**Sulfide Dissolution and Awaruite Formation in Continental Serpentinization Environments and Its Implications to Supporting Life**

E. M. Schwarzenbach, J. C. Vrijmoed, J. M. Engelmann, M. Liesegang, U. Wiechert, R. Rohne, and O. Plümper

1Institute of Geological Sciences, Freie Universität Berlin, Berlin, Germany, 2Department of Earth Sciences, Utrecht University, Utrecht, The Netherlands

**Abstract**  Serpentinization environments are key locations that support microbial communities by the abiogenic formation of reduced species associated with peridotite alteration. Here we studied partially serpentinized peridotites from the Chimaera seeps (Turkey), an active continental serpentinization system that vents highly methane-rich fluids, to investigate the impact of water-rock interaction on the sulfide and metal mineralogy and its implications on supporting microbial communities. Using high-resolution scanning electron microscopy, electron microprobe analysis, and transmission electron microscopy we found diverse pentlandite decomposition features with precipitation of secondary sulfides including millerite, heazlewoodite, as well as Cu-bearing sulfides, native Cu, and awaruite (Ni$_2$Fe). Awaruite forms dense veinlets to single crystal platelets tens of nanometers in size, which is formed by desulfurization of pentlandite. In addition, the nanometer-sized awaruite platelets are intimately intergrown with serpentine suggesting its growth during peridotite alteration by a dissolution-precipitation process, likely associated with the interaction of methane- and H$_2$-rich but highly sulfur-undersaturated fluids. Based on sulfur isotope signatures we infer a mantle and mid-ocean ridge origin of the sulfide minerals associated with the first stage of partial serpentinization and awaruite formation. Subsequent and ongoing continental fluid-rock interaction causes significant sulfide decomposition resulting in the formation of porosity and the release of, amongst others, H$_2$S and Fe. These species may likely provide a source of nutrients for active microbial communities in these comparatively nutrient-starved, low-temperature continental serpentinization environments.

1. Introduction

Metal and sulfide minerals in ultramafic rocks are ideal tracers for fluid-rock interaction processes. During hydrothermal alteration of ultramafic rocks—the so-called serpentinization reaction where the primary mantle minerals olivine and pyroxene are converted to serpentine, magnetite, talc, and brucite—H$_2$O is produced due to ferrous iron oxidation (Klein et al., 2009; McCollom et al., 2016). Simultaneously, H$_2$ can react abiotically with CO$_2$ or CO to produce CH$_4$ and higher hydrocarbons following Fischer-Tropsch Type and Sabatier reactions (e.g., Etiope et al., 2011). Associated with variations in water-rock ratios during ongoing serpentinization and rock fracturing, this imparts strong variations in fluid redox conditions, i.e., variations in $f$O$_2$, $f$H$_2$, and $f$S$_2$ conditions controlling the opaque mineralogy (Foustoukos et al., 2015; Frost, 1985; Klein & Bach, 2009). Effectively, changes in $f$O$_2$ and $f$S$_2$ cause precipitation of secondary opaque phases and/or decomposition of primary mantle sulfides (Alt & Shanks, 1998; Schwarzenbach et al., 2012). In fact, serpentinization environments are among the most reducing environments found on Earth allowing for formation and stabilization of native metals and metal alloys, for example, by desulfurization of magmatic pentlandite (e.g., Frost, 1985; Klein & Bach, 2009; Schwarzenbach, Gazel, & Caddick, 2014). Simultaneously, abiotically produced H$_2$ and/or CH$_4$ as well as other reduced carbon species, produced as a result of the serpentinization process, together with oxidants such as sulfate or CO$_2$, provide an ideal energy source for chemolithoautotrophic communities living at sites of active serpentinization (e.g., Brazelton et al., 2006; Kelley et al., 2005; Lang et al., 2018; McCollom, 2007). In this regard, these systems have gained increasing interest in the study of the evolution of life on Earth and in the search for life on other planets and planetary bodies (Martin & Russell, 2007; Russell et al., 2010; Vance & Melwani Daswani, 2020). The detection of
H₂ and CH₄ in the atmosphere of Saturn's icy moon Enceladus offers further evidence for serpentinization providing energy for extraterrestrial microbial life (Taubner et al., 2018).

Active sites of serpentinization have been found in oceanic settings where mantle rock is exposed to seawater near ultra-slow to slow spreading mid-ocean ridges (e.g., Kelley et al., 2001) and in continental sites where meteoric water circulates through ultramafic rocks that have been emplaced on the continent (e.g., Morrill et al., 2013; Sanchez-Murillo et al., 2014; Schrenk et al., 2013). At these sites, ongoing, low-temperature serpentinization is documented by the escaping alkaline (up to pH 12), H₂- and/or CH₄-rich, Ca-rich, but Mg- and CO₂-poor fluids (e.g., Bruni et al., 2002; Cipollini et al., 2004; Fritz et al., 1992; Kelley et al., 2001; Sanchez-Murillo et al., 2014; Schwarzenbach, Lang, et al., 2013). Microbial communities are found within chimney structures of hydrothermal vent fields and as microbial mats and biofilms around vent sites (Brazelton et al., 2011; Lang & Brazelton, 2020). They have been inferred to thrive within the serpentinite basement rock (Alt & Shanks, 1998; Schwarzenbach, Gill, & Johnston, 2018) and have been identified in emanating vent fluids (Brazelton et al., 2006, 2017; Morrill et al., 2013; Zwicker et al., 2018). Notably, in continental systems, the availability of vital elements such as sodium and sulfate is very limited, and concentrations are significantly lower than in marine environments where these species are abundant in seawater, which may limit the habitability of continental serpentinitization systems (Suzuki et al., 2013).

In this study, we investigate the opaque mineralogy of partly serpentinized harzburgites from the Chimaera seeps in Turkey. These rocks were initially partly serpentinized on the Jurassic ocean floor and currently are subject to extensive interaction with highly methane-rich fluids as documented by methane vents (Etiope et al., 2011). Microbial activity has been shown to be abundant around the methane-rich vents emanating from the ground, and methane-, nitrogen-, iron-, and hydrogen-oxidizing bacteria as well as archaea, and metal-resistant bacteria have been identified at these sites (Neubeck et al., 2017; Zwicker et al., 2018). Here, we use high-resolution microstructural and -chemical investigations to explore the impact of fluid chemistry, especially the methane-rich fluids, on sulfide stability, and its implication to supporting life in active serpentinitization systems, with a particular focus on pentlandite decomposition and awaruite formation. Sulfur isotopes are used to determine the origin of the sulfur and to infer sulfur speciation during the hydrothermal evolution of these rocks. We show that methane vents induce disequilibrium and destabilization of previously formed sulfides releasing H₂S and Fe to the fluid, forming porosity, and providing an additional energy source for microorganisms within serpentinites.

2. Geological Setting and Sample Selection

For this study, variably serpentinized harzburgites and iherzolites were collected near the Chimaera seep, close to the town of Çıralı in the Antalya Province, Turkey (Figure 1). The natural gas seeps, also known as Yanartaş, meaning “flaming rock” in Turkish, have been active for at least 2000 years and gas is emitted from around 50 vents, issuing along faults and from fractures in the rock (Etiope et al., 2011). The ultramafic rocks are part of the Tekirova ophiolitic unit. This unit belongs to the Antalya accretionary complex, which is one of the Mesozoic Neotethyan ophiolitic complexes in the eastern Mediterranean, and an accretionary wedge obducted onto an autochthonous carbonate platform during the closing of the Neotethyan Ocean (Aldanmaz et al., 2009). The Tekirova ophiolite includes an almost intact section of oceanic lithosphere including partly serpentinized harzburgites, minor Iherzolites, dunites and chromites, isotropic gabbros, and sheeted dikes (Bağcı et al., 2006). The Tekirova ophiolite formed in the southern Neotethys in the late Cretaceous likely along a mid-ocean ridge spreading center (Aldanmaz et al., 2009; Bağcı et al., 2006). Though both MOR type and later suprasubduction-type peridotites are preserved, the formation of the latter is likely associated with the closure of the ocean (Aldanmaz et al., 2009).

