virtual drill core of Ø 5.0 mm and 4.9 mm height. Avizo 9.0.1 (FEI) was employed for porosity evaluation. The structural thickness of the pores (i.e., "pore diameters") was evaluated using 3D local thickness measurements of the pore space model as implemented in the Skyscan software CTAn: subsequent to a weighted distance and medial axis extraction following Remy and Thiel (2002), a "sphere-fitting" local thickness measurement as defined by Hildebrand and Rüegsegger (1997) was made for all voxels lying

along this axis. This method defines local thickness at a given point in a structure as the diameter of the largest sphere which includes the point and which can be fitted completely inside the structure (it addresses the thickness of a pencil regardless of its length). In addition, "pore size" was assessed in terms of volume as the diameter of the pore volume-equivalent sphere (also CTAn). Pore size analysis based on diameters of equivalent area circles (or spheres in 3D) are widely used in 2D digital image analysis of thin sections (e.g., Klein and Reuschlé, 2003; Trautwein and Huenges, 2005). The volume-equivalent sphere method adds any connected voxel regions to the same pore. Thus, the diameter of the equivalent area circle of a single connected "pore region" (consisting of several interstices connected by narrow joints) can be much larger than the diameter of the biggest maximal sphere that can be fitted into the pore body (descriptively spoken, the diameter of the volume-equivalent sphere of a long pencil will deviate far from its thickness).

Geochemical reaction path modeling

A thermodynamic database containing equilibrium constants (log K values) for pure minerals, gases and aqueous species was assembled for temperature-pressure pairs along an assumed geothermal gradient (T °C/ P bar: 2/250, 50/270, 100/330, 150/400, 200/500, 250/600, 300/725, 350/860, 400/970, 450/1100, 500/1250). All log K values contained were calculated from the standard-state thermodynamic parameters using the SUPCRT92 computer program (Johnson et al., 1992). The SUPCRT92 database combines upgrades from *slop98.dat* and *speq02.dat* (Wolery and Jove-Colon, 2004), and contains some additional modifications, e. g., aqueous Al data from Tagirov and Schott (2001); data for Fe-serpentine, Fe-brucite and Fe-talc from McCollom and Bach (2009). The resulting logK-database was used for calculations of geochemical reaction paths with the computer code EQ3/6 (Wolery and Jarek, 2003). These calculations account for solid solutions of many minerals assuming ideal molecular mixing models. The end-members of solid solutions relevant to this study are:

serpentine (chrysotile, greenalite), talc (talc, minnesotaite), brucite (brucite, Fe-brucite), olivine (forsterite, fayalite), orthopyroxene (enstatite, ferrosilite), clinopyroxene (diopside, hedenbergite), tremolite (tremolite, Fe-actinolite), garnet (grossular, andradite), chlorite (clinochlore, daphnite), plagioclase (albite, anorthite) and carbonate (aragonite, strontianite). Certain minerals, which are unlikely to form under the conditions of rock alteration, were suppressed during the model runs (e.g., calcite, dolomite, phlogopite, andradite, corundum,...). For evaluation of the serpentinization conditions, the thermodynamic model involves speciation of seawater at 2°C, heating to 100°C and reaction with a harzburgite ‘special reactant’ (composition of the JP-1 standard from Imai et al., 1995) at a water-to-rock (w/r) mass ratio of unity. Harzburgite and seawater-derived fluid were then heated together to 500°C to evaluate the equilibrium mineral assemblage over the whole temperature range. To examine the low-temperature alteration and carbonate formation, seawater is speciated at 2°C and heated to 15°C. Then a harzburgite special reactant is added in a titration model, which allows for evaluating the mineral assemblage with reaction progress ξ , whereby increasing ξ corresponds to decreasing w/r mass ratio.

