Serpentinization, Carbonation, and Metasomatism of Ultramafic Sequences in the Northern Apennine Ophiolite (NW Italy)

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Abstract Fluid-rock interaction in ultramafic rocks considerably affects the chemical and isotopic composition of the oceanic lithosphere. We present a geochemical and petrological study of serpentinites and ophicalcites of the Northern Apennine ophiolite, Italy. This ophiolite sequence represents fragments of Jurassic oceanic lithosphere that have been denuded by low angle detachment faults, exposing peridotites on the ocean floor and triggering hydrothermal alteration. Seawater circulation is documented by (Jurassic) seawater-like 87Sr/86Sr values and δ13C values of 1.1–3.0‰ in carbonate veins of the ophicalcite. Bulk rock ophicalcites have low 87Sr/86Sr values of 0.70489–0.70599, elevated SiO₂ contents, and talc druses filling calcite veins that record Si-metasomatism. In contrast, underlying serpentinites have 87Sr/86Sr values above Jurassic seawater values. Bulk rock δD and δ18O values of ophicalcites are more negative than those of the serpentinites. The studied sequence represents an excellent example of the evolution from serpentinite to ophicalcite during continuous uplift and exposure of ultramafic rocks on the seafloor and documents the complex hydrothermal evolution of ultramafic rocks associated with this process. The extensive chemical transformation of mantle peridotites likely has an impact on geochemical cycles and subduction zone processes.

1. Introduction

Ocean ridge spreading centers produce around 18 km³ of oceanic crust each year (Cogné & Humler, 2006). Although the majority of newly formed oceanic crust is composed of mafic lithologies, approximately 9%–20% of the crust formed along slow spreading ridges comprises serpentenitized peridotite (Alt, Schwarzenbach, et al., 2013; Cannat et al., 1995, 2010). In these tectonic settings mantle rocks are exposed to seawater and altered via a complex interplay of magmatism, asymmetric extension, and detachment faulting, which is commonly linked to the formation of oceanic core complexes (Cannat, Sauter, et al., 2006; Früh-Green et al., 2018; John & Cheadle, 2010; Tucholke et al., 2008). During continuous mantle uplift, the ultramafic rocks undergo extensive chemical exchange with circulating fluids, resulting in pronounced chemical and mineralogical transformation (Früh-Green et al., 1990, 1996; Paullick et al., 2006; Schwarzenbach, Früh-Green, Bernasconi, Alt, & Plas, 2013). Seawater-rock interaction has been shown to influence the chemical evolution of the oceans (e.g., Früh-Green et al., 2004; von Damm, 1995) and circulation of seawater through mantle sequences affects rheology, strength, and seismic properties of the oceanic lithosphere (e.g., Escartin et al., 1997; Miller & Christensen, 1997). In addition, subduction of the altered oceanic lithosphere transports various elements into Earth’s interior (e.g., Alt, Schwarzenbach, et al., 2013; Scambelluri et al., 2004), affecting arc magmatism (e.g., Ulmer & Trommsdorff, 1995) and the chemical and isotopic evolution of Earth’s interior (e.g., Li et al., 2020).

Hydrothermal alteration in ultramafic rocks is primarily expressed by serpentinization—the reaction of the primary mantle minerals olivine and pyroxene with water to form a rock dominated by serpentine and
magnetite (Bach et al., 2004; Moody, 1976; O’Hanley, 1996). These reactions generally produce low-temperature, alkaline (pH ∼9–11), Ca-, and H2-rich fluids that induce carbonate formation upon interaction with seawater, such as those described from the Lost City hydrothermal field (LCHF) on the Atlantis Massif (AM) (Mid-Atlantic Ridge (MAR), 30°N; Kelley, Karson, et al., 2001; Ludwig et al., 2006). The LCHF represents one of the best examples of a modern serpentinite-hosted marine hydrothermal system and is characterized by up to 60 m high carbonate-brucite chimneys and towers that vent up to 95°C, high pH fluids and host diverse microbial communities (e.g., Brazelton et al., 2006; Kelley, Karson, Früh-Green, et al., 2005). Recent studies have shown that the evolution of peridotite-hosted hydrothermal systems is complex, commonly involving melt-rock interaction and a complex alteration history of serpentinitization, talc metasomatism, carbonation, and low-temperature seafloor weathering and oxidation (e.g., Früh-Green et al., 2018; Paulick et al., 2006). In many cases, interaction of water with interspersed gabbroic intrusions causes wide-spread or localized high-temperature imprint and changes the chemical signatures of the basement rocks, as documented by distinct enrichments in Si, Al, Ca, and assemblages of Ca-rich amphibole, talc, and chlorite (Boschi et al., 2006a, 2006b; Rounéjon et al., 2018). In addition, high-temperature fluid-rock interaction associated with magmatism can produce extensive sulfide deposits (e.g., Garuti et al., 2008; Marques et al., 2007), whereas low-temperature serpentinitization may facilitate formation of considerable amounts of microbially produced sulfide (e.g., Alt, Schwarzenbach, et al., 2013).

Here, we present a study of alteration processes and carbonate deposition in the Northern Apennine ophiolite in Italy with the aim to unravel its chemical evolution from serpentinite to ophicalcite formation. Ophiolites are fragments of oceanic lithosphere that have tectonically been emplaced on the continent (Coleman, 1977). Due to their exceptional exposure, they can provide unique insight into magmatic and hydrothermal processes that took place on the seafloor. The Northern Apennine ophiolite is considered a relic of oceanic lithosphere formed in the Piemont-Ligurian ocean. Previous research showed that this sequence records an oceanic alteration history similar to that described in a number of ultramafic core complexes along the MAR (e.g., Alt, Crispini, et al., 2018; Karson et al., 2006; Schwarzenbach, Früh-Green, Bernasconi, Alt, & Plas, 2013). The ophiolite only experienced a weak Alpine metamorphic overprint that did not exceed prehnite-pumpellyite facies conditions and did not modify the marine signatures (e.g., Cortesogno, Gianelli, & Piccardo, 1975; Garuti et al., 2008; Strating, 1991). Our study builds on previous work (Schwarzenbach et al., 2012, 2013, 2018), which was based on carbon and sulfur geochemistry and provided initial evidence for extensive seawater infiltration and variations in temperatures and fluid regime that also facilitated microbial activity in the serpentinites. Here, we present strontium, oxygen, and hydrogen isotope bulk rock data and in situ major and trace element compositions, which provide new, comprehensive insights into the hydrothermal and temporal evolution of this ophiolite sequence and the origin of the fluids that caused rock alteration. In particular, the good exposure of this sequence allows us to track its hydrothermal evolution during continuous uplift and exposure on the Jurassic ocean floor and the transition from serpentinite to ophicalcite formation. We compare this ancient system with the AM, which provides a modern analog for the N. Apennine ophiolite and allows us to evaluate the interplay of serpentinitization, metasomatism, and carbonation, and their effects on mass transfer during the hydrothermal evolution of ultramafic rocks. This allows us to better understand the chemical evolution of the oceanic lithosphere, which is eventually subducted along convergent margins and effectively controls long-term geochemical cycles.

2. Geological Overview and Samples

2.1. Regional Geology

The ophiolite successions in the N. Apennine (Eastern Liguria, Italy) represent relics of a former oceanic lithosphere of the Ligurian Tethys that separated the European and Apulian continental plates during the Late Jurassic-Cretaceous and locally developed a slow- to ultraslow-spreading ridge (Lagabrielle & Lemoiné, 1997; Strating, 1991; Tribuzio, Thirlwall, & Vannucci, 2004). Along these spreading centers mantle exhumation was prevalent, whereas mature oceanic spreading was comparatively short-lived (Le Breton et al., 2021). Accordingly, these ophiolite sequences are characterized by a heterogeneous basement made up of gabbroic intrusions in mantle peridotites and are discontinuously overlayed by ophicalcites, basaltic lavas, sedimentary breccias, and pelagic sediments (e.g., B. E. Treves and Harper, 1994). The peridotite basement varies in composition from depleted spinel harzburgites to fertile spinel lherzolites, and from dunites
Serpentinites, ophicalcites, and fault rocks from the Bracco Unit were systematically sampled in several active or abandoned quarries (Figure 1) allowing for the recovery of fresh sample material unaffected by long-term weathering. Talc-tremolite fault schists were sampled from a dome-shaped structure in the Cava dei Marmi that represents a several meters-wide zone of strongly sheared fault rocks along the contact between the ophicalcites and the underlying volcano-sedimentary sequence (from here on referred to as Cava dei Marmi fault schists). We classify the ophicalcites into two groups according to their oxidation state and tectonic history: green and red ophicalcites. The green ophicalcites are defined here as completely serpentinitized and variable calcite-veined massive peridotites. They have been fractured in situ and are characterized by the presence of cross-cutting generations of calcite veins. Locally, oxidation is observed along the calcite veins (Figure 2a). The red ophicalcites typically overlie the green ophicalcites and are highly fractured, partly brecciated, and are interpreted as tectonic breccias (Figure 2b). They are characterized by an intense red color, crosscut by a myriad of calcite veins commonly containing talc in druses. The transition from serpentinites, to green and then to red ophicalcites is gradual and reflected by an increase in calcite veining and SCHRZENBACH ET AL. 10.1029/2020JB020619 3 of 24
Figure 2. (a) Strongly veined and partly oxidized green ophicalcite with oxidation initiating along calcite veins. (b) Highly oxidized, red ophicalcite characterized by intense fracturing and brecciation, showing crosscutting relationships of multiple generations of calcite-veins and talc in druses. (c and d) Lens of tremolite-rich fault schist at the contact between massive serpentinites and brecciated pillow basalts at the Libiola mining site (LLB) (e–h) Microphotographs of replacement textures in green ophicalcites using crossed polarized light: (e) Chlorite-amphibole-vein with fan-shaped chlorite, serpentine, amphibole blades (hornblende to actinolite-hornblende), and fine-grained talc at the vein rim. (f) Fibrous serpentine in a bastite replacing pyroxene with talc forming a rim around bastite. (g) Late serpentine-vein with fragments of calcite formed by reactivation of an older calcite-vein that cuts the serpentine mesh texture. (h) Chlorite replacing pyroxene in a bastite with fine-grained tremolite and hornblende forming a rim around bastite. Abbreviations: cc–calcite; chl–chlorite; hbl–hornblende; serp–serpentine; tlc–talc; trem–tremolite.
oxidation from bottom to top of the exposed sequence. A transect through all three lithologies was sampled to account for variations in veining and oxidation.