The gas seeps are mostly venting from ultramafic rocks near the contact of the Tekirova ophiolite and shallow water carbonate-dominated sediments of the Kemer zone (Zwicker et al., 2018). The gas seeps consist mainly of methane (~87 vol.%), hydrogen (~10 vol.%), and N₂, with CH₄ formation having been associated with a thermogenic and abiotic origin linked to ongoing serpentinization in the subsurface (Etiope et al., 2011), though a partially microbial origin cannot be excluded (Zwicker et al., 2018). Active fluid seeps have only been reported at one location and, most likely, they only escape periodically with the fluid being of meteoric origin (Meyer-Dombard et al., 2015). Very similar to other continental sites of active
serpen
tinization, a fluid pH of 11.95 was measured, with the fluid being very Ca\textsuperscript{2+}-
rich—showing some of the highest concentrations yet detected in serpen
tinization systems—and Mg\textsuperscript{2+} and CO\textsubscript{2}-poor (Meyer-Dom
bard et al., 2015). Equilibrium formation temperatures for methane currently being emitted has recently been estimated based on clumped isotope signatures to 235°C ± 29°C (Douglas et al., 2017), which is higher than previous estimates of <50°C–100°C using the H\textsubscript{2}-CH\textsubscript{4} δD geothermometer (Etiope et al., 2011). Though a temperature of <100°C coincides with maximum temperatures at the base of the ophiolite and thus, maximum temperatures for current, continental fluid-peridotite interaction (Etiope et al., 2011).

Variably serpen
tinized harzburgites were collected from three outcrops and are shown in Figure 1. At all sampling sites, methane is venting from the ground, as previously described by Etiope et al. (2011).

3. Methods

For this study 19 rock samples were investigated (Table 1). For all samples, 30 µm thin sections and bulk rock powders were prepared. The mineralogy and petrology of the samples were examined on thin sections by transmitted and reflected light microscopy, and by electron microprobe analysis (EMPA), and scanning electron microscopy (SEM). EMP analyses were carried out on a JEOL 8200 Superprobe at the Freie Universität Berlin using 15 kV acceleration potential, a 20 nA current, and a 1 µm beam size using natural and synthetic reference material. High-resolution backscatter electron (BSE) images and element distribution maps were obtained with the Zeiss ATLAS software using a Zeiss Sigma 300 VP Field-Emission Scanning Electron Microscope equipped with two Bruker Quantax Xflash 6i 60 mm\textsuperscript{2} SSD EDX Detectors for qualitative and quantitative element analysis also at the Freie Universität Berlin. Quantitative EDX maps were measured at 5 kV with a pixel size of 11 nm using the Ni-Lα, Cu-Lα, Fe-Lα, S-Kα, Mg-Kα, and As-Lα lines.

On one thin section site-specific, electron-transparent foils were prepared using a Thermo Fischer (form\er FEI) Helios G3 focused ion beam scanning electron microscope (FIB-SEM) to examine the micro-
morphology of awaruite-pentlandite intergrowths. FIB-SEM foils were subsequently investigated using the
| Sample name | Lithology | Macroscopic description | Degree of serpentinization (in %) | Mineralogy$^b$ |
|-------------|-----------|-------------------------|----------------------------------|----------------|
| CS-01       | Carbonate-veined serpentinite | Covered with white serpentinite, pervaded by serpentine and calcite veins (mm sized) | >95 | T - T T XX T O | rare ptl |
| CS-05†      | Serpentinite | Bastites visible macroscopically | No thin section | T | none detected |
| CS-06†      | Serpentinite | Mesh texture with bastites present | 90–95 | T - T T XX O | T | ptl, aw |
| CS-07†      | Serpentinite | Bastites visible macroscopically | No thin section | T T T XX | none detected |
| CS-09†      | Serpentinite | Mesh texture with bastites present | >95 | T T T T XX T | none detected |
| CS-10       | Serpentinite | Mesh texture with bastites present | >95 | T T T T XX T | none detected |
| CS-11†      | Carbonate-veined serpentinite breccia | Various sizes of the components, carbonate as veins and as aggregates | 100 | - - - XX O | none detected |
| CS-13†      | Serpentinite | 80–85 | O O - T XX | none detected |
| CS-14       | Serpentinized harzburgite | Bastites visible | 50–60 | X O - T XX T | none detected |
| CS-16       | Serpentinite | 2 mm thick vein | 70–75 | O O T T XX | T | none detected |
| CS-17†      | Serpentinite | Carbonate-veined serpentinite | 100 | - - - T XX O | none detected |
| CS-19†      | Serpentinite | Mesh texture with rare bastites present | 100 | - - - T XX T | none detected |
| CS-20†      | Serpentinite | Covered with thick serpentinite veins | 90 | O - T T XX | none detected |
| CS-22       | Serpentinite | Mesh texture with rare bastites present | 100 | - - - T XX T T T | none detected |
| CS-25†      | Serpentinite | Mesh texture with rare bastites present | 80–90 | O T - T XX | none detected |
Table 1 continued

| Sample name | Lithology | Degree of serpentinization (in %) | Macroscopic description | Mineralogy | Sulfide | Edx mode | Sulfur isotope compositions |
|-------------|-----------|-----------------------------------|-------------------------|------------|---------|----------|---------------------------|
| CS-26       | Harzburgite | 30–40 | Thick 3-5 mm serpentine vein | Olivine, opx, cpx | none detected | Fe, Cr, pl, Co-pl, Cu-pl, Ni-pl, Cu-ple, Ca-pl, Mg-pl | Thermo Fischer (former FEI) Talos 200FX transmission electron microscope (TEM) operating at 200 kV and equipped with four energy-dispersive X-ray (EDX) detectors. EDX maps were collected and analyzed using the Bruker Esprit 2.1 software. All FIB-SEM and TEM investigations were carried out at the Utrecht University electron microscopy center. |
| CS-30       | Serpentinite | 60–70 | Fe-oxide very finely dispersed, mesh texture with bastites present | Olivine, cpx, opx, spinel, serpentine, talc, chlorite, amphibole, pyroxene, olivine, spinel, serpentine, talc, chlorite, amphibole | none detected | Fe, Cr, pl, Co-pl, Cu-pl, Ni-pl, Cu-ple, Ca-pl, Mg-pl | Precipitates were analyzed for their $^{34}$S/$^{32}$S ratios on a Thermo Fisher Scientific MAT 253 mass spectrometer combined with an Eurovector elemental analyzer from HEKAtech by combustion to SO$_2$ gas. The international sulfide (Ag$_2$S) standards IAEA-S1, IAEA-S2, and IAEA-S3, the sulfate (BaSO$_4$) standards NBS-127, IAEA-SO$_5$, and IAEA-SO$_6$, and an in-house sulfate ($K_2$SO$_4$) standard were used as reference materials. Sulfur isotope compositions are reported in the conventional delta-notation ($\delta^{34}S$) and reported against V-CDT. Analytical reproducibility of the analyses of the standards is better than $\pm 0.12\%$ for sulfides and $\pm 0.26\%$ for sulfates. The measurement error on S contents is typically better than 5%. For individual samples the error can be higher due to either sample heterogeneity and/or very low sulfide and sulfate concentrations, and was constrained from duplicate sample extractions and sample analyses, and is given in Table 2. |
| CS-34       | Serpentinite | 100 | Calcite veins | Olivine, cpx, opx, spinel, serpentine, talc, chlorite, amphibole, pyroxene, olivine, spinel, serpentine, talc, chlorite, amphibole | none detected | Fe, Cr, pl, Co-pl, Cu-pl, Ni-pl, Cu-ple, Ca-pl, Mg-pl | |
| CS-36       | Harzburgite | 30–40 | Partly serpentinized, pyroxene more decomposed than olivine | Olivine, cpx, opx, spinel, serpentine, talc, chlorite, amphibole, pyroxene, olivine, spinel, serpentine, talc, chlorite, amphibole | none detected | Fe, Cr, pl, Co-pl, Cu-pl, Ni-pl, Cu-ple, Ca-pl, Mg-pl | |

4. Results

4.1. Mineralogy

The studied samples are highly serpentinized clinopyroxene-bearing harzburgites with variable degrees of serpentinization (degree to which primary minerals are replaced by serpentine ± brucite ± talc) from ~30% to 100% (Table 1). In general, orthopyroxene is more extensively serpentinized compared to olivine. Most samples show a typical mesh texture where serpentine progressively replaces olivine, and bastites forming as orthopyroxene is progressively replaced by serpentine. Locally, chlorite, talc, and amphibole occur either as veins or replacing bastites. In a few samples, brucite occurs as veins or as aggregates in the serpentine groundmass. Some samples contain Cr-rich spinel. Fine-grained iron oxides and iron hydroxides locally replace serpentine in the groundmass leading to a brown to reddish, variably oxidized groundmass. In addition, some entirely serpentinized peridotites are cut by carbonate veins and some samples are carbonate-veined serpentinite breccias.
4.2. Sulfide Mineralogy and Chemistry

The opaque phases are comprised, apart from magnetite and fine-grained Fe-oxides/hydroxides, of sulfides, native metals, and metal alloys of manifold compositions. These include pentlandite [(Fe,Ni)S₂], Co-pentlandite [(Co,Fe,Ni)₃S₄], Cu-rich pentlandite (sugakite [Cu(Fe,Ni)₃S₄] and sanamiite [Cu₄(Fe,Ni)₃S₈]), heazlewoodite [Ni₃S₂], millerite [NiS], chalcocylite [Cu₄S₃], chalcocite [CuS], native copper and awaruite (Ni₃Fe) (Figure 2, Tables 1 and S1). While in some samples no sulfide minerals, native copper, or awaruite could be detected, awaruite was found in samples of highly variable degree of serpentinization, from around 30% to around 90%–95%. Accordingly, there is no correlation between sulfide, alloy, or native metal mineralogy and either degree of serpentinization or silicate mineralogy.