SAMPLE CHARACTERIZATION

Sample 1270D-R-01W 75-78cm is an almost completely serpentinized harzburgite. Primary olivine is only found as rare relict included in spinel and is elsewhere completely replaced by serpentine and magnetite. Spinel and orthopyroxene are locally preserved. Chromium spinel ($X_{Mg} = Mg/[Mg+Fe^{2+}] = 0.50-0.57$; $Cr/[Cr+Al+Fe^{3+}] \approx 0.55$) has anhedral shape and occurs in vicinity of orthopyroxene. Clinopyroxene (average: $En_{0.49}Fs_{0.03}Wo_{0.48}$; $Na_2O = 0.1-0.2$ wt.%) is only found as exsolution lamellae in or at the rims of larger orthopyroxene crystals. Orthopyroxene (average: $En_{0.90}Fs_{0.08}Wo_{0.02}$; $Al_2O_3 = 1.3-1.9$ wt.%) is rimwards replaced by magnetite-free serpentine ($X_{Mg} = 0.93$; up to 2.2 wt.% Al_2O_3) and contains tiny amounts of talc on cracks. In some orthopyroxene aggregates, replacement by

amphibole (tremolite to Mg-hornblende; $X_{\text{Mg}} = 0.92\text{-}0.94$; $\text{TiO}_2 < 0.15$ wt.%) is observed. The former presence of olivine is inferred from typical mesh textures, which make up approximately 80 vol.% of the rock. The mesh rims consist of a network of magnetite aligned along trails and serpentine ($X_{\text{Mg}} = 0.93\text{-}0.96$; $\text{NiO} = 0.2\text{-}0.5$ wt.%) filling the spaces in between. This mesh texture is locally flattened, indicating that serpentinization took place pre- to syn-tectonically. Additionally, serpentine forms some larger veins, which are magnetite-free and crosscutting the mesh texture. These veins are typically undeformed, but locally follow pre-existing deformational structures. Brucite, which is elsewhere a breakdown product of olivine, has neither been observed visually nor detected by means of X-ray diffraction or electron microprobe analysis. Iowaite, another mineral phase occurring during low-temperature serpentinization, has also not been observed. Aragonite (containing ca. 3% strontianite component) occurs in different textures (see Fig. 2c,d): 1) as narrow ($< 50\text{ }\mu\text{m}$) veins following pre-existing serpentine veins; 2) as common filigree veinlet network ($< 20\text{ }\mu\text{m}$) irregularly crosscutting the whole rock; 3) intergrown with serpentine in centers of the mesh texture.

In thin sections, the centers of mesh textures appear brownish in color, but frequently the mesh centers are void. To confirm the presence of these voids and to preclude that they are preparation artifacts, detailed SEM examinations on broken sample surfaces (Fig. 2a,b) as well as X-ray microtomography measurements (Fig. 1) were undertaken. Combining results from these different analyses, the centers of mesh textures appear to have variable degrees of porosity. Locally, voids of up to $120\text{ }\mu\text{m}$ diameter are present. Their inner walls are lined with fine needles ($< 0.25\text{ }\mu\text{m}$) of iron-rich minerals, which could not be identified unambiguously (Fig. 2b). We assume that they are either ferrihydrite or hematite or goethite or a mixture of these minerals. Additionally, serpentine in the immediate vicinity of voids is commonly intergrown with aragonite (Fig. 2c,d). These carbonatized mesh center areas are connected by a network of up to $20\text{ }\mu\text{m}$ wide aragonite veins. Noticeable carbonation is only observed

where carbonate veins crosscut mesh centers; however, some mesh centers only show a porous structure of sponge-like serpentine, but no aragonite formation. In some places, where carbonate veins are absent, voids with Fe-rich linings lack the adjacent carbonation. X-ray element distribution maps of individual mesh centers (Fig. 3) generally show a pronounced iron enrichment in the center and a surrounding Ca-Sr-enrichment due to aragonite formation. Carbonate veins in orthopyroxene follow the well-developed cleavage, and where veins leave orthopyroxene crystals, porous structures are observed as well. Spinel appears to be unaffected by the carbonate formation.