Serpentinites and tremolite-schists from the Val Graveglia Unit were sampled at one abandoned mining site close to the village of Libiola. In the study area, the serpentinites over-thrust the brecciated basalts and are therefore not associated with the underlying stockwork deposits. A prominent lens of tremolite-schist at the contact between the serpentinites and the brecciated basalts was sampled as well (Figures 2c and 2d) (from here on referred to as Libiola fault schists). In addition, gabbro samples from the Bracco Unit investigated by Molli (1995) were used in this study for strontium isotope analyses.

3. Analytical Procedures

3.1. Petrographic Characterization

The mineralogy and petrology were investigated on thin sections with transmitted light microscopy and using a JEOL JSM-6390 LA scanning electron microscope with energy dispersive X-ray spectroscopy capabilities. Quantitative element concentrations were obtained by electron microprobe analysis carried out on a JEOL JXA-8200 at ETH Zurich. The beam was set to 15 kV accelerating potential, 1–10 µm beam size, and 5–20 nA beam current. Natural and synthetic standards were used for calibration. Additionally, X-ray diffraction (XRD) spectra were acquired on vein powders with a LynxEye X-ray diffractometer (Bruker AXS D8 Advance) at ETH Zurich to determine the carbonate mineralogy.

3.2. Major and Trace Element Analysis

Bulk rock powders of the serpentinites and ophicalcites were prepared by cutting away the outermost rind to remove contamination, crushing in a steel mortar, and grinding to a powder in an agate mill. Major and trace element analysis of the powders were obtained by Panalytical Axios wave-length dispersive X-ray fluorescence spectrometry (WD-XRF, 2.4 kV) at ETH Zurich after fusing the bulk rock powders to glass beads with Lithium-Tetraborate (ratio 1:5). Bulk rock trace element compositions were measured on glass beads with a laser-ablation micro-sampler coupled to an inductively coupled Elan 6000 plasma mass spectrometer (LA-ICP-MS). Boron and REE concentrations in ultramafic rocks were determined at the commercial Activation Laboratories Ltd. (Ancaster, Canada) by PGNAA Elemental Analyzer and by using its research quality Lithium Metaborate/Tetraborate Fusion ICP-MS method, respectively. Mineral REE compositions were measured on thin sections with a Resonetics Resolution 155 laser ablation system, coupled to a Thermo Element XR Sectorfield ICP-MS and using a diameter of 20–40 µm. Data reduction was performed using the Matlab-based code SILLS (Guillong et al., 2008).

3.3. Strontium Isotope Analyses

To prepare whole-rock powders of gabbros and ultramafic rocks for isotope analysis, rock samples were cut, separated from major calcite veins, crushed in a steel mortar, and ground in an agate mill. Strontium isotope analyses were performed on a Thermo Finnigan Neptune 53 MC-ICP-MS at ETH Zurich, after dissolution in a mixture of HF and HNO₃ according to ion exchange procedures developed by de Souza et al. (2010) and Deniel and Pin (2001). Because of the highly heterogeneous carbon content, the carbonate-rich green and red ophicalcites were decarbonized at least twice (to ensure complete carbonate removal) with 2M HCl prior to dissolution and the final residues were analyzed with a coulometer to determine if all carbonate had been dissolved (Vogel, 2016).

Calcite veins were micro-drilled to extract different vein generations and were dissolved with the following procedure: carbonate powders were dissolved in concentrated HCl, dried down, re-dissolved in concentrated HNO₃, dried down and diluted 150 times with 2% HNO₃ prior to analysis. The long-term average value for $^{87}\text{Sr}/^{86}\text{Sr}$ of the NBS987 standard measured during the period of analysis is 0.710243 with a 2σ standard deviation of 21 µg/g (N = 43). The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios were adjusted for mass bias by normalizing to a $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.1194 and are reported relative to the certified value of $^{87}\text{Sr}/^{86}\text{Sr}$ = 0.71024 for the NBS987 standard. In addition, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios have been corrected for their age by using the measured Rb/Sr to an average age of 160 Ma (Jurassic).
3.4. Stable Isotope Analyses

Hydrogen and oxygen isotope analyses of silicates were carried out on bulk rock powders of the serpentinites and green ophicalcites. Hydrogen isotope ($\delta^D$) compositions were analyzed using the high-temperature (1,400°C) reduction method with He as a carrier gas and a TC-EA (Flash1112HT, Thermo Fisher) interfaced to a Delta Plus XP IRMS at IGG-CNR, Pisa (Italy). Oxygen isotope values were determined on whole-rock powders after decarbonization of all the samples with 2M HCl (see Section 3.3). Measurements were conducted at the Institute of Earth Sciences at the University of Lausanne (Switzerland) using a CO$_2$ laser fluoration system coupled to a Finnigan MAT-253 mass spectrometer. Results are given in standard $\delta$-notation, expressed relative to the Vienna Standard Mean Ocean Water (V-SMOW) in permil ($‰$). Replicate hydrogen isotope analyses of internal standards give an average precision better than $±5‰$. Oxygen analyses were duplicated or triplicated and corrected to the LS-1 in house standard, which yielded an average value of 18.1 $±$ 0.6‰. However, typical precision for the standard analyses is $±0.2‰$. Higher errors during analysis were likely caused by oxidation during fluorination of the fine-grained powders, leading to higher background interferences.

Oxygen and carbon isotope analyses of micro-drilled calcite veins were analyzed on a GasBench II with a continuous-flow IRMS setup, after the method of Breitenbach and Bernasconi (2011). Isotope ratios are reported in permil ($‰$) using the conventional $\delta$-notation and with respect to the V-SMOW for oxygen and Vienna Pee Dee Belemnite (V-PDB) for carbon. Standard deviation was 0.05‰ for both $\delta^{13}C$ and $\delta^{18}O$.

4. Results

4.1. Sample Description

Macroscopic and microscopic investigation of the serpentinites, and green and red ophicalcites indicate a similar protolith but highly variable alteration characteristics. The serpentinites from the basement of the Bracco Unit are completely serpentinized harzburgites and clinopyroxene-poor lherzolites. The serpentinites and ophicalcites show a typical mesh texture with no relicts of primary minerals except for Cr-rich spinel, which is a common magmatic mineral in peridotites and is strongly altered, as well as rare diopsidic and partly serpentinized clinopyroxene that is also most likely of primary magmatic origin. The groundmass of the ophicalcites commonly contains talc and chlorite as microscopic intergrowths in the serpentine mesh and amphibole either around bastites that replace orthopyroxene or forming veins (Figure 2). Oxidation is observed in both green and red ophicalcites. In the green ophicalcites, oxidation of the serpentinite mesh texture initiates along calcite veins locally producing a reddish halo along the veins (Figure 2a). In contrast, the red ophicalcites show pervasive oxidation of the groundmass as defined by the high abundance of hematite (as determined by polarization microscopy) and/or other Fe-oxides and -hydroxides finely dispersed in the groundmass, which gives the intense red color (Figure 2b). Similarly, calcite veining is significantly more abundant in the red ophicalcites, where calcite veins mostly follow mm to cm wide fractures. In the red ophicalcites, numerous generations of calcite veins can be distinguished based on fabrics and crosscutting relationships (Figure 3): (1) Early calcite veins, in long planar fractures and locally including fragments of serpentine fibers; (2) Thinner ribbon calcite veins as bands of subparallel calcite veins that commonly show extensional structures; (3) Vein networks including jigsaw puzzle breccias, consisting of a disarray of calcite veinlets with complex geometry and a clear hydrofracture texture; (4) Breccias with pink/gray calcite-micrite matrix and serpentinite clasts; and (5) Late-stage calcite veins filling thick and branching irregular fractures. These latter veins cut across older features and reactivate older surfaces. Furthermore, late-stage calcite veins are associated with talc druses in the center of the veins, as previously reported in detail by B. Treves et al. (1995).