In almost all samples investigated here, the sulfides and metals occur within the serpentine groundmass, that is, they are surrounded by serpentine. In all samples, pentlandite is the dominant sulfide mineral. Pentlandite is in most samples highly decomposed (Figures 3 and 4) and often intergrown with other mineral phases such as awaruite, magnetite, Cu-rich pentlandite (up to a composition of sanamiite and sugakite), chalcocite and/or native copper, or in one sample with millerite and heazlewoodite.

Pentlandite has a highly variable composition ranging (in the case of Cu-free pentlandite) from Fe contents up to 42.7 wt.% to Ni contents up to 55.7 wt.%, and up to 67 wt.% in the case of the Ni-rich godlevskite end member [Ni₄FeS₄] (Figure 2a). In most samples, Co contents in pentlandite are below 4 wt.%, except one sample (CS22) containing pentlandite with up to 14.5 wt.% Co. Heazlewoodite contains up to 3.4 wt.% Fe and millerite up to 1.9 wt.% Fe. For both minerals, Cu, Co, Zn, and As concentrations are below the detection limit. Heazlewoodite and millerite have only been detected intergrown with decomposing pentlandite, but not as single grains. Cu-bearing sulfides include sugakite and sanamiite with up to 17 wt.% Cu that substitutes for Ni (16.0–39.3 wt.%) or Fe (17.8–40.7 wt.%). The Co content of these sulfides is typically below 1 wt.%. Chalcocite is very rare and contains 3.4 to 4.4 wt.% Fe. It was only detected intergrown with Cu-bearing pentlandite (Figure 3b). Co-pentlandite, parallel exsolutions, and highly decomposed pentlandite occur (Figure 3c). Accordingly, spot analysis of the exsolved domains yields mixed analyses due to mineral intergrowth on the submicrometer scale (Figure 2). Similarly, in a few samples, Cu-rich sulfide minerals were detected, which, however, could not be classified due to their small grain sizes and their being intergrown with the pentlandite (Figures 3a–3d). Native copper could only be quantified by EMPA in sample CS26, though in several samples submicrometer-sized veins of native copper, formed within the center of serpentine veins, could be identified by EDX mapping (Figures 3d and 3e).

4.3. Awaruite Microstructure

The Fe-Ni alloy awaruite occurs exclusively next to or intergrown with pentlandite (Figures 3a and 4) and can be categorized into three distinct growth morphologies and assemblages: (i) awaruite intergrown with pentlandite as micrometer-scale dense veinlets or rims (e.g., Figures 4b and 4e, see also suppl. material Figure S2), (ii) as tens of nanometers thick platelets lacking magnetite (e.g., Figures 4e and 4f), or (iii) in a few samples as micrometer-scale vein-like features with magnetite, and/or native copper (Figure 3e). The dense awaruite veinlets or rims (i and iii) are up to 5 μm thick and represent a gen-
Figure 2. Ternary diagrams of (a) Fe-S-(Ni + Cu + Co) and (b) Cu-S-(Fe + Ni + Co) showing the range of chemical compositions detected in the studied samples (in wt.%). Gray triangles represent analyses containing >3 wt.% Cu, circles represent analyses containing <3 wt.% Cu. Note, numerous analyses represent mixed analyses due to mineral intergrowth at the submicrometer-scale. (c) Pentlandite-awaruite pairs of grain CS06_R71 with the stability fields in the S-Fe-Ni space for 230°C redrawn from Misra and Fleet (1973) (in atom%). Yellow pentagons = pentlandite, blue hexagons = awaruite, black circles = mixed pentlandite-awaruite analyses. Red stars represent the stoichiometric composition of Cu-bearing sulfides, black stars represent stoichiometric compositions of Fe- and Ni-sulfides and metals.

Figure 1. Binary Fe-S-Ni phase diagrams for (a) Fe-Ni and (b) Ni-Cu with the stability fields in the S-Fe-Ni space for 230°C. Red stars represent the stoichiometric composition of Cu-bearing sulfides, black stars represent stoichiometric compositions of Fe- and Ni-sulfides and metals.}

4.4. Sulfur Isotope Composition

Bulk rock sulfur isotope compositions and contents are highly variable and reach in one sample up to 1.33 wt.% S in the bulk rock total sulfur content (Table 2, Figure 6). However, most samples yielded no detectable sulfide nor sulfate by wet chemical extraction. In samples with detectable sulfur, sulfate is typically the dominant sulfur phase (SO\(_4^{2-}\) total sulfur = 0.475 to 1.000) with sulfate contents of 70–6,306 µg/g, though mostly below 490 µg/g. AVS contents are typically between 5 and 499 µg/g, except for one sample with 6,972 µg/g AVS, and chromium reducible sulfide (CRS) contents are between 17 and 246 µg/g. While \(\delta^{34}\)S values of sulfate have a relatively narrow range of 13.3–20.7‰, \(\delta^{34}\)S values of AVS and CRS have a larger range of −0.1‰ to +22.3‰ and −0.6 to +19.4‰, respectively (Figures 6a and 6b). In general, the sulfide content determined from powdered samples agrees well with the sulfide abundance observed in thin sections, with a few exceptions that suggest sample heterogeneity in terms of sulfide mineral occurrence (e.g., sample CS-1) as reflected by slightly larger errors (Table 2).

5. Discussion

5.1. Origin of Sulfide and Metal Mineral Phases

Primary, unaltered mantle rocks have sulfide mineralogy typically consisting of pentlandite, pyrrhotite, and rare chalcopyrite (e.g., Lorand, 1987; Lorand, 1989), with sulfur being present only in its reduced state (S\(^{-}\), S\(^{2-}\)). The distinction between primary and secondary sulfide
minerals can be based on mineralogical evidence (e.g., crystal shape, mineralogy), but is often challenging particularly with regards to pentlandite and pyrrhotite unless they occur as inclusions in primary minerals (e.g., olivine, spinel) (Lorand, 1987). A second and relatively reliable tool to determine the origin of the sulfur is to use sulfur isotope compositions as the average depleted mantle is estimated to have a narrow range in $\delta^{34}S_{\text{sulfide}}$ values of $0 \pm 1\%$ (Figure 6c) (Sakai et al., 1984; Shanks, Böhlke, & Seal, 1995).

Based on the $\delta^{34}S_{\text{sulfide}}$ values of the studied samples some pentlandite is most likely of depleted mantle origin as reflected by $\delta^{34}S$ values of $-0.6\%$–$2.1\%$ (Figure 6c). However, a range in $\delta^{34}S_{\text{sulfide}}$ values of up to
+22.3‰ clearly documents at least in part a secondary origin of the sulfide, which is further supported by a dominance of oxidized sulfur in the bulk rock (Figure 6b), both documenting introduction of reduced and oxidized sulfur most likely associated with serpentinization of the peridotite. Furthermore, a secondary origin of the sulfide and metal mineral, as well as extensive water-rock interaction and changing fluid redox conditions associated with peridotite alteration, is evidenced by the abundance of strongly decomposed pentlandite and pentlandite intergrown with diverse Cu-bearing sulfides, metals, or metal alloys (Figures 3 and 4).