RESULTS AND DISCUSSION

Development of porosity

X-ray microtomography measurements (Fig. 1) confirm the presence of porosity developed preferentially in centers of mesh textures, where either large voids or filigree aggregates of porous serpentine are observed. As serpentinization and carbonation typically lead to volume increase and clogging of fluid pathways, the observed porosity is likely due to dissolution of pre-existing minerals. The microporosity observed therefore differs from nanoscale porosity, which is known to be generated during serpentinization (Tutolo et al., 2016), but not detectable by means of X-ray microtomography. The distribution of pore sizes has been evaluated using a smaller sub-volume of the sample (a tetragonal prism of 3.4 x 3.4 x 4.9 mm) and is shown in Fig. 4a,b,c. From the pore thickness analyses based on local thickness determinations we observe that ca. 75 % of the porosity is hosted by voids smaller than 17.75 μm , with pores around 10 μm thickness are most abundant (Fig. 4a). However, from pore size analyses assessing the diameter of the pore volume-equivalent sphere we gain complementary insight into the pore size distribution: although ca. 85 % of the pores are smaller than 17.75 μm , it is obvious that most of the porosity is located in only a few pores that are larger than 40 μm equivalent sphere diameter (Fig. 4b). The combination of these

findings uncovers a pronounced elongation of preferentially the large pores. This deviation of mainly the large pores from sphericity (a measure of how round a 3D object is; it is the ratio of the surface area of a sphere with the same volume as the given particle to the surface area of the particle) can be seen in Fig. 2, e.g. parts (a) and (c), and is confirmed by sphericity analyses of pore shapes (see Fig. 4c): while pores larger than 60 μm equivalent sphere diameter plot between 0.5-0.3 sphericity, pores smaller than 20 μm plot at a higher sphericities of 0.6-0.8. The presence of such distinct pore structures, evident from BSE (Fig. 2) and μ -CT image material (Fig. 1), is interpreted as evidence for two different dissolution reactions: we propose that slightly porous serpentine aggregates (Fig. 2c) are former serpentine-brucite intergrowth zones, from which brucite was dissolved during low-temperature interactions with seawater. Brucite as an olivine breakdown product is elsewhere commonly observed (e.g., Mumpton and Thompson, 1966; Klein et al., 2009; Klein et al., 2014; Kahl et al., 2015; Schwarzenbach et al., 2016) and explained by the reaction: Olivine + $\text{H}_2\text{O} \Rightarrow \text{Serpentine} + \text{Brucite} + \text{Magnetite} + \text{H}_2$. This interpretation is in agreement with the absence of porous serpentine in the immediate vicinity of orthopyroxene, where one would not expect brucite to form alongside with serpentine due to locally increased silica activity ($\text{brucite} + \text{SiO}_2 = \text{serpentine}$). The second type of voids is larger and developed in the mesh centers. These larger voids (Figs. 1a,c and 2a,d) are interpreted as a result of dissolution of relict olivine grains, which had survived the preceding serpentinization event.

The rock studied reveals complex textural relationships that impede with an unambiguous interpretation of the detailed history of water-rock reactions. The serpentinization and veining patterns are typical for oceanic serpentinites from detachment faults (Andreani et al., 2007), and we suggest the following plausible scenario: Serpentinization starts when temperatures fall below ca. 400°C during unroofing and uplift of the footwall of a detachment fault. The products of serpentinization differ along the cooling path. At high temperatures (ca. 350-420°C) breakdown of olivine and orthopyroxene to form