The Cava dei Marmi fault schists are strongly sheared, highly heterogeneous, and characterized by the abundance of talc, tremolite, and calcite. Serpentinite occurs as rare clasts and chlorite in pockets. Such assemblages are typical for metasomatic rocks observed in detachment fault zones on the seafloor and suggests an ocean floor setting (Boschi et al., 2006a, 2006b; Karson et al., 2006). However, tectonic reworking during the Alpine orogenesis cannot be excluded completely.

Mg-rich gabbros, sampled in the Bracco Pass and the Bonassola area, intrude the serpentinites in the Bracco Massif and commonly show medium- to coarse-grained porphyroblastic textures, consisting mainly of
clinopyroxene and plagioclase. High temperature shear zones are preserved within sections of undeformed gabbros. In the Bonassola area the effect of hydrothermal circulation in the gabbros is also apparent. Wide-spread fractures filled with Mg-hornblende (± plagioclase), which replaces the clinopyroxene, occur as parallel swarms crosscutting the high-T shear zones. For a detailed description of the gabbros, we refer to Molli (1995) and Tribuzio, Renna, et al. (2014).

4.2. Mineralogy and Mineral Chemistry

4.2.1. Serpentine, Talc and Chlorite

The texture and chemical composition of serpentine strongly depends on the primary mineral phases it replaces. Serpentine after olivine is the main phase forming the groundmass and commonly develops a mesh or ribbon texture. The meshes typically are formed by fibrous serpentine at the rims and very fine-grained, homogeneous, and locally isotropic serpentine in the mesh cores suggesting a dominance of lizardite and chrysotile. Orthopyroxene has been completely replaced by aggregates of fibrous serpentine minerals that retain the prismatic shape of the original orthopyroxene grains and form bastites. In some of the ophiolites, serpentine veins cut the mesh texture and were reactivated by calcite veining or vice versa (Figure 2g). No evidence of serpentine recrystallization was observed that would indicate a regional metamorphic

Figure 3. Rock slab of a red ophiolite from Cava dei Marmi showing (a) crosscutting relationships between different vein generations: (1) early calcite veins, (2) thinner ribbon veins, (3) vein networks with clear hydrofracture texture (hydrofracture veinlets), (4) micritic calcite matrix, and (5) late calcite veins (see text for more details). (b) Temperature variations (yellow ellipses) calculated from δ18Ocarb values of different micro-drilled veins.
overprint, which is consistent with maximum metamorphic conditions around prehnite-pumpellyite facies as constrained by Garuti et al. (2008).

The chemical variation of serpentine (serpentine mesh texture, bastite, and veins), chlorite, and talc from serpentinites, green and red ophicalcites is presented in Figure 4. In the serpentinites, only serpentine with compositions very close to lizardite was analyzed and no talc or chlorite was detected. In all samples (i.e., serpentinites, green and red ophicalcites), serpentine after olivine shows a large variation in Mg# (Mg/(Mg + Fe)) of 0.76–0.89, whereas bastites have a narrower range (0.81–0.93). Mesh cores have lower Mg# than mesh rims, indicating an enrichment in FeOtot from rim to core of the serpentine meshes with up to 9.8 wt.% FeOtot in mesh cores (with no magnetite present). Bastites have highly variable compositions within individual grains and show higher contents of Cr2O3 and Al2O3, and low contents of NiO compared to mesh serpentine, reflecting the primary orthopyroxene composition (see Table S2). Serpentine veins are generally poorer in FeOtot compared to groundmass serpentine.

Mineral assemblages with talc and chlorite were only detected and analyzed in the ophicalcites. In addition, mixing trends between serpentine and chlorite, and between serpentinite and talc suggest fine-grained mineral intergrowths on a submicrometer scale (Figure 4). Polarization microscopy indicates that talc occurs in pockets in the core of the serpentine mesh texture, as fine-grained rims around bastites, and intergrown within serpentinite in the bastites (Figures 2e and 2f). It is also present as fine intergrowths with amphibole and chlorite forming veins. In some red ophicalcites, coarse-grained talc-druses (up to 3 cm wide) occur in late-stage calcite veins (Figures 2b and 3). In the Cava dei Marmi fault schists that border the ophicalcites, talc occurs as fine-grained aggregates in pockets and, rarely, within the cores of serpentine meshes. Only analyses of talc veins (within calcite veins) from the red ophicalcite yielded pure talc analyses, whereas all other occurrences are fine serpentine-talc intergrowths. Chlorite forms either fan-shaped aggregates in the serpentinite groundmass, where it occurs with talc and amphibole as vein-like features, or replaces pyroxene...
in bastites (Figures 2g and 2h). In most cases, chlorite forms fine-grained intergrowths with serpentine (Figure 4). In addition, chlorite is associated with altered Cr-rich spinel in the serpentinites and ophicalcites.

4.2.2. Amphibole

Amphiboles are present mostly in the ophicalcites and in the Cava dei Marmi and Libiola fault schists. They are colorless, calcic in composition, and form needles and blades at the rim of bastites or partly replacing bastites. They are also found as veins and in pockets, or in the serpentine mesh texture as very fine intergrowths with serpentine, talc, and chlorite (Figures 2e and 2h). In the fault schists, amphiboles are present as veins or in pockets together with chlorite. Following the classifications of Leake et al. (1997), the amphiboles are mostly magnesio-hornblende with lesser tremolites (Figure 5) and show no clear distinction between occurrences in veins and the fault schists. However, the chemical compositions of the amphiboles that form rims around bastites and those that replace bastites are more variable and also include edenite compositions.

4.2.3. Calcite Veins

The ophicalcites have a complex network of multiple generations of veins, ranging in size from a mm-scale microscopic network that appears to hydrofracture the mesh texture, to macroscopic veins that are several centimeters thick and several meters in length. The veins are composed mainly of calcite as previously also determined by Schwarzenbach, Früh-Green, Bernasconi, Alt, and Plas (2013). No aragonite, Mg-calcite or dolomite were detected by XRD or microscopic observations, although B. E. Treves and Harper (1994) described calcite fibers and rosettes that may represent pseudomorphs of former aragonite crystals. Locally, calcite is present in the core of the serpentine meshes.

4.2.4. Minor Phases and Oxides

All magnetite is most likely of secondary origin associated with serpentinitization and carbonation. Very small magnetite grains and oxide needles are distributed homogeneously in the serpentinite mesh texture or form thick oxide bands at the rim of serpentine veins as observed by polarization microscopy. Magnetite also occurs locally as euhedral crystals in calcite and serpentine veins. Hematite, Fe-oxides and/or Fe-hydroxides give the noticeable red color in the red ophicalcites and occur along calcite veins in the green ophicalcites. In some cases, ghost-structures of hematite in calcite veins can be found, reflecting older serpentine mesh structures. Almost no magnetite could be observed in the bastites.

Cr-rich spinel is observed in all thin sections and shows incipient alteration to Fe-chromite ± chlorite along the edges. The composition of Cr-spinel varies strongly between the different samples: Cr₂O₃-contents range from 25.8 to 38.1 wt.%, MgO-contents are between 7.8 and 17.5 wt.% and Al₂O₃-contents are between 18.9 and 39.0 wt.%. Sulfide minerals are abundant in calcite veins and occur locally within the serpentine mesh. Sulfides include pentlandite, pyrrhotite, pyrite, millerite, siegenite and rare chalcopyrite, and are described in detail by Schwarzenbach, Früh-Green, Bernasconi, Alt, Shanks III, et al. (2012).

4.3. Bulk Rock Major and Trace Element Geochemistry

Bulk rock major element compositions of serpentinites and ophicalcites are plotted (on an anhydrous basis) in Figure 6 together with serpentinites and talc-ampibole schists from the AM (Boschi et al., 2006a) and fresh peridotites from the Internal Ligurian units (Mt. Fucisa; Rampone et al., 1996). The chemical composition of the serpentinites overlaps with the serpentinites from the AM and with the Internal Ligurian peridotites; however, our samples on average show high Fe₂O₃ and higher Al₂O₃ contents compared to the AM serpentinites. The gradual transition from serpentinite to ophicalcite from the Bracco Unit is highlighted by an increase in CaO (up to 6.4 wt.%), due to carbonate veining, and by an increase in SiO₂ and a decrease in MgO, due to the formation of amphibole/talc. A similar trend is found for the AM talc schists, especially with regard to SiO₂ and MgO contents.
Trace element patterns reveal typical enrichments in fluid mobile elements (FMEs) particularly Cs, Sr, and U (Figures 7a and S1). On average, Cs, Rb, and Sr are more enriched in the ophicalcites than in the basement serpentinites. Ba concentrations of basement serpentinites show both enrichment and depletion compared to the primitive mantle. The ophicalcites have intermediate Ba compositions. Overall, the serpentinites from the Bracco Unit overlap with the trace element patterns found in serpentinites from the AM. Metals (e.g., Cu, Zn) show similar concentrations in the serpentinites and ophicalcites.