Figure 4. Backscattered electron (BSE) images of variably decomposed pentlandite with dense awaruite (aw_{(i)}) forming along orthogonal cleavage planes of the pentlandite (a–c) or locally cutting pentlandite as irregular veins (e). Awaruite (aw_{(i)}) forming nanometer thin platelets are highlighted in (e) with awaruite increasingly consuming pentlandite (red arrows) and replacing it pseudomorphically (original pentlandite grain boundary is indicated) with awaruite platelets often intersecting at an angle of 90°. Locally pentlandite is consumed along orthogonal cleavage planes forming awaruite platelets (f). (b, e, and f) are magnifications of areas shown in (a, c, and d), respectively. Abbreviations as in Figure 3.
Figure 5. (a–f) BSE images and quantitative EDX maps measured with a pixel size of 11 nm (see area shown in Figure 4c) for S, Ni, Fe, Mg, of pentlandite (ptl) replaced by two generations of awaruite: dense awaruite (aw(i)) and platelet aggregates (aw(ii)). Panel (b) is a magnification of (a) (dashed-orange rectangle) and represents the mapped area in (c–f). (g) Bright-field (BF-STEM), and (h) High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image, as well as element mappings (i–l) of the same area (red line in (a) indicates the cut FIB-SEM-section). Columnar aw(i) crystals are oriented with their long axis normal to the parent pentlandite surface and separated from this substrate by a thin serpentine layer. Later aw(ii) platelets are up to 2 μm long single crystals and 70 nm thick. They intersect at an angle of $\sim90^\circ$ and are intergrown with late serpentine. BSE, backscattered electron; EDX, energy dispersive X-rays.
Interestingly, no secondary sulfides other than pentlandite were detected as single mineral grains. In other words, heazlewoodite, millerite, and Cu-bearing sulfide minerals have been exclusively detected intergrown with pentlandite. This indicates that pentlandite (and possibly pyrrhotite and chalcopyrite) decomposition and alteration were a major mechanism for secondary sulfide formation. In oceanic serpentinites and serpentinized peridotites, precipitation of sulfide minerals associated with microbial sulfate reduction or introduction of high-temperature S-bearing fluid result in either massif sulfide deposits, euhedral to fracture filling sulfides, finely disseminated sulfides (<1 μm) in the serpentine mesh texture, or in rare cases framboidal sulfide minerals, with their mineralogy reflecting prevalent fO2, fH2, and a(H2S) conditions (Alt et al., 2007; Delacour et al., 2008; Marques et al., 2007; Schwarzenbach et al., 2012). This implies that only rare secondary sulfide minerals formed in the studied samples during hydrothermal alteration and/or that subsequent fluid-rock interaction destabilized these mineral phases, that is, resulted in their decomposition and partial dissolution if, example, a(H2S) decreased as shown by thermodynamic modeling (Foustoukos et al., 2015; Frost, 1985; Klein & Bach, 2009). A change in sulfide/metal mineralogy has previously been shown particularly associated with the formation of awaruite, which forms due to the high H2 concentrations released during serpentinization that cause desulfurization of pentlandite according to the reaction (Klein & Bach, 2009; Schwarzenbach et al., 2014):

\[
Ni_{4/3}Fe_{1/3}S + 4 H_2, aq + 4 H_2O = 1.5 NiFe + Fe_3O_4 + 8 H_2S, aq
\]  

(1)

This reaction has been inferred from dense awaruite as reaction rims on or veinlets within pentlandite in, example, serpentinites from ODP Leg 209 along the Mid-Atlantic Ridge (Alt et al., 2007; Klein & Bach, 2009), peridotites from the Santa Elena ophiolite (Schwarzenbach et al., 2014), or serpentinized dunites of the Muskox intrusion (Chamberlain et al., 1965).

Similarly, the micromorphology of the Cu-bearing sulfides in the partly serpentinized harzburgites studied here points to a secondary origin. Copper-bearing sulfide minerals and native copper have been described in variably serpentinized peridotites from the Santa Elena ophiolite in Costa Rica. These have been attributed to a mostly secondary origin and formation associated with high-temperature (~350°C) fluids that contain small amounts of copper within a mid-ocean ridge environment (Schwarzenbach et al., 2016). The mineral precipitation took place at very low water-rock ratios, effectively leading to positive δ34Ssulfide values due to fluid evolution toward a closed system (Figure 6c) (Schwarzenbach et al., 2014, 2016). The sulfur isotope composition of the here studied rocks coincides with such a scenario; the δ34Ssulfide Values of the Chimaera samples mostly overlap with the isotope composition of the Santa Elena ophiolite suggesting that (Cretaceous) seawater-derived sulfate was abiogenically reduced to form sulfide and that sulfide was added by the hydrothermal fluids in a seafloor setting (Figure 6c). (Note, Santa Elena and Chimaera peridotites were both serpentinized in the Cretaceous where δ34Sseawater-sulfate values were around 16–19‰; Present et al. [2020]). However, the abundance of vein-like native copper forming in the center of serpentine veins (see Figure 3e) indicates that native copper formed during a later stage of fluid-rock interaction. Copper is a relatively reactive element and precipitates in its native state at high concentrations. In other cases, native copper has been described in hydrothermal systems that formed by supergene alteration and oxidation of sulfide deposits by ambient seawater in the TAG (Trans-Atlantic Geotravers) field (Hannington et al., 1988) or during low-temperature, epigenetic hydrothermal alteration of comparatively Cu-rich basalts (e.g., Bing-Quan et al., 2007; Pinto et al., 2011).

Hence, based on the sulfur isotope compositions, we infer that hydrothermal alteration of the peridotites associated with seafloor spreading was accompanied by localized high-temperature fluids that introduced sulfide and trace amounts of copper to form copper-bearing sulfides similar to the process observed in the Santa Elena ophiolite (Schwarzenbach et al., 2014). This was associated with thermochemical sulfate reduction with sulfur isotope fractionation by closed system fluid evolution resulting in δ34Ssulfide Values up to 22.3‰ (Table 2). A seafloor origin of the pentlandite is further corroborated, as thermochemical sulfate reduction is not proceeding efficiently at <250°C (Shanks et al., 1981) and hence is not proceeding at the low temperatures currently prevailing in the subsurface of the Chimaera hydrothermal field (<100°C) (Etiope et al., 2011). In contrast, the textural relations of the native copper veinlets within the center of serpentine veins suggest these formed after ophiolite emplacement, most likely by subsequent alteration of Cu-sulfides related to meteoric fluid circulation.
Figure 6. Bulk rock sulfur isotope compositions of the studied samples compared to peridotites from the Santa Elena ophiolite in Costa Rica (Schwarzenbach et al., 2016) (only samples that yielded detectable sulfur are shown). (a) $\delta^{34}$S of sulfate against $\delta^{34}$S of the sulfide fractions (AVS and CRS) indicating later addition of sulfate either from modern or an ancient seawater sulfate reservoir. The light gray area indicates $\delta^{34}$S composition of Paleozoic to Mesozoic seawater (after Kampschulte & Strauss, 2004; Present et al., 2020). (b) Most samples from the Chimaera hydrothermal system are dominated by sulfate over sulfide and have a relatively narrow range in $\delta^{34}$S values. (c) $\delta^{34}$S of AVS and CRS extracts shown against total sulfide contents. Chimaera samples have sulfide compositions very similar to those found in the Santa Elena peridotites that have been associated with thermochemical sulfate reduction at increasingly limited sulfate input, that is, low water-rock ratios. Processes indicated by the arrows and average depleted mantle composition (red star) after Alt et al. (2007). AVS, acid volatile sulfide; CRS, chromium reducible sulfide.
5.2. Mechanisms Resulting in Awaruite Formation

The two generations of awarute micromorphologies (columnar awarute, vs. up to 2 μm long, 40–70 nm thin awarute, single crystals, see Figure 4) strongly indicate formation during contrasting episodes of hydrothermal circulation, that is, different replacement episodes resulting from differing reaction kinetics imposed by changing temperatures and/or fluid properties, as discussed in the following. The chemical composition of the μm-scale vein-like awarute-pentlandite pairs indicates formation temperatures of around 230°C using the phase relations in the Fe-S-Ni system from Misra and Fleet (1973) (Figure 2c). This infers formation during ocean floor alteration rather than low-temperature interaction with meteoric fluids and coincides with previous observations of dense awarute rims or veinlets intergrown with magnetite and pentlandite from oceanic settings (Alt et al., 2007; Klein & Bach, 2009). Based on the micromorphologies it is likely that most of the denser awarute, that either forms veinlets, rims, or forms along the octahedral parting planes of pentlandite is associated with this stage of water-rock interaction. Interestingly, this temperature overlaps with temperatures constrained from clumped isotope thermometry for abiogenic methane formation of 235°C ± 29°C (Douglas et al., 2017). This may suggest a concurrent formation of methane and the early awarute generation in an ocean floor setting. However, these temperatures can only be constrained where awarute forms up to micrometer-thick intergrowths with pentlandite. The small size of the later platy awarute, does not allow quantification of the exact chemical composition and hence no precipitation temperatures can be constrained.

Overall, the uniform orientation of columnar awarute, single crystals in rims (Figures 5g and 5h) and particularly the replacement front between nanometer-scale awarute, platelets and pentlandite octahedral parting planes (Figure 4e) evidence a coupled dissolution-precipitation process. Such a mineral replacement mechanism proceeds when fluid comes into contact with a solid phase with which it is not in equilibrium (Putnis, 2009). A coupled dissolution-precipitation process is characterized by the preservation of the morphology of the parent phase (in our case pentlandite) (Figures 4a and 4c), a distinct replacement front (Figure 4e), and formation of porosity, which allows continuous transport of fluid to the parent phase and reaction of fluid with the parent phase to produce the reaction product (in our case awarute) (Plümper et al., 2017; Putnis, 2009; Putnis & Putnis, 2007).