serpentine and magnetite is expected, whereas serpentinization of olivine at $T < 350^{\circ}\text{C}$ yields additional brucite. At lower temperatures, lower amounts of magnetite and larger amounts of more Fe-rich brucite are proposed to form (e.g., Jöns et al., 2010; Klein et al., 2014). This idea is in agreement with the observation of typical mesh textures containing magnetite (higher T), and brucite forming in the centers of meshes upon further cooling. In the immediate vicinity of bastite (i.e. serpentinized orthopyroxene), a more or less magnetite-free corona of massive serpentine is observed. This texture indicates that increased silica activity from Opx breakdown inhibited brucite formation. Such a chemical gradient between olivine-rich and orthopyroxene-rich regions is a common observation in serpentinized ultramafic rocks (Klein et al., 2013; Schwarzenbach et al., 2016). In the studied sample, both mesh textures and bastites are slightly deformed, indicating syntectonic serpentinization in a fault zone setting. Upon further cooling of the serpentinized harzburgite, brittle fracturing opened pathways for seawater ingress. Where cracks cross brucite-bearing regions, brucite is missing. Nesbitt and Bricker (1978) already showed that brucite will dissolve more rapidly than any alteration phase forms. We hence propose that brucite dissolution may lead to the porous structure observed.

Although brucite is nowhere preserved in the studied sample, we consider it as a likely precursor mineral of the voids nowadays present. The mode of the rock (olivine > orthopyroxene) is such that brucite must have formed during serpentinization. Brucite dissolves in seawater and is removed from serpentinized peridotites in the course of seafloor weathering (e.g., Bach et al., 2004). Malvoisin (2015) recently argued that there is no thermodynamic drive for brucite dissolution in seawater. However, the water-to-rock ratios in Malvoisin's model calculations were much too low to represent rock weathering at the seafloor. Partial dissolution of serpentine minerals could hypothetically also explain the spongy texture, but this process would likely lead to formation of talc (Nesbitt and Bricker, 1978), which is - except minor occurrences within bastite textures - nowhere observed.

Another possibility is that iowaite was the precursor mineral of the voids. Iowaite is structurally related to brucite, but incorporates several weight percent of chlorine (Kohls and Rodda, 1967). However, even with extensive X-ray mapping of porous mesh textures we were not able to find elevated chlorine contents that would indicate the presence of relict iowaite. But even if iowaite was present, it would likely be a breakdown product of brucite, forming when Cl^- is supplied and some Fe^{2+} oxidized to Fe^{3+} upon seawater ingress (Heling and Schwarz, 1992). However, no definite statement about the previous existence of either brucite or iowaite can be made.

A further observation is that in pressure shadows of larger bastites voids occur in greater abundance and reach larger size (Figs. 1d, 2e). These voids cannot represent former brucite, because the higher SiO_2 activity prevailing close to orthopyroxene would inhibit brucite formation. We hence propose that these voids represent olivine, which survived the synkinematic serpentinization event in the pressure shadows of orthopyroxene, which behaved more rigid than the already formed serpentine of the mesh textures. Subsequent lower-temperature serpentinization under static conditions then led to the formation of larger amounts of brucite. At that moment, the pyroxene was already serpentinized and therefore did not impose increased silica activity conditions that would inhibit brucite formation. The following ingress of seawater at even lower temperatures dissolved brucite and left a highly porous structure behind. Alternatively, relict olivine could have dissolved directly in circulating seawater. Olivine dissolution would not be expected in a serpentinization setting, but may have taken place close to the seafloor (i.e. in the position, in which the rock was before it was cored). A sketch summarizing the proposed textural evolution of the harzburgite is given in Fig. 5.

Carbonation of peridotites

Aragonite veins form a pervasive network throughout the serpentinized harzburgite. As there is no preferred orientation of carbonate veins, their formation is interpreted to have