Bulk rock REE patterns of the serpentinites and ophicalcites are characterized by variable LREE enrichments and a nearly flat pattern of the HREE (Figure 7b). The serpentinites and the ophicalcites mostly have overlapping bulk rock REE patterns. However, the ophicalcites have a smaller range of HREE.
Figure 7. (a) Spider diagram showing trace element variations of selected bulk rock serpentinites, ophicalcites, and Cava dei Marmi fault schists normalized to primitive mantle (after McDonough & Sun, 1995). Atlantis Massif serpentinites (light gray field) and metasomatic serpentinites (dark gray field) are shown for comparison (data from Boschi et al., 2006a). Noticeable are enrichments in Fluid Mobile Elements (FME) particularly Cs, U, and Sr. (b) Chondrite-normalized REE pattern (after Sun & McDonough, 1989) of selected bulk rock serpentinites, ophicalcites, and Cava dei Marmi fault schists. Peridotite REE compositions from Internal Liguride (IL) Units are plotted for comparison (Rampone et al., 1996). Serpentinites and ophicalcites have a relatively flat REE pattern and elevated LREE compositions compared to unaltered IL peridotites. (c) Chondrite-normalized REE concentration patterns (after Sun & McDonough, 1989) determined in situ on minerals from ophicalcites and fault schists. Orthopyroxenes (Opx) and clinopyroxenes (Cpx) of the Internal Liguride Peridotites (IL) from fresh clinopyroxene-poor lherzolites are plotted for comparison (Rampone et al., 1996).
concentrations than the serpentinites and tend to have lower average LREE concentrations. In comparison to the peridotites from the Internal Liguride Units (Rampone et al., 1996), the studied serpentinites and ophicalcites are enriched in LREE.

In situ mineral analyses of the mesh serpentine and bastite minerals yielded different REE patterns than the serpentinite bulk rock analyses (Figure 7c). They are characterized by highly variable and depleted LREE compositions and a nearly flat pattern for the HREE. Both groundmass serpentine and bastites display slight positive Eu anomalies, but variable (positive and negative) Ce anomalies. Some of the bastites have slightly higher REE compositions than the serpentine groundmass and reflect the precursor pyroxene: LREE depletion, and a flat HREE pattern. One analysis of clinopyroxene yielded elevated REE compositions compared to the bastites and serpentines.

4.4. Isotope Compositions

4.4.1. Bulk Rock Isotope Systematics

The δ18O values of the serpentinites and ophicalcites in the Bracco Unit range between 6.2 and 7.5‰. The Cava dei Marmi fault schists—dominated by talc and tremolite—have the highest value with 14.7‰. The serpentinites and Libiola fault schists from the Val Graveglia Unit yield δ18O values of 8.6 and 5.1‰, respectively (Table 1).

The average δD values of the ophicalcites is slightly higher (δD = −68 ± 6‰) than the serpentinites (δD = −74 ± 6‰), whereas the Cava dei Marmi fault schists have values of δD = −75 and −59‰. With the exception of the Libiola fault schist that has a δD value of −40‰, the serpentinites from the Val Graveglia Unit are similar to the Bracco Unit with an average δD value of −76 ± 2‰ (Table 1).

In addition to the serpentinites and ophicalcites, gabbros from the Bracco unit were analyzed for their Sr isotope composition. Overall, the studied samples have a large range in 87Sr/86Sr ratios (Figure 8). The gabbros have the lowest 87Sr/86Sr ratios and range from 0.70295 to 0.70457; these values are close to depleted MORB mantle compositions (0.7025; Rehkämper & Hofmann, 1997) but also show moderate exchange with seawater-derived hydrothermal fluids. The (decarbonated) ophicalcites and the Cava dei Marmi fault schists have similar 87Sr/86Sr ratios and display values between the gabbros and Jurassic seawater (0.7068–0.7070 for 165–160 Ma; Wierzbowski et al., 2017). The micro-drilled carbonate veins have a range in 87Sr/86Sr ratios of 0.70503–0.70718, which are mostly lower than Jurassic seawater compositions but on average higher than the ophicalcites. Remarkable is the fact that the Bracco serpentinites have 87Sr/86Sr ratios ranging from 0.70337 to 0.70857, whereby most serpentinites display 87Sr/86Sr ratios higher than Jurassic seawater. The 87Sr/86Sr ratios of the Val Graveglia serpentinites are comparably high with values of 0.70703–0.70864, and the Libiola fault schist has the highest value of 0.71400.

4.4.2. Carbon and Oxygen Isotope Systematics of Calcite Veins

The carbonate veins have δ13C values of 1.1–3.0‰ (V-PDB) (Figure 9a). The δ18O values range from 15.4 to 24.6‰ (V-SMOW) and record variations in precipitation temperatures (Figures 3 and 9b, Table S4). Calcite precipitation temperatures were calculated using the calcite-water fractionation equation of Friedman and O’Neil (1977) assuming an initial seawater composition of δ18O = −1‰ for an ice-free Earth. This yields an overall trend of decreasing temperature from 108°C in the early and ribbon calcite veins to 41°C in the late stage calcite veins. These temperatures agree with results of Schwarzenbach, Früh-Green, Bernasconi, Alt, & Plas (2013) that showed a decrease with age from 151°C to 49°C. This trend is associated with early calcite veins with the lowest δ13C values (≈1‰) and 87Sr/86Sr ratios close to seawater composition, and late calcite veins with δ13C values of 2–3‰ and lower 87Sr/86Sr ratios (Figure 9a).