We infer that the first stage of fluid-rock interaction produced columnar (dense) awarute, on dissolving pentlandite and took place within an ocean floor setting induced by H2 production during ongoing serpentinization at >200°C. Based on the distinctly different awarute morphologies we infer that the second stage pentlandite decomposition to awarute platelets was most likely the effect of higher disequilibrium conditions with the fluid phase caused by changes in fluid chemistry and/or temperature. These conditions resulted in the formation of up to 2 μm long and 40–70 nanometer thin awarute single crystals (Figures 5g and 5h). The morphology of the serpentinite crystals in cracks and in the pore space between awarute platelets suggests serpentine either formed during pentlandite replacement or after it fills the pore space, documenting that this stage of awarute formation was also associated with serpentinization of the peridotite. Disequilibrium could be caused by two different factors; First, at decreasing a(H2S) pentlandite becomes thermodynamically unstable (e.g., Frost, 1985; Klein & Bach, 2009), suggesting that highly S-undersaturated fluid conditions effectively result in decomposition of pentlandite to form awarute (see Equation 1). While seawater has sulfate concentrations of around 2,650 mg/L (28 mM), SO42− concentrations in the Chimaera springs are on the order of 8 mg/L (Meyer-Dombard et al., 2015). Similarly, H2S concentrations are likely exceedingly low as well in the Chimaera springs (though they have not been reported yet for these springs), as is also typical in other continental serpentinization systems (Sabuda et al., 2020). Such low fS2 (aH2S) conditions could induce pentlandite decomposition and awarute formation releasing H2S to the fluid as a consequence (Klein & Bach, 2009). Second, the Chimaera vents comprise ~87 vol% CH4 and ~10 vol% H2 (Etiope et al., 2011). The formation of awarute due to high fH2 has been constrained thermodynamically (Klein & Bach, 2009) and may be used as a proxy for the sulfide stabilities. Since both CH4 and H2 act as strong reducing agents, it is most likely that both species have the same redox potential stabilizing metal alloys, that is, destabilizing pentlandite. The lack of magnetite in the pentlandite-awarute intergrowths studied here, which is usually found together with pentlandite-awarute assemblages (Klein & Bach, 2009), further suggests that magnetite was either not stable, that is, conditions were more reducing, temperatures were too low (Klein, Bach, Humphris, et al., 2014), and/or that Fe3+—typically taken up by magnetite—was
incorporated by another phase, such as serpentine. A similar process may also take place when awaruite precipitates as single grains in a serpentine matrix such as described in serpentinites from the Cache Creek terrain (Britten, 2017). In that case, awaruite forms during ongoing serpentinization at high $f_{O_2}$ with Fe and Ni derived from olivine and pyroxene breakdown, whereas Fe$^{3+}$ would be taken up by the surrounding serpentine. Most likely, in the Cache Creek samples the formation of awaruite crystals took place close to equilibrium enabling massive, well-developed crystals, which is in contrast to the effectively more dendritic awaruite observed in our study that is typical for formation far from equilibrium (Sunagawa, 2005).

This overall indicates that the awaruite platelets formed as a result of the interaction of the methane-rich, sulfur-poor fluids during continental serpentinization, possibly in the presence of a free gas phase and, hence, at a later stage than some of the denser awaruite. However, in a few samples, we cannot exclude that some of the denser awaruite could have formed also during late-stage interaction associated with continental serpentinization. This is especially the case where the awaruite, platelets merge into denser, a few 100-nm-thin awaruite, veinlets (e.g., Figures 4e and 5a). Importantly, the pore space had to be fluid-saturated as long as the reaction proceeded to allow for fluid flow toward the reaction interface and to allow for continuous pentlandite decomposition and awaruite formation, whereas in the absence of available fluid the reaction would have stopped. This has been demonstrated previously by for example, Putnis (2009). Platy awaruite, formation was most likely facilitated as the rock had already been partly serpentinitized, which provided additional fluid pathways due to the presence of nanometer-scale pore space within the serpentinite groundmass (Tutolo et al., 2016) rather than the grains being enclosed within primary minerals.

Accordingly, our analytical results provide evidence that pentlandite is either of magmatic origin or formed during peridotite alteration along an oceanic spreading center. Based on the composition of pentlandite-awaruite pairs and the temperature constraints for thermochemical sulfate reduction discussed above, seafloor serpentinization would have taken place at a temperature range around 230°C–350°C induced by the introduction of Cretaceous seawater. As shown in many oceanic serpentinites this stage was associated with fluids of different origin (see e.g., Schwarzenbach et al., 2018) precipitating Cu-sulfides by high-T fluid influx and on the other hand producing awaruite by lower T (i.e., ~230°C) fluid circulation of highly reducing fluids. In particular, during this stage, stress-induced fracturing of the sulfide minerals caused parting along octahedral parting planes of the pentlandite (Figures 7a and 7b), whereas micrometer-thick awaruite, rims composed of columnar single crystals formed along these fractures (Figure 7c), as the peridotite was undergoing serpentinization. A change toward highly S undersaturated and highly reducing (high $f_{O_2}$ and $f_{H_2}$ conditions) most likely associated with interaction with meteoric water during continental serpentinitization—caused further pentlandite breakdown and pseudomorphic replacement by nanometer-scale awaruite, platelet aggregates, while serpentine precipitated in the newly formed pore space.

Effectively, the replacement of pentlandite by the awaruite, platelets leads to a considerable increase in pore space (though subsequently filled by serpentine) as well as a loss of Fe (the Ni/Fe ratio changes from ~0.8 in pentlandite to ~2.8 in awaruite) and $H_2S$. This $H_2S$ loss is also evident in the widespread decomposition of sulfide minerals in most of the studied samples (e.g., Figure 2b). We infer that the very low $a(H_2S)$ in the meteoric fluids caused general sulfide mineral breakdown and the formation of Cu-rich sulfide minerals that are stable at highly variable $f_{O_2}$ and $f_{H_2}$ conditions (Schwarzenbach, Gazel, & Caddick, 2014). It is likely that within continental serpentinization environments redox conditions are highly variable and may range from highly oxidizing where fresh, oxygenated meteoric water enters the system to strongly reducing where the methane-hydrogen-rich fluids are circulating. This likely also explains the observed variety in opaque phases.

The loss of $H_2S$ is also reflected in the low sulfide yields during wet chemical sulfur extraction, with sulfur contents below detection limit for most studied samples. Some of the sulfide minerals may have been oxidized to sulfate. Though the low sulfate contents of most samples and $\delta^{34}S_{sulfate}$ values of 13.2‰–20.7‰ rather point to the addition of seawater-derived sulfate because oxidative weathering of sulfide minerals is associated with an enrichment factor $\varepsilon \approx 0$‰, which could not be observed here (Figure 6a) (Alt et al., 2007; Rye et al., 1992). Seawater sulfate could have been introduced by the methane-rich fluids. These have been inferred to circulate through the lower lying Upper Paleozoic to Lower Mesozoic shales that are the source rock of the methane seeps (Hosgörmez, 2007). The $\delta^{34}S$ composition of seawater sulfate in the Paleozoic and Mesozoic varied between +10‰ and +35‰ (Kampfshulte & Strauss, 2004; Present et al., 2020).
and hence could have contributed trace amounts of sulfate to the rock (Figure 6a). The input of modern seawater-sulfate can, however, not be excluded. Overall, the sulfur geochemistry clearly points to multiple generations of sulfur cycling in the studied samples.

5.3. Implications for Microbial Activity

Previous studies have shown that microbial communities are found within ultramafic basement rocks, as documented by negative δ^{34}S signatures of serpentinites from the Iberian Margin, the Northern Apennine, and various drill core samples from the Mid-Atlantic Ridge (e.g., Alt et al., 2007; Alt & Shanks, 1998; Delacour et al., 2008; Schwarzenbach et al., 2018). In these rocks, evidence for microbial sulfate reduction can be traced to at least 150 m depths of the basement (Alt & Shanks, 1998). Similarly, sulfate reducers, sulfide oxidizers, and microbes using intermediate thiosulfate species have been detected within fluids of continental sites of serpentinization (e.g., Sabuda et al., 2020; Zwicker et al., 2018). While sulfate-reducing microbes may live within fractures and cracks, the occurrence of finely disseminated sulfide minerals with biogenic signatures also suggests that they possibly live within the pore space of serpentinites (Schwarzenbach et al., 2018). Tutolo et al. (2016) showed that the porosity of a peridotite can considerably increase as a result of the serpentinization reaction. Although in their case the pore space is most likely within the nanometer scale but has recently been shown to potentially play a pivotal role in the synthesis of abiotic carbon compounds (Nan et al., 2020). Alternatively, we suggest that low temperature water-rock interaction that causes destabilization of sulfide minerals, example, pentlandite-awaruite replacement (Figure 4) or pentlandite dissolution (Figure 3b), can result in considerable porosity that potentially provides a habitat for microbial communities. The increase of porosity effectively produced during pentlandite-awaruite replacement is on the order of 40%, with pores in the range of a few tens of nanometers between the platelets and larger pore space in the range of up to one micrometer in fractures of the sulfides (e.g., Figures 2d and 3e). Simultaneously, Fe, H_{2}S as well as other trace elements such as Co are released during sulfide decomposition. The porosity formed between the awaruite platelets and the extensive reactive mineral surface created by the replacement process is thereby key in allowing for continuous and coupled dissolution-reprecipitation to proceed and thus to continuously serve as an H_{2}S source for microbial life, for example, in adjacent fractures, whereby the pore space serves as ideal pathways for fluids to continuously react with the minerals.