occurred under static conditions. The veins locally follow the magnetite-rich borders of mesh textures, but crosscut them in other places (Fig. 2c). Where the vein network is in contact with mesh cell centers, carbonate spreads out to either replace brucite or fill open spaces formed due to brucite dissolution (Fig. 2c). Notably, where larger voids are present (probably representing former olivine), aragonite does not fill the large open space, but grows within the neighboring serpentine matrix (Fig. 2d). Two distinct processes could lead to this kind of microtexture: 1) Carbonation occurred prior to void formation, and hence carbonate did not grow inside the void. Dissolution of the void precursor (olivine or brucite) followed, but no additional carbonation was possible due to lack of appropriate fluid chemistry (i.e. no carbonate ions and/or insufficient Ca present); 2) Carbonation was coeval with void formation, but carbonate grew preferentially in porous serpentine matrix as carbonate supersaturation was more easily reached in smaller fluid pathways than in larger open voids. In any case, we interpret the fact that not all open spaces were filled with carbonate as evidence that carbonation leads to a reduced permeability of the serpentinite, an issue that is elsewhere controversially discussed (Ulven et al., 2014). Additionally, textural observations indicate that the relative timing of the carbonation process could be variable, depending on the microtextural context. While porous serpentine in mesh-cell centers becomes carbonate-filled coeval with dissolution of the former void-filling material, carbonate precipitation probably predates the void formation in the cases where large voids are now present. A plausible link between mineral dissolution and carbonate formation is based on the fact that dissolution of brucite leads to an increasing pH of the fluid ($\text{Mg}[\text{OH}]_2 = \text{Mg}^{2+} + 2[\text{OH}]^-$). Under alkaline pH the speciation of the dissolved carbonate changes towards carbonate ions ($\text{HCO}_3^- + [\text{OH}]^- = \text{H}_2\text{O} + \text{CO}_3^{2-}$), which can then react with Ca^{2+} to precipitate carbonate ($\text{CO}_3^{2-} + \text{Ca}^{2+} = \text{CaCO}_3$). This mechanism can be visualized using reaction path models in which a serpentinized harzburgite reacts with seawater. The transition from the rock-dominated to the fluid-dominated regime involves pronounced changes in both mineral

assemblage and fluid composition (Fig. 6). Most obvious is a steep gradient in pH, which coincides also with replacement of magnetite by hematite. Furthermore, as the amount of brucite is predicted to decrease, aragonite is expected to form preferentially. The fluid-dominated regime is further characterized by a more Mg- and Fe-rich composition of the fluid (compared to the rock-dominated system), which is also in accordance with previous observations on Mg-loss during marine weathering (Snow and Dick, 1995). The fact that aragonite formed instead of calcite could be explained with the retarding effect of dissolved Mg on calcite precipitation (Berner, 1975).

The carbonation process documented here is not restricted to the studied locality; in fact, a link between carbonate formation and the occurrence of ultramafic rocks is commonly observed. This has been demonstrated from in-situ oceanic crust (e.g., Eickmann et al., 2009; Bach et al., 2011; Schroeder et al., 2015) and ophiolite complexes (e.g., Kelemen and Matter, 2008; Beinlich et al., 2012) and was also supported by laboratory experiments (e.g., Andreani et al., 2009; Hövelmann et al., 2011; Hövelmann et al., 2012; van Noort et al., 2013). The observation of incomplete carbonation, i.e. partially carbonatized porous mesh textures (Fig. 2c) and large voids that are not carbonate-filled, supports the hypothesis that the extent of carbonation reactions is limited by permeability reduction under static conditions and that net volume increase is not sufficient to cause additional fracturing of the serpentinite. In contrast to analysis of the pore sizes, quantification of the extent of carbonation by segmentation of the greyscale images from the microtomography is hindered by the very similar X-ray transmissivity of thin carbonate veins and other phases like orthopyroxene, late serpentine veins and bastites. Therefore, we decided to not give an estimate of the carbonate volume as this value would be subjected to a large error.

Implications for fluid flow through the lithosphere

It is generally accepted that hydrothermal seawater circulation through oceanic crust at mid-oceanic ridges is critical for cooling of the lithosphere (e.g., Sleep and Wolery, 1978;