5. Discussion

5.1. Alteration History Based on Microstructures

The mineralogical and geochemical characteristics of the studied serpentinites indicate a multiphase alteration process with infiltration of fluids along passive tension fractures and locally focused along fault zones. The chemical zoning of the mesh-texture serpentine after olivine (i.e., Fe-poor rim vs. Fe-rich core)
| Sample | Rock type | Location | Coordinates | Sr (μg/g) | δ²⁰Sr/⁶⁰Sr | 2 Standard error | δD | δ¹⁸O (‰, V-SMOW) | % stdv |
|--------|-----------|----------|-------------|-----------|-------------|----------------|-----|----------------|--------|
| LBR5   | Serpentinite | Bonassola outcrop (close to Rodingite) | 44°10′32″ 09°35′08″ | 19 | 0.703370 | 0.000039 |      |                |        |
| LCA4   | Serpentinite | Carro old mining site | 44°16′41″ 09°35′26″ | 4 |           | −74 |      |                |        |
| LCA5   | Serpentinite | Carro old mining site | 44°16′41″ 09°35′26″ | 5 |           | −71 |      |                |        |
| LCA6A  | Serpentinite | Carro old mining site | 44°16′41″ 09°35′26″ | 6 |           | −68 |      |                |        |
| LCA7   | Serpentinite | Carro old mining site | 44°16′41″ 09°35′26″ | 5 |           | −67 |      |                |        |
| LCG10  | Serpentinite | Cava Galli | 44°10′28″ 09°36′22″ | 6 | 0.708481 | 0.000022 | −73 |      |        |
| LCG11  | Serpentinite | Cava Galli | 44°10′28″ 09°36′22″ | 7 | 0.708154 | 0.000026 | −67 | 7.3 | 0.2 |
| LCG9   | Serpentinite | Cava Galli | 44°10′28″ 09°36′22″ | 7 |           | −72 |      |                |        |
| LCM18  | Serpentinite | Cava dei Marmi | 44°11′51″ 09°35′20″ | 8 | 0.707849 | 0.000025 | −77 |      |        |
| LCM21  | Serpentinite | Cava dei Marmi | 44°11′51″ 09°35′20″ | 6 | 0.707867 | 0.000026 | −86 |      |        |
| LCP12  | Serpentinite | Cava Piazza | 44°13′52″ 09°32′59″ | 9 | 0.708154 | 0.000026 |      |                |        |
| LPM1   | Serpentinite | Punta dei Marmi | 44°11′53″ 09°33′39″ | 11 | 0.703510 | 0.000022 |      |                |        |
| LSP10  | Serpentinite | Along road cut on SS332 | 44°13′06″ 09°35′16″ | 9 | 0.708578 | 0.000026 | −78 | 7.5 | 0.5 |
| LSP11  | Serpentinite | Along road cut on SS332 | 44°13′45″ 09°35′21″ | 15 | 0.709740 | 0.000016 | −81 |      |        |
| LSP12  | Serpentinite | Along road cut on SS332 | 44°13′45″ 09°35′21″ | 11 |           | −81 |      |                |        |
| LSP3   | Serpentinite | Along road cut on SS332 | 44°12′35″ 09°35′26″ | 11 | 0.706650 | 0.000044 | −68 |      |        |
| LA1    | Green ophicalcite | Cava dei Marmi | 44°11′51″ 09°35′20″ | 27 | 0.705589 | 0.000022 |      |                |        |
| LA3a   | Green ophicalcite | Cava dei Marmi | 44°11′51″ 09°35′20″ |           | −71 |      |                |        |
| LA9a   | Green ophicalcite | Cava dei Marmi | 44°11′51″ 09°35′20″ | 44 | 0.705456 | 0.000028 | −74 | 7.0 | 0.1 |
| LA12a  | Green ophicalcite | Cava dei Marmi | 44°11′51″ 09°35′20″ | 13 | 0.705732 | 0.000036 | −63 | 6.2 | 0.3 |
| LA14a  | Green ophicalcite | Cava dei Marmi | 44°11′51″ 09°35′20″ |           | −65 |      |                |        |
| LA15a  | Green ophicalcite | Cava dei Marmi | 44°11′51″ 09°35′20″ |           | −77 |      |                |        |
| LA16a  | Green ophicalcite | Cava dei Marmi | 44°11′51″ 09°35′20″ | 17 | 0.705129 | 0.000031 | −67 |      |        |
| LCG3   | Green ophicalcite | Cava Galli | 44°10′28″ 09°36′22″ | 11 | 0.705770 | 0.000027 | −63 |      |        |
| LCM6   | Cava dei Marmi fault schist (Serp-Talc-Trem Schist) | Cava dei Marmi | 44°11′51″ 09°35′20″ | 114 | 0.705501 | 0.000034 | −59 |      |        |
| LCM7   | Cava dei Marmi fault schist (Serp-Talc Schist) | Cava dei Marmi | 44°11′51″ 09°35′20″ | 28 | 0.705779 | 0.000036 | −75 | 14.8 | 0.3 |
| LCM2   | Red ophicalcite | Cava dei Marmi | 44°11′51″ 09°35′20″ | 22 | 0.705419 | 0.000016 |      |                |        |
| LCM3   | Red ophicalcite | Cava dei Marmi | 44°11′51″ 09°35′20″ | 14 | 0.704896 | 0.000033 |      |                |        |
| LCG4   | Red ophicalcite | Cava Galli | 44°10′28″ 09°36′22″ | 12 | 0.705753 | 0.000016 |      |                |        |
| LCG5   | Red ophicalcite | Cava Galli | 44°10′28″ 09°36′22″ | 11 | 0.705995 | 0.000030 |      |                |        |
| G61b   | Banded metagabbro | Bracco Pass | n.r. | 222 | 0.703355 | 0.000028 |      |                |        |
| G28b   | Banded metagabbro | Bracco Pass | n.r. | 204 | 0.703789 | 0.000023 |      |                |        |
| G29b   | Banded metagabbro | Bracco Pass | n.r. | 185 | 0.702956 | 0.000027 |      |                |        |
| GC2b   | Gabbro | Bracco Pass | n.r. | 249 | 0.704079 | 0.000022 |      |                |        |
| G22b   | Gabbro | Bracco Pass | n.r. | 253 | 0.703995 | 0.000021 |      |                |        |
| LCC2   | Gabbro | Castagnola | 44°13′51″ 09°34′57″ | 201 | 0.704574 | 0.000039 |      |                |        |
| LCC5   | Gabbro | Castagnola | 44°13′51″ 09°34′57″ | 190 | 0.704509 | 0.000039 |      |                |        |
| GC1b   | Gabbro | Bracco Pass | n.r. | 279 | 0.704246 | 0.000021 |      |                |        |
reflects the multistage process of serpentinization. A first stage of alteration likely resulted in the formation of Fe-rich brucite (as an intermediate phase and not preserved) and Fe-poor serpentine, which was followed by increasing H₂O- and Si-activities that resulted in progressive dissolution and replacement of olivine and Fe-rich brucite by Fe-poor serpentine and magnetite forming the magnetite-bearing veins (e.g., Beard et al., 2009; Boschi, Dini, Baneschi, et al., 2017; Schwarzenbach, Caddick, et al., 2016). A later stage of alteration is indicated by relict olivine in the core of the meshes replaced by Fe-rich serpentine, which suggests that Si-activities increased to the point where brucite and magnetite were unstable (e.g., Früh-Green et al., 2004; Grozeva et al., 2017; Klein et al., 2014; Mayhew & Ellison, 2020). This interpretation is supported by local occurrences of talc in the mesh cores as well as fine-grained serpentine-talc intergrowths in the mesh texture (Figure 4). In addition to serpentinization and extensive carbonation, variations in bulk rock chemistry associated with talc, chlorite, and amphibole with highly variable compositions (Figure 6) indicate variations in fluid/rock ratios and/or fluid compositions and temperatures during progressive rock alteration (Malvoisin, 2015). Secondary amphibole and/or talc rims around bastites have been described in many oceanic serpentinites and their origins are commonly linked to early stages of mantle hydration associated with the interaction of peridotites with hydrothermal fluids during mantle upwelling (e.g., Agrinier & Girardeau, 1988; Früh-Green et al., 1996). However, in the N. Apennine serpentinites, the amphibole veins and patches cutting the serpentine mesh texture, and amphibole of hornblende to edenite composition replace bastites, which document a later stage of localized fluid infiltration likely at amphibolite-facies conditions (e.g., Schmidt, 1992). Calcite veins and talc druses filling preexisting calcite veins in the opal-calcites document the final stages of serpentine/opal-calcite alteration, whereby the abundance of talc points to late stage Si-metasomatism. These observations indicate that multiple phases of fluid-rock interaction with different fluid sources at varying temperatures have affected the N. Apennine serpentinites and opal-calcites during their hydrothermal evolution.

| Sample | Rock type | Location | Coordinates | Sr (µg/g) | 87Sr/86Sr | δ²⁰⁰O (‰, V-SMOW) | δD | Sr n.d. | Sr stdv |
|--------|-----------|----------|-------------|----------|-----------|-------------------|----|---------|--------|
| LPB6   | Mylonitic metagabbro | Bracco Pass | n.r. | 266 | 0.703507 | 0.000039 |
| LBR13  | Mylonitic metagabbro | Bonassola | 44°10′49″ 09°35′04″ | 219 | 0.703370 | 0.000039 |
| LBR11  | Mylonitic metagabbro | Bonassola | 44°10′49″ 09°35′04″ | 185 | 0.703470 | 0.000039 |
| G18a   | Porphyroclastic metagabbro mylonites | Bracco Pass | n.r. | 185 | 0.703551 | 0.000024 |
| G19a   | Porphyroclastic metagabbro mylonites | Bracco Pass | n.r. | 225 | 0.703907 | 0.000022 |
| G7a    | Porphyroclastic metagabbro mylonites | Bracco Pass | n.r. | 231 | 0.702990 | 0.000022 |
| GC11a  | Porphyroclastic metagabbro mylonites | Bracco Pass | n.r. | 286 | 0.704215 | 0.000022 |

Val Graveglia Unit

| Sample | Rock type | Location | Coordinates | Sr (µg/g) | 87Sr/86Sr | δ²⁰⁰O (‰, V-SMOW) | δD | Sr n.d. | Sr stdv |
|--------|-----------|----------|-------------|----------|-----------|-------------------|----|---------|--------|
| LLB16  | Serpentinite | Libiola old mining site | 44°18′13″ 09°26′58″ | 8 | 0.707505 | −78 |
| LLB17  | Serpentinite | Libiola old mining site | 44°18′13″ 09°26′58″ | 7 | 0.707566 | −78 | 8 | 1.1 |
| LLB28  | Serpentinite | Libiola old mining site | 44°18′13″ 09°26′58″ | 10 | 0.708464 | −74 |
| LLB27  | Serpentinite | Libiola old mining site | 44°18′13″ 09°26′58″ | 7 | 0.707322 | 0.00002 |
| LLB18  | Libiola fault schist (mostly Trem) | Libiola old mining site | 44°18′13″ 09°26′58″ | 10 | −40 | 5.1 | 0.8 |
| LLB19  | Libiola fault schist (mostly Trem) | Libiola old mining site | 44°18′13″ 09°26′58″ | 9 | 0.714003 | 0.000035 |

Note. Reported Sr. n.r. = not reported; n.d. = not determined.

bSamples from Schwarzenbach, Früh-Green, Bernasconi, Alt, Shanks III, et al., 2012, 2013, analyzed for this study.
bSamples collected by Molli (1995) and analyzed for this study.
Trace and rare Earth element patterns as well as stable and radiogenic isotope signatures provide ideal tracers for fluid sources and fluid-rock interaction processes. Importantly, major and trace element concentrations in peridotites are also modified by melting and refertilization by melt-rock interaction (Niu, 2004; Paulick et al., 2006). In the following, we first discuss the REE patterns to account for possible melt-rock interaction that could have taken place before, during or after hydrothermal alteration and then combine these observations with isotope signatures to constrain the hydrothermal alteration history and the impact of different fluid sources during serpentinization, carbonation and Si-metasomatism.