At the Chimaera hydrothermal field, the presence of sulfate-reducing bacteria has been inferred based on biomarker studies and DNA extractions from surface rock samples (Neubeck et al., 2017; Zwicker et al., 2018). For Chimaera as well as other sites of active serpentinization, it has been suggested that sulfate reducing (and potentially sulfide oxidizing) microbes exist in microenvironments where active fluid-peridotite interaction provides niches for both sulfate-reducing bacteria but also methanogens, which are the more abundant species (Zwicker et al., 2018). Hence, we suggest that H_{2}S and Fe released by sulfide decomposition serve as energy sources for sulfide- and Fe oxidizing microbes at depth. Some H_{2}S may be transported toward shallower depths where mixing with oxygenated meteoric water takes place and sulfide is oxidized to sulfate serving as an energy source for sulfate reducers. In addition, sulfate leached from underlying...
carbonate sequences and preserved as traces in the serpentinites may serve as an additional energy source for sulfate reducers.

6. Conclusions

Variably serpentinized peridotites from the methane-rich Chimaera hydrothermal field in Turkey have experienced multiple phases of fluid-rock interaction. Peridotite alteration by Cretaceous seawater along an ocean ridge spreading center took place at around 230°C–350°C and resulted in pentlandite precipitation associated with thermochemical sulfate reduction, likely at low water-rock ratios causing positive $\delta^{34}S_{\text{sulfide}}$ values as a result of isotope fractionation following closed system processes. This stage of water-rock interaction was associated with the introduction of high-temperature fluids that contributed small amounts of Cu. Within the same setting, dense polycrystalline awaruite, rims formed along octahedral parting planes of pentlandite due to the highly reducing conditions imposed by ongoing serpentinization. The formation of awaruite generations at different fluid conditions is strongly supported by their different growth morphologies. We suggest that skeletal, nanometer-sized awaruite platelets formed following the obduction of the ophiolite and interaction with meteoric water. At this stage of water-rock interaction, the fluids are rich in CH$_4$ and H$_2$, whereas a(H$_2$S) is very low. We infer that the very low a(H$_2$S) of the circulating meteoric fluids and the high CH$_4$ concentrations induced strong disequilibrium conditions particularly with respect to pentlandite, as well as other sulfide phases, and induce their destabilization. Due to the heterogenous nature of these systems, redox conditions may be highly variable ranging from oxidizing where oxygenated meteoric water enters the system to highly reducing where the CH$_4$--H$_2$--rich fluids are channelized, but conditions are throughout sulfur-poor. These variations are reflected in the diverse opaque mineralogy from native copper, millerite, and heazlewoodite to the Fe-Ni alloy awaruite.

We infer that especially in these energy-limited systems the release of chemical species by mineral decomposition reactions induced by sulfur-undersaturated, meteoric fluids may be essential. In particular, the availability of S, Fe, and potentially other trace metals such as Co, and the formation of porosity that allows for fluid pathways and potentially serves as habitats for microbial communities may be key in supporting life within the basement of active serpentinization environments. Above all, these reactions may also be essential in supporting life on other water-bearing planets and planetary bodies, where water-peridotite interaction may take place in their crust or mantle.

Data Availability Statement

All datasets for this research are included in this study and its supplementary information files Table S1. In addition, all data are available in the Zenodo Repository, at https://doi.org/10.5281/zenodo.4700157.

Acknowledgments

The authors thank Alexander Schwarz and Sabine Meister for their help during analytical work. Benjamin Tutolo and Wolf-Achim Kahl are thanked for constructive comments and suggestions and Susanne Straub for editorial handling. Funding for this research was in parts provided by the Deutsche Forschungsgemeinschaft (DFG) grant SCHW 1889/4-1 to Esther Schwarzenbach. Oliver Pilipner is supported by a European Research Council (ERC) starting grant “nanoEARTH” (852069). We acknowledge support by the German Research Foundation and the Open Access Publication Fund of the Freie Universität Berlin. Open Access funding enabled and organized by Projekt DEAL.

References

Aldanmaz, E., Schmidt, M. W., Gourgaud, A., & Meisel, T. (2009). Mid-ocean ridge and supra-subduction geochemical signatures in spinel-peridotites from the Neotethyan ophiolites in SW Turkey: Implications for upper mantle melting processes. Lithos, 113, 691–708. https://doi.org/10.1016/j.lithos.2009.03.010

Alt, J. C., & Shank, W. C. (1998). Sulfur in serpentinized oceanic peridotites: Serpentinization processes and microbial sulphate reduction. Journal of Geophysical Research, 103, 9917–9929. https://doi.org/10.1029/98JB00576

Alt, J. C., Shank, W. C., Bach, W., Paulick, H., Garrido, C. J., & Beaudoin, G. (2007). Hydrothermal alteration and microbial sulphate reduction in peridotite and gabbro exposed by detachment faulting at the Mid-Atlantic Ridge, 15° 20’ N (ODP Leg 209): A sulfur and oxygen isotope study. Geochemistry, Geophysics, Geosystems, 8. https://doi.org/10.1029/2007GC001617

Bagci, U., Parlak, M., & Höck, V. (2006). Geochemical character and tectonic environment of ultramafic to mafic cumulate rocks from the Tekirova (Antalya) ophiolite (southern Turkey). Geological Journal, 41, 193–219.

Bing-Quan, Z., Yao-Guo, H., Zheng-Wei, Z., Xue-Jun, C., Tong-Mo, D., Guang-Hao, C., et al. (2007). Geochemistry and geochronology of native copper mineralization related to the Emeishan flood basalts, Yunnan Province, China. Ore Geology Reviews, 32, 366–380. https://doi.org/10.1016/j.oregeorev.2006.10.004

Brazelton, W. J., Mehta, M. P., Kelley, D. S., & Baross, J. A. (2011). Physiological differentiation within a single-species biofilm fueled by serpentinization. mBio, 2. https://doi.org/10.1128/mBio.00127-11

Brazelton, W. J., Schrenk, M. O., Kelley, D. S., & Baross, J. A. (2006). Methane- and sulfur-metabolizing microbial communities dominate the Lost City hydrothermal field ecosystem. Applied and Environmental Microbiology, 72, 6257–6270. https://doi.org/10.1128/aem.00574-06

Bağci, U., Parlak, O., & Höck, V. (2006). Geochemical character and tectonic environment of ultramafic to mafic cumulate rocks from the Tekirova (Antalya) ophiolite (southern Turkey).

Aldanmaz, E., Schmidt, M. W., Gourgaud, A., & Meisel, T. (2009). Mid-ocean ridge and supra-subduction geochemical signatures in spinel-peridotites from the Neotethyan ophiolites in SW Turkey: Implications for upper mantle melting processes. Lithos, 113, 691–708. https://doi.org/10.1016/j.lithos.2009.03.010

Alt, J. C., & Shank, W. C. (1998). Sulfur in serpentinized oceanic peridotites: Serpentinization processes and microbial sulphate reduction. Journal of Geophysical Research, 103, 9917–9929. https://doi.org/10.1029/98JB00576

Alt, J. C., Shank, W. C., Bach, W., Paulick, H., Garrido, C. J., & Beaudoin, G. (2007). Hydrothermal alteration and microbial sulphate reduction in peridotite and gabbro exposed by detachment faulting at the Mid-Atlantic Ridge, 15° 20’ N (ODP Leg 209): A sulfur and oxygen isotope study. Geochemistry, Geophysics, Geosystems, 8. https://doi.org/10.1029/2007GC001617

Bagci, U., Parlak, M., & Höck, V. (2006). Geochemical character and tectonic environment of ultramafic to mafic cumulate rocks from the Tekirova (Antalya) ophiolite (southern Turkey). Geological Journal, 41, 193–219.