Stein and Stein, 1994), and an important driver of chemical exchange between the lithosphere and the hydrosphere (e.g., Wolery and Sleep, 1976; Mottl and Wheat, 1994; Snow and Dick, 1995). Of major importance are oceanic detachment fault systems, which are common at intermediate- to slow-spreading ridges (e.g., Schroeder and John, 2004; Smith et al., 2006), and provide conditions favorable for seawater ingress into greater crustal depths. McCaig et al. (2007) even propose that the fluid flow focused on detachment fault systems is intimately linked with occurrences of ocean floor hydrothermal black smoker venting. The combination of tectonically induced permeability, large volumes of circulating fluids and reasonably high temperatures (up to ca. 400°C) makes these detachment faults especially important for fluid-rock interaction processes. However, detachment faults actively channelizing high-temperature fluid upflow are likely localized phenomena and unlikely to account for the large volumes of ocean crust alteration, which are of relevance for global geochemical budgets (i.e. the global carbon cycle). Alteration at low to ambient temperature conditions, in contrast, is widespread and - although water-mineral reactions are more sluggish - probably more important than localized high-temperature fluid-rock interaction in global exchange budgets.

In the studied sample we find evidence that mineral dissolution caused increasing permeability and porosity, but also evidence for clogging of permeability due to carbonate precipitation. The presence of open pore spaces close to carbonate-filled veins (Fig. 2c) indicates that volume increase due to carbonate formation may not have been sufficient for inducing further cracking and related increase of the permeability. The low-temperature aragonite formation, which is linked to alkalinity-generating mineral dissolution reactions, occurs in comparatively young ocean crust. This demonstration of early inorganic carbonate precipitation is crucial for using carbonates as archives for past-seawater compositional changes, as demonstrated by Coggon et al. (2010) and Rausch et al. (2013). In a recent work by Coogan et al. (2016) it was also shown using U-Pb dating of calcite from comparatively old (>80Ma) ocean crust that carbonate formation takes place soon after crustal accretion. U-

Pb dating of carbonate in crust younger than 80 Ma is analytically challenging. If carbonates from younger ocean crust should be used as seawater archives, we propose the preferable use of carbonate contained in ultramafic or olivine-bearing mafic host rocks, because these rocks will more likely undergo early alkalinity-generating mineral reactions supporting early carbonate precipitation.

Implications for life on the ocean floor

In recent years, considerable progress has been made in understanding the abiogenic requirements for microbial activity in the deep sea. In an environment where photosynthesis is not possible, microbial communities depend on gaining energy from inorganic redox reactions. At the lithosphere-hydrosphere interface, the strong contrast between oxidized seawater and reduced rock-dominated fluids can provide conditions favorable for catabolic and anabolic processes. This is the reason that the nearby Logatchev vent field, which is an ultramafic-hosted hydrothermal system, shows a complex deep-sea ecosystem, which is based on chemosynthetic energy. The Logatchev vent fluids are rich in hydrogen, the production of which is related to iron oxidation during serpentinization reactions (McCollom and Bach, 2009). During serpentinization, ferrous iron from primary olivine and pyroxene is oxidized and the resulting ferric iron is incorporated into magnetite. However, not all Fe^{2+} is oxidized during serpentinization: secondary minerals like serpentine and brucite also incorporate Fe^{2+} . The lower serpentinization temperatures are, the more Fe-rich are secondary serpentine and brucite (Klein et al., 2009; Jöns et al., 2010). Even if some of the Fe contained in brucite and serpentine is trivalent (Klein et al., 2014), serpentinites still bear the potential to be exploited by microorganisms to gain metabolic energy at ambient temperature conditions. We observe that brucite was dissolved and minerals containing trivalent Fe (e.g., goethite, ferrihydrite, hematite) were formed (Figs. 2, 3). Mineral textures indicate that Fe-bearing minerals precipitated from the fluid contained in the voids, probably during the latest stages of the rock history when temperatures were low. Assuming oxidation of a pure Fe^{2+} -brucite to goethite