5.2. Distinguishing Melt-Rock and Fluid-Rock Interaction Processes

Melt impregnation and melting processes are typically reflected by the addition of SiO₂, REE, and HFSE (e.g., Nb, Ta, Zr, Hf). Melt-rock interaction causes addition of LREE and HFSE to the rock in about equal proportions, whereas interaction with aqueous solutions leads to a more distinct enrichment in LREE than in HREE and HFSE (Paulick et al., 2006). In the Bracco Unit, the chondrite-normalized REE patterns of the ophicalcites are similar to the basement serpentinites (Figure 7b). HREE (Gd-Lu) patterns are rather flat in both serpentinites and ophicalcites, whereas the LREE (La-Eu) contents are more variable and enriched compared to the unaltered peridotites of the Internal Ligurian units (Rampone et al., 1996). Interestingly, the in situ analyses of the minerals show no LREE enrichment in the serpentinites nor the ophicalcites (Figure 7c).

LREE enrichment in serpentinites compared to unaltered peridotites has been broadly documented in mid-ocean ridge serpentinites and has been associated with the mobility and incorporation of LREE in serpentinites during hydrothermal processes (Niu, 2004; Paulick et al., 2006). Records of hydrothermal processes are preserved in both the serpentinite minerals and some ophicalcite bulk rocks that display negative Ce anomalies in the REE patterns (Figure 7b) and have been linked to the presence of seawater-derived fluids or the oxidation of Fe³⁺ during serpentinization (Niu, 2004). However, some researchers (Bodinier & Godard, 2003; Boschi et al., 2006a) suggest that the LREE enrichment observed in ophiolitic and oceanic harzburgites may result from the infiltration of small volumes of evolved, LREE-enriched melts that precipitate minute amounts of barely detectable LREE-rich mineral phases. Because the in situ REE analyses of the serpentinite minerals in the N. Apennine sequences show strong LREE depletions, we infer that a small-scale, "cryptic" melt impregnation may have occurred before serpentinization began, and any LREE-enriched phase that contributes to the LREE-enriched bulk rock pattern was not measured by the in situ analyses of the major mineral phases.
5.3. Fluid Sources During Serpentinization and Carbonation

Seawater is the primary fluid source in peridotite-hosted hydrothermal systems, as is reflected by seawater-like $^{87}$Sr/$^{86}$Sr values found in serpentinites and their carbonate veins, such as from the Atlantic Ocean (e.g., Delacour et al., 2008; Vils et al., 2009). In the N. Apennine ophiolite, geochemical evidence for seawater-infiltration is documented in the carbon isotope compositions (see also Schwarzenbach, Früh-Green, Bernasconi, Alt, & Plas, 2013) and the $^{87}$Sr/$^{86}$Sr values of some micro-drilled carbonate veins (Figure 9a). The early calcite veins have $^{87}$Sr/$^{86}$Sr ratios of 0.70661–0.70718 and $\delta^{13}$C values around 1‰, both reflecting average mid- to late Jurassic seawater compositions ($^{87}$Sr/$^{86}$Sr $\approx$ 0.7068–0.7070, $\delta^{13}$C $\approx$ 1‰, respectively) (Veizer et al., 1999; Wierzbowski et al., 2017). The effects of seawater infiltration within the serpentinites and ophiolites are further documented by the enrichment of FMEs with distinct positive anomalies in Cs, U, and Sr (Figure 7a). These enrichments are typical for seafloor-exposed serpentinites (Deschamps et al., 2012; Peters et al., 2017) and indicate infiltration of seawater-derived fluids during the main stages of serpentinization. The N. Apennine ophiolites show stronger enrichments in Cs, Sr, and Rb (and variable enrichments in U) (see Figure S1) suggesting overall higher fluid-rock ratios during formation of the ophiolites compared to the serpentinites.

Oxygen and hydrogen isotope compositions provide further constraints on fluid sources, water-rock ratios, and temperatures during water-rock interaction (e.g., Früh-Green et al., 1996; Sakai et al., 1990). Previous studies have suggested that fluid-rock interaction in the N. Apennine serpentinites took place at $\sim$150°C–240°C based on bulk rock $\delta^{18}$O values of 6.7–9.9‰ and assuming interaction with Jurassic seawater (Schwarzenbach, Früh-Green, Bernasconi, Alt, & Plas, 2013). The $\delta^{18}$OWR values of the samples studied here are within a slightly larger range (5.1–14.8‰; Table 1), but overall suggest a similar temperature range of 180°C–280°C depending on which fractionation factor is used (see Figure S2). Comparison to available $\delta$D and $\delta^{18}$O data from mid-ocean ridge serpentinites shows considerable overlap (Figure 10a). The range in $\delta^{18}$O data mostly reflects variable serpentinization temperatures and variable water-rock ratios, with $\delta^{18}$O values $>5.5$‰ (i.e., mantle values) generally suggesting temperature $<250$°C and $\delta^{18}$O values $<5.5$‰ indicating higher temperatures (e.g., Alt, Shanks, et al., 2007; Barnes, Paulick, et al., 2009; Boschi, Bonatti, et al., 2013; Früh-Green et al., 1996; Sakai et al., 1990; Wenner & Taylor, 1973). In addition, the range in $\delta$D values of $-86$ to $-59$‰ determined in our study provide further evidence that most serpentinites studied to date have strongly negative $\delta$D values (Figure 10a). The origin of these negative $\delta$D values is still controversial. A common interpretation is that they require interaction with either evolved seawater-derived and/or magmatic waters, which are characterized by negative $\delta$D values (Früh-Green et al., 1996; Shanks et al., 1995; Wenner & Taylor, 1973). Alternatively, Früh-Green et al. (1996) proposed that the negative $\delta$D values are correlated to the formation of considerable amounts of H$_2$ due to oxidation of ferrous iron in olivine ± pyroxene. Finally, negative $\delta$D values in ophiolites potentially also derive from interaction with meteoric waters, which could have interacted with the serpentinites subsequent to their emplacement on the continent. This has previously been inferred based on highly variable $\delta$D values that correlated with mineral textures (Kyser et al., 1999). In this case, the $\delta$D values are lowered to more negative values commonly reaching $\delta$D values of $-100$‰ and lower (Barnes, Selverstone, & Sharp, 2006; Kyser et al., 1999). In the N. Apennine samples, the $\delta$D values have a relatively narrow range, which overlaps considerably with
...fluids affected the ophicalcites. Serpentinites display higher percentages for Sr, indicating mixing proportions between gabbro by altered seawater and assumed to have similar compositions as the serpentinite end-member and a gabbro-derived fluid, formed lines represent simple fluid-rock interaction trajectories, indicating mixing by two possible mechanisms: 1) seawater mixing with fluids generated from peridotite or gabbro alteration at depth, which resulted either in pervasive talc alteration in the peridotites (Paulick et al., 2006) or by localized influx of oxidizing, Si-Al-Ca-rich fluids produced talc, amphibole, and chloride schists along fault zones (e.g., at the AM; Boschi et al., 2006a, 2006b). Accordingly, we suggest that in the rocks studied here, Si-metasomatism could have been caused by two possible mechanisms: 1) seawater mixing with fluids generated from the serpentinitization of peridotites, specifically pyroxenes, at increasing water-rock ratios or 2) interaction with fluids with a component derived from a mafic source. Both processes have been thermodynamically modeled by Malvoisin (2015) and resulted in formation of talc co-existing with either serpentine or carbonate. Considering the amount of talc precipitated as druses in the ophicalcites and the shift to higher SiO₂ bulk content from the basement serpentinites to the ophicalcites, and affected both bulk serpentinites and ophicalcites in about equal proportions (Früh-Green et al., 1996; Shanks et al., 1995).

Figure 10. Geochemical models of interacting fluids. (a) δ⁸⁷Sr/⁸⁶Sr vs. 1/Sr for bulk rock samples. Dotted gray lines represent simple fluid-rock interaction trajectories, indicating mixing between a serpentinite end-member and a gabbro-derived fluid, formed by altered seawater and assumed to have similar compositions as the analyzed gabbros. Percentages indicate mixing proportions between gabbro and serpentinite. Ophicalcites plot within the mixing trends, suggesting mafic-derived fluids affected the ophicalcites. Serpentinites display higher δ⁸⁷Sr/⁸⁶Sr compositions than Jurassic seawater, suggesting the influence of fluids with more radiogenic Sr. Jurassic seawater and mantle as in Figure 8.