Bing-Quan, Z., Yao-Guo, H., Zheng-Wei, Z., Xue-Jun, C., Tong-Mo, D., Guang-Hao, C., et al. (2007). Geochemistry and geochronology of native copper mineralization related to the Emeishan flood basalts, Yunnan Province, China. Ore Geology Reviews, 32, 366–380. https://doi.org/10.1016/j.oregeorev.2006.10.004

Brazelton, W. J., Mehta, M. P., Kelley, D. S., & Baross, J. A. (2011). Physiological differentiation within a single-species biofilm fueled by serpentinization. mBio, 2. https://doi.org/10.1128/mBio.00127-11

Brazelton, W. J., Schrenk, M. O., Kelley, D. S., & Baross, J. A. (2006). Methane- and sulfur-metabolizing microbial communities dominate the Lost City hydrothermal field ecosystem. Applied and Environmental Microbiology, 72, 6257–6270. https://doi.org/10.1128/aem.00574-06
Brazelton, W. J., Thornton, C. N., Hyer, A., Twing, R. L., Longino, A. A., Lang, S. Q., et al. (2017). Metagenomic identification of active methanogens and methanotrophs in serpentinizing springtime soils of the Voltri Massif. Italy. PeerJ, 5, e2945. https://doi.org/10.7717/peerj.2945

Britten, R. (2017). Regional metallogeny and genesis of a new deposit type-disseminated awaruite (Ni3Fe) mineralization hosted in the cache creek terrane. Economic Geology, 112, 517–550. https://doi.org/10.2113/econgeo.112.3.517

Bruni, J., Canepa, M., Chiodini, G., Cioni, R., Cipolli, F., Longinelli, A., et al. (2002). Irreversible water-rock mass transfer accompanying the generation of the neutral, Mg-HCO3, and high-pH, Ca-OH spring waters of the Genova province, Italy. Applied Geochemistry, 17, 455–474. https://doi.org/10.1016/s0883-2970(01)00115-5

Canfield, D. E., Raiswell, R., Westrich, J. T., Reaves, C. M., & Berner, R. A. (1986). The use of chromium reduction in the analysis of reduced inorganic sulfur in sediments and shales. Chemical Geology, 54, 149–155. https://doi.org/10.1016/0009-2517(86)90078-1

Chamberlain, J. A., McLeod, C. R., Trall, R. J., & Lachance, G. R. (1965). Native metals in the Muskox intrusion. Canadian Journal of Earth Sciences, 2, 188–215. https://doi.org/10.1007/bf00455-017

Cipolli, F., Gambardella, B., Marinì, L., Ottolino, G., & Vetuschi Zuccolini, M. (2004). Geochemistry of high-pH waters from serpentinites of the Gruppo di Voltri (Genova, Italy) and reaction path modeling of CO2 sequestration in serpentinite aquifers. Applied Geochemistry, 19, 787–802. https://doi.org/10.1016/j.jgeochem.2003.10.007

Delacour, A., Früh-Green, G. L., Bernasconi, S. M., & Kelley, D. S. (2008). Sulfur in peridotites and gabbros at Lost City (30°N, MAR): Implications for hydrothermal alteration and microbial activity during serpentinization. Geochimica et Cosmochimica Acta, 72, 5090–5110. https://doi.org/10.1016/j.gca.2008.07.017

Douglas, P. M. J., Stolper, D. A., Eller, J. M., Sessions, A. L., Lawson, M., Shuai, Y., et al. (2017). Methane clumped isotope: Progress and potential for a new isotopic tracer. Organic Geochemistry, 113, 263–282. https://doi.org/10.1016/j.orggeochem.2017.07.016

Etiöpe, G., Schoell, M., & Högström, H. (2011). Abiotic methane flux from the Chimaera seep and Tekirova ophiolites (Turkey): Understanding gas exhalation from low temperature serpentinization and implications for Mars. Earth and Planetary Science Letters, 310, 96–104. https://doi.org/10.1016/j.epsl.2011.08.001

Foustoukos, D. I., Bizimis, M., Frisyb, C., & Shirey, S. B. (2012). Redox controls on Ni-Fe-PGE mineralization and Re/Os fractionation during serpentinization of abyssal peridotite. Geochimica et Cosmochimica Acta, 150, 11–25. https://doi.org/10.1016/j.gca.2014.11.025

Fritz, P., Clark, I. D., Tones, J., Whiticar, M. J., & Faber, E. (1992). Deuterium and 13C evidence for low temperature production of hydrogen and methane in a highly alkaline groundwater environment in Oman. Khadha and Maest. https://doi.org/10.3917/puf.fritz.1992.01

Frost, B. R. (1985). On the stability of sulfides, oxides, and native metals in serpentinite. Geochimica et Cosmochimica Acta, 49, 135–138. https://doi.org/10.1016/0016-7037(85)90201-9

Früh-Green, G. L., Bernasconi, S. M., & Kelley, D. S. (2008). Sulfur in peridotites and gabbros at Lost City (30°N, MAR): Implications for hydrothermal alteration and microbial activity during serpentinization. Geochimica et Cosmochimica Acta, 72, 5090–5110. https://doi.org/10.1016/j.gca.2008.07.017

Klein, F., & Bach, W. (2009). Fe-Ni-Co-O-S phase relations in peridotite-seawater interactions. Journal of Petrology, 50, 37–59. https://doi.org/10.1093/petrology/epn131

Klein, F., Bach, W., Humphris, S. E., Kahl, W.-A., Jöns, N., Moskowitz, B., & Berque, T. S. (2014). Magnetite in seafloor serpentinite—Some like it hot. Geology, 42, 135–138. https://doi.org/10.1130/G35068.1

Klein, F., Bach, W., Jöns, N., McCollom, T., Moskowitz, B., & Berqué, T. (2009). Iron partitioning and hydrogen generation during serpentinization of abyssal peridotites from 15°N on the Mid-Atlantic Ridge. Geochimica et Cosmochimica Acta, 73, 6868–6893. https://doi.org/10.1016/j.gca.2009.08.021

Lang, S. Q., & Brazelton, W. J. (2020). Habitability of the marine serpentine subsurface: A case study of the Lost City hydrothermal field. Philosophical Transactions of Royal Society A., 378, 20180429. https://doi.org/10.1098/rsta.2018.0429

Lang, S. Q., Früh-Green, G. L., Bernasconi, S. M., Brazelton, W. J., Schrenk, M. O., & McGonigle, J. M. (2018). Deeply-sourced formate fuels sulphate reducers but not methanogens at Lost City hydrothermal field. Scientific Reports, 8, 755. https://doi.org/10.1038/s41598-017-10902-5

Liebmann, J., Schwarzenbach, E. M., Früh-Green, G. L., Boschi, C., Roumèjone, S., Strauss, H., et al. (2018). Tracking Water-Rock Interaction at the Atlantis Massif (MAR, 30°N) Using Sulfur Geochemistry. Geochimica et Geophysica, Geosystems, 19, 4561–4583. https://doi.org/10.1029/2018gc007810

Lorand, J. P. (1987). Cu-Fe-Ni-S mineral assemblages in upper-mantle peridotites from the Table Mountain and Blow-Me-Down Mountain ophiolite massifs (Bay of Islands area, Newfoundland): Their relationships with fluids and silicate melts. Lithos, 20, 59–76. https://doi.org/10.1016/0021-2533(87)90024-7

Lorand, J. P. (1989). Mineralogy and chemistry of Cu-Fe-Ni sulfides in orogenic-type spinel peridotite bodies from Ariege (Northeastern Pyrenees, France). Contribution to Mineralogy and Petrology, 103, 335–345. https://doi.org/10.1007/bf00402929

Marques, A. F. A., Barriga, F. J. A. S., & Scott, S. D. (2007). Sulfide mineralization in an ultramafic-rock hosted seafloor hydrothermal system: From serpentinization to the formation of Cu-Zn-(Co)-rich massive sulfides. Marine Geology, 245, 20–39. https://doi.org/10.1016/j.margeo.2007.05.007

Martin, W., & Russell, M. J. (2007). On the origin of biochemistry at an alkaline hydrothermal vent. Philosophical Transactions of the Royal Society B, 362, 1887–1926. https://doi.org/10.1098/rstb.2006.1881

McCollom, T. M. (2007). Geochemical constraints on sources of metabolic energy for chemolithoautotrophy in ultramafic-hosted deep-sea hydrothermal systems. Astrobiology, 7, 933–950. https://doi.org/10.1089/ast.2006.0119