according to the reaction " $4 \text{Fe}(\text{OH})_2 + \text{O}_2(\text{aq}) = 4 \text{FeO}(\text{OH}) + 2\text{H}_2\text{O}$ ", we can calculate the affinity of this reaction depending on the temperature of the system and compare it to other energy-yielding reactions (Fig. 7). High affinities point to the fact that microbial life catabolizing this reaction could be supported. Figure 7 shows that the calculated reaction affinities for Fe-brucite oxidation increase with decreasing temperature and are higher than for sulfate reduction, which is another process linked to hydrothermal alteration of ultramafic rocks (Alt et al., 2007). Even in anoxic environments, dissolution of olivine may yield energy for microbial catabolism, as enough hydrogen would be produced for hydrogenotrophic microorganisms irrespective of the nature of the secondary ferric phase (Bach, 2016). Our study does not provide explicit evidence for microbial exploitation of these reactions in the studied sample. But the water-rock reactions that apparently took place within the void spaces we imaged indicate that serpentinites undergoing low-temperature interactions with seawater may constitute a suitable microbial habitat. This could also be true for Fe oxidation reactions taking place during ophiolite weathering. Literature on serpentinite springs in ophiolite settings is typically discusses the release of hydrogen and methane through subsurface serpentinization reactions as the main energy source for microbial activity (Brazelton et al., 2012; Brazelton et al., 2013). But oxidation of Fe^{2+} -bearing brucite and serpentine could also take place in a sub-aerial setting under the influence of fresh water and support microbial life (cf. Okland et al., 2012). However, in oceanic and in continental settings, clogging of fluid pathways through carbonate precipitation could cause this habitat to be available only for a restricted time period in the serpentinite alteration history.

SUMMARY AND CONCLUSIONS

We were able to demonstrate, using high-resolution 3D-microtomography, that open cavities are present in a serpentinized harzburgite from the uppermost oceanic crust. This porosity is interpreted to have formed due to dissolution of brucite and/or olivine. Petrographic

observations indicate that voids are integrated in a network of carbonate veins, the formation of which is linked to changing alkalinity in conjunction with dissolution reactions. Incomplete carbonate filling of pore spaces indicates low-temperature carbonation under static conditions leads to clogging of fluid pathways and thus to a reduction in permeability. The mechanism that leads to carbonate formation is intimately linked to dissolution reactions in ultramafic rocks. Therefore, carbonate precipitation in abyssal ultramafic rocks is likely to occur soon after crustal accretion, which might make those carbonate veins particularly useful as archives for reconstructions of palaeo-seawater compositions. Iron-rich precipitates on the inner walls of open voids highlight the possibility that oxidation of divalent iron in brucite, serpentine or olivine is a potential source of catabolic energy for deep-sea microbial communities.

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FIGURE CAPTIONS

Figure 1: Results of high-resolution X-ray microtomography. a) Slice of a virtual core (5mm diameter) showing mesh and bastite textures. Voids are found in the center of mesh cells. b) Overview of a virtual core from which the other sub-figures are taken. c) Textural details from the virtual core and volume rendering and segmentation. Magnetite (displayed in red colour) forms the outer border of the mesh cells, voids (yellow) are present in the mesh texture centers. Growth of Fe-oxide/hydroxide phases (blue) on outer walls of voids can also be visualized. d) Section of the virtual sample core showing a bastite texture. A larger amount of voids is found in pressure shadows of the former orthopyroxene. Carbonate veins follow pre-existing serpentine veins. e) Bastite and mesh texture crosscut by later serpentine veins. Late carbonate veins (indicated by white arrows) are found to follow the pre-existing serpentinization structures. f) Section of the virtual core showing several sub-parallel carbonate veins (indicated by white arrows) crosscutting both pre-existing serpentine veins and regions containing voids.

Figure 2: Electron optical images of the studied sample (mineral abbreviations after Kretz, 1983). a) Secondary electron (SE) image showing a truncated void at a broken sample surface. Aragonite occurs close to the void, ferric iron bearing minerals (Fe-oxi) on inner walls of the void. b) Close-up of inner walls of a void with sub-micron size overgrowths of Fe³⁺-bearing minerals (SE image), probably precipitated from the void-filling fluid. c) Backscattered-electron (BSE) image of a mesh texture featuring a porous serpentine structure in the center of the mesh (representing former serpentine-brucite intergrowths). Aragonite veins crosscut the texture. Where aragonite veins meet mesh centers, more extensive carbonation is observed. d) Open void in the center of a mesh texture, probably representing former olivine. Carbonation occurs in immediate vicinity of the void. Fe-enrichment is found

on inner walls of the void (BSE image). e) BSE image showing a bastite formed after orthopyroxene, which features a higher abundance of voids on opposing sides. These voids are interpreted to form in pressure shadows of the pyroxene (see text for further discussion).