5.4. Silica Metasomatism

The abundance of talc (macroscopically seen in Figures 2b and 3) and amphibole in the ophicalcites as well as serpentine-talc intergrowths in the serpentinite mesh textures (Figure 4) document an increase in SiO₂ bulk content from the basement serpentinites to the ophicalcites, and suggests localized Si-metasomatism. Si-metasomatism in the ophicalcites is also expressed by lower MgO/SiO₂ ratios (Figure 6) compared to the basement serpentinites, as is seen in a plot of MgO/SiO₂ vs. Al₂O₃/SiO₂ (Figure 11), where the terrestrial array is defined by the successive magmatic depletion of a primitive mantle during partial melting (Hart & Zindler, 1986; Jagoutz et al., 1979). An off-set to lower MgO/SiO₂ values in most abyssal serpentinites has previously been related to partial MgO loss during seafloor weathering through brucite dissolution and incongruent olivine dissolution (Niu, 2004; Paulick et al., 2006; Snow & Dick, 1995). However, the macroscopic abundance of talc in the Bracco ophicalcites leads us to infer that the lower MgO/SiO₂ ratios are more likely the result of Si addition rather than extensive Mg loss (Malvoisin, 2015).

Si-metasomatism and/or talc formation have previously been documented in peridotites from the MAR, including ODP Leg 209 near the 15°20’N fracture zone (Paulick et al., 2006) and the AM (Boschi et al., 2006a, 2006b). In both cases, alteration is associated with the input of fluids derived from peridotite or gabbro alteration at depth, which resulted either in pervasive talc alteration in the peridotites (Paulick et al., 2006) or by localized influx of oxidizing, Si-Al-Ca-rich fluids produced talc, amphibole, and chloride schists along fault zones (e.g., at the AM; Boschi et al., 2006a; Boschi et al., 2006b). Accordingly, we suggest that in the rocks studied here, Si-metasomatism could have been caused by two possible mechanisms: 1) seawater mixing with fluids generated from the serpentinitization of peridotites, specifically pyroxenes, at increasing water-rock ratios or 2) interaction with fluids with a component derived from a mafic source. Both processes have been thermodynamically modeled by Malvoisin (2015) and resulted in formation of talc co-existing with either serpentine or carbonate. Considering the amount of talc precipitated as druses in the ophicalcites and the shift to higher SiO₂ bulk rock contents in most ophicalcites, we tend toward an externally derived fluid to account for the late stage Si-metasomatism.
Higher enrichments in Sr, Rb, and Cs in the ophicalcites provide further evidence for a mafic source of the fluid, such as gabbroic intrusions or basaltic lavas (von Damm, 1990) (Figure 7a). Interestingly, Ba, which is considered to be highly mobile in high-temperature fluids and can be enriched in fluids derived from young gabbroic intrusions, is not markedly enriched. In addition, there is a lack of metal enrichments (e.g., Cu or Zn), which is also typical for high-temperature fluid-rock interaction (e.g., Niu, 2004; von Damm, 1990). This would suggest that the fluids that produced the Si-metasomatism in the ophicalcites were dominantly lower temperature fluids and hence, would not have affected Ba and metal concentrations. Additional evidence for mafic-derived fluids is provided by the Sr isotope signatures. The final formation of talc filling druses within pre-existing carbonate veins in the ophicalcites (Figure 3) correlates with an increase in the $^{87}$Sr/$^{86}$Sr ratios from seawater-like compositions in the early calcite veins toward mantle or MORB-like $^{87}$Sr/$^{86}$Sr ratios in the later stage carbonate veins (Figure 9c). In addition, we calculated simple isotope mixing trajectories between serpentinites and mafic-derived end-member fluids (Figure 10b). For this we used different Sr concentrations for the serpentine ($4–15 \mu g/g$), the highest serpentinite compositions ($^{87}$Sr/$^{86}$Sr = 0.7085) and the average of the analyzed gabbroic rocks ($^{87}$Sr/$^{86}$Sr = 0.7037), which is assumed to approximate the composition of the mafic-derived fluids. All the ophicalcites and Cava dei Marmi fault schists indicate variable proportions of mixing between the two end-members. Similarly, most late calcite veins have $^{87}$Sr/$^{86}$Sr ratios between those of Jurassic seawater and the gabros (Figures 9 and 10b). We infer that the trend to lower $^{87}$Sr/$^{86}$Sr ratios reflect increasing influx of mafic-derived fluids with ongoing rock fracturing associated with more pronounced Si-influx in the ophicalcites than the underlying serpentinites. Associated $\delta^{13}$C-values of 2–3‰ overlap with values from carbonate vent samples, breccias, and carbonate infillings of the LCHF and are attributed to the input of $^{13}$C-enriched carbon associated with ongoing microbial activity (e.g., methanogenesis) (Früh-Green et al., 2003). An abundance of methanogenesis agrees with the decreasing temperatures preserved in the $\delta^{18}$O values (Figure 9b), which increasingly favors microbial activity. Alternatively, they may be the result of closed system fluid evolution of the dissolved inorganic carbon during water-rock interaction with the mafic lithologies.

The Cava dei Marmi fault schist that displays a high $\delta^{18}$O value yielded low $^{87}$Sr/$^{86}$Sr ratios (Figure 10b), which are in the same range as the ophicalcites, suggesting that these fault schists and the ophicalcites were altered by the same or compositionally similar fluids. In contrast, the Libiola fault schist is characterized by elevated $^{87}$Sr/$^{86}$Sr ratios (up to 0.71847), and based on the oxygen composition, has the highest formation temperatures (lowest $\delta^{18}$O value). Such compositions may imply that a sedimentary influx took effect during hydrothermal alteration on the ocean floor or that the schists may have been reactivated during Alpine orogenesis.

### 5.5. Evidence for Fluid Input From Continental Basement Rocks

Interestingly, most of the serpentinites have higher $^{87}$Sr/$^{86}$Sr values than Jurassic seawater (Figure 8), which varied between 0.7068 and 0.7072 in the Middle to Late Jurassic (Wierzbowski et al., 2017), whereas $^{87}$Sr/$^{86}$Sr values above 0.7078 were only reached at ~74 Ma (Jones et al., 1994). $^{87}$Sr/$^{86}$Sr values above seawater compositions have also been documented in some serpentinites from the MAR (e.g., Mével, 2003; Snow et al., 1993) suggesting a $^{87}$Sr reservoir during hydrothermal circulation. Snow et al. (1993) argue that high $^{87}$Sr/$^{86}$Sr ratios could be generated by infiltration of detrital sediments penetrated through micro-cracks into serpentinites. This process is not directly related to serpentization but can considerably alter the $^{87}$Sr/$^{86}$Sr compositions of abyssal serpentinites (Mével, 2003). Thus, one possibility would be that interaction of fluids with the sedimentary Framura Breccia overlying the ophicalcites could have had an effect on the serpentinites. However, the ophicalcites, which are underlying the sedimentary Framura Breccia and overlying the...
serpentinites, do not show this more radiogenic Sr enrichment. Alternatively, continental basement rocks have high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (>0.720 to 0.750; Allègre, 2008) similar to sedimentary rocks and, thus, fluids that interacted with continental basement could have modified the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the serpentinites. Recent models suggest that continental basement was likely present during initial stages of rifting and opening of the Piemont-Ligurian ocean, where subcontinental mantle was sporadically exposed to seawater in a narrow ocean basin (Le Breton et al., 2021). Similarly, felsic continental crust associated with subcontinental mantle in the N. Apennines have been interpreted as evidence for the early stages of continental breakup and opening of the oceanic basement within an OCT (Marroni et al., 1998) and have been compared to observations from the Iberia-Newfoundland margins where tilted continental basement blocks and oceanic crust periodically occur over a distance of 150 km within the OCT (McCarthy et al., 2018; Whitmarsh et al., 2001). Such a setting would allow infiltration of fluids that had interacted with continental basement rocks during initial stages of peridotite hydration, shifting the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the serpentinites to higher values. This interpretation, however, assumes that the early continental Sr isotope signatures are preserved throughout the hydrothermal evolution of the system. Alternatively, we would have to envisage exchange with continental rocks and preferential fluid circulation solely in the serpentinites during the Alpine orogeny, for which we have no further evidence.

6. Hydrothermal Evolution of the Northern Apennine Ophiolite

The data presented above suggest a complex alteration history and indicate that the serpentinites were dominated by different fluids than the overlying ophicalcites, but all record multiple phases of water-rock interaction, some of which result in pervasive alteration whereas other events were more localized (e.g., forming distinct veins). Using our new data with previously published interpretations, we reconstruct the temporal and chemical evolution of the studied rocks and infer the alteration history of the N. Apennine ophiolite sequence.