McCollom, T. M., Klein, F., Robbins, M., Moskowitz, B., Berqué, T. S., Jöns, N., et al. (2016). Temperature trends for reaction rates, hydrogen generation, and partitioning of iron during experimental serpentinization of olivine. Geochimica et Cosmochimica Acta, 181, 175–200. https://doi.org/10.1016/j.gca.2016.03.002

Meyer-Dombard, D. A. R., Woychese, K. M., Yargöçlu, E. N., Cardace, D., Shock, E. L., Güleç-Pektas, Y., & Temel, M. (2015). High pH microbial ecosystems in a newly discovered, ephemeral, serpentinizing fluid seep at Vanartas (Chimera), Turkey. Frontiers in Microbiology, 5. https://doi.org/10.3389/fmicb.2014.00723
Zwicker, J., Birgel, D., Bach, W., Richoz, S., Smrzka, D., Grasemann, B., et al. (2018). Evidence for archeal methanogenesis within veins at the Vance, S. D., & Melwani Daswani, M. (2020). Serpentinite and the search for life beyond Earth. Tuttle, M., Goldhaber, M. B., & Williamson, D. L. (1986). An analytical scheme for determining forms of sulfur in oil shales and associated Sunagawa, I. (2005). Shanks, W. C., Bischoff, J. L., & Rosenbauer, R. J. (1981). Seawater sulphate reduction and sulfur isotope fractionation in basaltic systems: Interaction of seawater with fayalite and magnetite at 200-350°C. Schwarzenbach, E. M., Gazel, E., Caddick, M. J. (2014). Hydrothermal processes in partially serpentinized peridotites from Costa Schrenk, M. O., Brazelton, W. J., Lang, S. Q., & Jamtveit, B. (2017). Fluid-driven metamorphism of the continental crust governed by nanoscale fluid flow. Nature Geosciences, 10, 685–690. https://doi.org/10.1038/ntgeo3009 Present, T. M., Adkins, J. F., & Fischer, W. W. (2020). Variability in sulfur isotope records of Phanerzoic seawater sulphate. Geophysical Research Letters, 47, e2020GL088766. https://doi.org/10.1029/2020gl088766 Putnis, A. (2009). Mineral replacement reactions. Reviews in Mineralogy and Geochemistry, 70, 87–124. https://doi.org/10.2138/rmg.2009.70.3 Putnis, A., & Putnis, C. V. (2007). The mechanism of reequilibration of solids in the presence of a fluid phase. Journal of Solid State Chemistry, 180, 1783–1786. https://doi.org/10.1016/j.jssc.2007.03.023 Robertson, A. H. F., & Woodcock, N. K. (1980). Strike-slip related sedimentation in the Antalya Complex, Southwest Turkey. Special Publication on the International Association of Sedimentologists, 4, 127–145. https://doi.org/10.1016/S0144-3037(35)ch8 Russell, M. J., Hall, A. J., & Martin, W. (2010). Serpentinization as a source of energy at the origin of life. Geobiology, 8, 355–371. https://doi.org/10.1111/j.1472-4669.2010.00249.x Rye, R. O., Belkbe, P. M., & Wasserman, M. D. (1992). The stable isotope geochemistry of acid sulphate alteration. Economic Geology and the Bulletin of the Society of Economic Geologists, 87, 225–262. https://doi.org/10.2113/gsecongeo.87.2.225 Sabuda, M. C., Brazelton, W. J., Putman, L. I., McCollom, T. M., Hoehler, T. M., Kubo, M. D. Y., et al. (2020). A dynamic microbial sulfur cycle in a serpentinizing continental ophiolite. Environmental Microbiology, 22, 2329–2345. https://doi.org/10.1111/1462-2920.15006 Sakai, H., Marais, D. J. D., Ueda, A., & Moore, J. G. (1984). Concentrations and isotope ratios of carbon, nitrogen and sulfur in ocean-floor basalts. Geochimica et Cosmochimica Acta, 48, 2433–2441. https://doi.org/10.1016/0016-7037(84)90295-3 Sánchez-Murillo, R., Gazel, E., Schwarzenbach, E. M., Crespo-Medina, M., Schrenk, M. O., Roli, J., & Gill, B. C. (2014). Geochemical evidence for active tropical serpentinization in the Santa Elena Ophiolite, Costa Rica: An analogy of a humid early Earth? Geochimistry, Geophysics, Geosystems, 15, 1803–1800. https://doi.org/10.1002/2013gc005213 Schrenk, M. O., Brazelton, W. J., & Lang, S. Q. (2013). Serpentinization, carbon, and deep life. Reviews in Mineralogy and Geochemistry, 75, 575–606. https://doi.org/10.2138/rmg.2013.75.18 Schwarzenbach, E. M., Früh-Green, G. L., Bernasconi, S. M., Alt, J. C., Shanks, III, W. C., III, Gaggero, L., & Crispini, L. (2012). Sulfur geochemistry of peridotite-hosted hydrothermal systems: Comparing the Ligurian ophiolites with oceanic serpentinites. Geochimica et Cosmochimica Acta, 91, 283–305. https://doi.org/10.1016/j.gca.2012.05.021 Schwarzenbach, E. M., Gazel, E., & Caddick, M. J. (2014). Hydrothermal processes in partially serpentinized peridotites from Costa Rica: Evidence from native copper and complex sulfide assemblages. Contributions to Mineralogy and Petrology, 168, 1–21. https://doi.org/10.1007/s00410-014-1079-2 Schwarzenbach, E. M., Gill, B. C., Gazel, E., & Madrigal, P. (2016). Sulfur and carbon geochemistry of the Santa Elena peridotites: Comparing oceanic and continental processes during peridotite alteration. Lithos, 252–253, 92–108. https://doi.org/10.1016/j.lithos.2016.02.017 Schwarzenbach, E. M., Gill, B. C., & Johnston, D. T. (2018). Unraveling multiple phases of sulfur cycling during the alteration of ancient ultramafic oceanic lithosphere. Geochimica et Cosmochimica Acta, 223, 279–299. https://doi.org/10.1016/j.gca.2017.12.006 Schwarzenbach, E. M., Lang, S. Q., Früh-Green, G. L., Lilley, M. D., Bernasconi, S. M., & Mélly, S. (2013). Sources and cycling of carbon in continental, serpentine-hosted alkaline springs in the Voltri Massif, Italy. Lithos, 177, 226–244. https://doi.org/10.1016/j.lithos.2013.07.009 Shanks, W. C., Bischoff, J. L., & Rosenbauer, R. J. (1981). Seawater sulphate reduction and sulfur isotope fractionation in basaltic systems: Interaction of seawater with fayalite and magnetite at 200-350°C. Geochimica et Cosmochimica Acta, 45, 1977–1995. https://doi.org/10.1016/0016-7037(81)90065-4 Shanks, W. C., Böhlke, J. K., & Seal, R. R. (1995). Stable isotopes in mid-ocean ridge hydrothermal systems: Interactions between fluids, minerals, and organisms. American Geophysical Union. Sunagawa, I. (2005). Crystals grow, morphophilia and perfection. Cambridge University Press. https://doi.org/10.1017/cbo9780511610349 Suzuki, S., Ishii, S., Wu, A., Cheung, A., Tenney, A., Wagner, G., et al. (2013). Microbial diversity in The Cedars, an ultrabasic, ultrareducing, and low salinity serpentinizing ecosystem. Proceedings of the National Academy of Sciences, 110, 15386–15391. https://doi.org/10.1073/pnas.1302428110 Taubner, R.-S., Pappenreiter, P., Zwicker, J., Smrzka, D., Pruckner, C., Kolar, P., et al. (2018). Biological methane production under putative Enceladus-like conditions. Nature Communications, 9, 748. https://doi.org/10.1038/s41467-018-02876-y Tutoyo, B. M., Mildner, D. R. F., Gagnon, C. V. Y., Saar, M. O., & Seyfried, W. E. (2016). Nanoscale constraints on porosity generation and fluid flow during serpentinization. Geology, 44, 103–106. https://doi.org/10.1130/g37349.1 Turtle, M., Goldhaber, M. B., & Williamson, D. L. (1986). An analytical scheme for determining forms of sulfur in oil shales and associated rocks. Tectonics, 33, 953–961. https://doi.org/10.1029/94tc00424x Vance, S. D., & Melwani Daswani, M. (2020). Serpentinite and the search for life beyond Earth. Philosophical Transactions of the Royal Society A, 378, 20180421. https://doi.org/10.1098/rsta.2018.0421 Zwicker, J., Birgel, D., Bach, W., Richoz, S., Smrzka, D., Graesemann, B., et al. (2018). Evidence for archaic methanogenesis within veins at the onshore serpentinite-hosted Chimaera seeps, Turkey. Chemical Geology, 483, 567–580. https://doi.org/10.1016/j.chemgeo.2018.03.027