Figure 3: BSE image (a) of a void with carbonate vein; X-ray element maps of Ca (b), Fe (c), Si (d), Sr (e) and Mg (f). The distribution of Ca (b) and Sr (e) reflects the carbonation process. Where a massive carbonate vein meets a porous mesh cell center, more extensive carbonation is observed. Besides magnetite, which forms the borders of the mesh texture, enrichment of Fe (c) is observed on the inner walls of the void, where Fe-oxides/hydroxides grow. Silica- (d) and Mg-rich (f) areas consist of serpentine.

Figure 4: Size distribution analyses of the 3D pore space model derived from X-ray microtomography data. (a) Distribution of pore thickness based on local thickness determinations: ca. 75 % of the porosity is hosted by voids smaller than 17.75 μm , with pores around 10 μm thickness being most abundant. (b) Pore size distribution analyses determining the diameter of the pore volume-equivalent sphere, assessing both the number of pores and the associated volume in size class. See text for a detailed description of quantitative 3D analytical procedures. (c) Plot of sphericity Ψ vs. equivalent sphere diameter of the pores. The sphericity is a measure of how round a 3D object is. It is defined as the ratio of the surface area of a sphere with the same volume as the given particle (V_p) to the surface area of a particle (A_p).

Figure 5: Sketch representing the different stages of the textural evolution of the studied harzburgite. (a) Massive unaltered harzburgite consisting of orthopyroxene and olivine (minor amounts of clinopyroxene and spinel are not shown). (b) Upon uplift in the detachment fault system, the harzburgite cools and ingress of seawater-derived fluids causes syntectonic

serpentinization. The deformation is weak, but causing the olivine in pressure shadows of orthopyroxene to be less affected by alteration than olivine in the rock matrix, where serpentine, magnetite and brucite are the olivine breakdown products. (c) Ongoing serpentinization also affects orthopyroxene, which is transformed into bastite. (d) At even lower temperatures carbonatizing fluids infiltrate the harzburgites. These fluids preferentially follow pre-existing fluid pathways. Dissolution of serpentine, brucite and olivine starts, leading to aragonite precipitation. (e) The fluid network extends leading to ubiquitous mineral dissolution and carbonate precipitation (see text for a detailed description of the different textures).

Figure 6: Results of reaction path modeling illustrating mineralogical (a) and fluid chemical (b) changes due to seawater interaction with serpentinized harzburgite at 15°C. Increasing reaction progress ξ corresponds to decreasing water/rock mass ratio. The model predicts that during alteration the pH decreases, aragonite forms, the amount of brucite decreases and magnetite is replaced by hematite. See text for further details.

Figure 7: Affinities of three reactions that could potentially provide catabolic energy to deep-sea microbial communities. In the calculation it was assumed that $H_2(aq)$ for the hydrogenotrophic reactions is set by the Fe-brucite-goethite equilibrium. $O_2(aq)$ concentrations are assumed to decline by an order of magnitude per 10°C temperature increase (starting at 100 $\mu\text{mol/kg}$ $O_2(aq)$ at 0°C). The activity of water and goethite was set to unity, the activity of Fe-brucite was assumed 0.1. Most relevant for the studied rock sample is oxidation of Fe-brucite to form goethite, which has an intermediate affinity.

Figure 4

(a)

(b)

(c)

Figure 5
(a) Unaltered Harzburgite

(b) Syntectonic serpentinization

(c) Ongoing serpentinization

(d) Infiltration of carbonatizing fluids

(e) Pervasive fluid infiltration

Figure 6

Figure 7