The formation of tremolite to hornblende rims around pyroxene suggests that the peridotites of the N. Apennine were initially hydrated at relatively high temperatures likely during initial mantle upwelling. These stages of mantle hydration as well as continuous mantle exhumation were affected by fluids that had reacted with either the continental basement or with sediments prior to peridotite infiltration (Figure 12—stage 1). Since continental basement rocks and sedimentary sequences have considerably more radiogenic Sr compared to peridotites, even low amounts of fluid that had interacted with basement rocks or sediments would have substantially shifted the $^{87}\text{Sr}/^{86}\text{Sr}$ values of the serpentinized peridotites to higher values. The serpentinites from the Bracco and the Val Graveglia Units both show the same trends further supporting wide-spread and relatively pervasive fluid infiltration with a more radiogenic Sr signature. Seawater influx was overall relatively restricted as suggested by the lesser enrichment of FMEs such as Cs, Rb, Sr, U in the serpentinites compared to the ophicalcites. Based on the flat REE patterns of the peridotites cryptic melt impregnation likely also affected these rocks.

Serpentinization was also associated with the local influx of higher temperature fluids. This is documented by the formation of edenite and Mg-hornblende, indicating amphibolite-facies conditions, that form veins together with chlorite or replace bastites. In addition, high-temperature fluid influx is recorded by sulfur isotope signatures. Using in situ $\delta^{34}\text{S}$ values in sulfide minerals and bulk rock multiple sulfur isotope signatures, Schwarzenbach, Gill, and Johnston (2018) document the impact of thermochemical sulfate reduction, which took place at $\sim$350°C–400°C and was associated with input of $\text{H}_2\text{S}$ leached from mafic rocks. This stage of alteration likely took place during continuous uplift of the peridotites during the main stage of serpentinization as some of the amphibole-chlorite-veins cut the serpentine mesh texture. Gabброic intrusions most likely provided the heat for high-T fluid circulation (Figure 12—stage 2). At a similar time, the Cava dei Marmi fault schists likely formed within fault zones during peridotite exposure, similar to the processes described at the AM (e.g., Boschi et al., 2006a; Früh-Green et al., 2018; Rouméjon et al., 2018).

By continuous uplift of the peridotites, these rocks were exhumed to the seafloor where serpentinization fluids mixed with seawater in cracks and fractures producing carbonate veins in the serpentinites and ophicalcites (Figure 12—stage 3). These veins document temperatures decreasing from 150°C to 41°C with increasing seawater influx (this study and Schwarzenbach, Früh-Green, Bernasconi, Alt, & Plas, 2013). As
the system cooled, microbial activity took place as documented by sulfur isotope compositions in sulfide minerals (Schwarzenbach, Gill, & Johnston, 2018) and the δ13C values of the carbonates that point to methanogenesis. At this stage the highly oxidized ophicalcites would have been directly exposed to seawater. Extensive and pervasive interaction with seawater in the ophicalcites is indicated by greater enrichments in FMEs (Cs, Rb, Sr, and locally U) compared to the serpentinites. However, some of this enrichment may also be linked to later Si-metasomatism.

Interestingly, most of the Sr values of the calcite veins in the ophicalcites are significantly below Jurassic seawater and only a few of the veins reflect unmodified seawater based on their 87Sr/86Sr ratios. As discussed above, these low 87Sr/86Sr ratios can be correlated with the Si-metasomatism recorded in the ophicalcites and are likely produced by Si input from mafic rocks. However, the serpentinites underlying the ophicalcites have significantly higher 87Sr/86Sr ratios than the ophicalcites suggesting that the Si-metasomatism was most pronounced in the top most sections and decreased downwards, consistent with the presence of talc filling late stage carbonate veins. Underlying gabbro intrusions are therefore unlikely the fluid source. The most likely scenario is that the fluids leading to Si-metasomatism were derived from interaction with basalts, which are locally found overlying the ophicalcites (B. E. Treves and Harper, 1994). Consequently, we infer that seawater-derived fluids infiltrated the basalts after their emplacement, picked up the 87Sr/86Sr signal of the basalts and then infiltrated the ophicalcites to produce talc in druses within preexisting carbonate veins. As the fluids would have come from the top, restricted fluid infiltration associated with Si-metasomatism would not have affected the underlying serpentinites. In addition, it should be noted that the serpentinite protolith of the ophicalcites would initially have had an 87Sr/86Sr ratio above Jurassic seawater and would have later entirely shifted (during their conversion from serpentinites to ophicalcites) toward basalt-like 87Sr/86Sr values. This shift would have accompanied extensive alteration and precipitation of talc in druses. Finally, the bulk rock δD and δ18O values record the integrated history of fluid infiltration, which was overall dominated by evolved, seawater-derived fluids, but that possibly contained a magmatic fluid component.
7. Conclusions

This study summarizes the extensive alteration history of ophiolites and serpentinites in the N. Apennine ophiolite. The mineralogical and geochemical signatures of the serpentinites and ophiolites record extensive metasomatism by fluids with variable chemical compositions and a cryptic melt impregnation pre-dating hydrothermal alteration. In particular, the chemical variations attest to fluids of variable origin, i.e., seawater-derived fluids that have interacted with different lithologies and imprint a chemical signature on the ultramafic basement as it is undergoing hydration. The serpentinites thereby record 1) hydration processes during early mantle upwelling within an opening ocean basin with input of a continental basement-derived fluid—as preserved in the high $^{87}$Sr/$^{86}$Sr ratios; and 2) localized high-temperature fluid influx likely associated with continuous mantle exposure and local gabbroic intrusion as documented by amphiboles with hornblende to edenite composition and sulfide isotope compositions as previously reported. In contrast, the ophiolites mostly record the late stages of seawater-rock interaction with extensive carbonation and interaction with basalt-derived fluids at low-temperatures as the mantle sequence was emplaced at the ocean floor, resulting in a gain of SiO$_2$, CaO, and FMEs. Although all studied rocks record multiple phases of water-rock interaction, their chemical signatures are dominated by different and distinct events. Accordingly, the transition from serpentinite to ophiolite as preserved in the N. Apennine ophiolite records the history of uplift and exposure on the seafloor. In addition, this alteration sequence documents that serpentinites can undergo a very complex hydrothermal evolution from serpentinization, carbonation to Si-metasomatism. The complex hydrothermal evolution of these systems is essential to understand the chemical and petrophysical evolution of the oceanic lithosphere and processes of mass transfer. Extensive carbonation and Si-metasomatism may eventually affect subduction zone processes, i.e., change the expected rheology, for example, due to higher Si contents, and mineral stabilities within the subducting slab and the subduction zone channel, and as a consequence may affect element cycling within subduction zones.

Data Availability Statement

All data sets for this research are included in this paper and its supplementary information files Tables S1–S5. In addition, all supplementary data is available online on PANGAEA at https://doi.org/10.1594/PANGAEA.921751.
Boschi, C., Dini, A., Früh-Green, G. L., & Kelley, D. S. (2008). Isotopic and element exchange during serpentinization and metasomatism at the Atlantis Massif (MAR 30°N): Insights from B and Sr isotope data. *Geochimica et Cosmochimica Acta*, 72, 1801–1823. https://doi.org/10.1016/j.gca.2008.01.013

Boschi, C., Früh-Green, G. L., Delacour, A., Karson, J. A., & Kelley, D. S. (2006a). Mass transfer and fluid flow during detachment faulting and development of an oceanic core complex, Atlantis Massif (MAR 30°). *Geochemistry, Geophysics, Geosystems*, 7. https://doi.org/10.1029/2005GC000704

Boschi, C., Früh-Green, G. L., & Escarit, J. (2006b). Occurrence and significance of serpentinite-hosted, talc- and amphibole-rich fault rocks in modern oceanic settings and ophiolite complexes: An overview. *Ofioliti*, 31, 129–140.

Brazielton, 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

Breitenbach, S. F. M., & Bernasconi, S. M. (2011). Carbon and oxygen isotope analysis of small carbonate samples (20–100 µg) with a GasBench II preparation device. *Rapid Communications in Mass Spectrometry*, 25, 1910–1914. https://doi.org/10.1002/rcm.5952

Cannat, M., Fontaine, T., & Escarit, J. (2010). Serpentinization and associated hydrogen and methane fluxes at slow spreading ridges. In P. A. Rona, C. W. Devey, J. Dyment, & B. J. Murton (Eds.), *Diversity of hydrothermal systems on slow spreading ocean ridges*. *Geophysical monograph*. Washington: American Geophysical Union.

Cannat, M., Mevel, C., Maia, M., Deplus, C., Durand, C., Gente, P., et al. (1995). Thin crust. ultramafic exposures, and rugged faulting patterns at the Mid-Atlantic Ridge (22°-24°N). *Geology*, 23, 49–52. https://doi.org/10.1130/0091-7613(1995)023<0049:tcufrf>2.3.co;2

Cortesogno, L., Gianelli, G., & Piccardo, G. (1975). Preorogenic metamorphic and tectonic evolution of the ophiolite mafic rocks (Northern Apennine and Tuscany). *Italian Journal of Geosciences*, 94, 291–327.

Delacour, A., Früh-Green, G. L., Frank, M., Gutjahr, M., & Kelley, D. S. (2008). Sr- and Nd-isotope geochemistry of the Atlantis Massif (30°N, MARY): Implications for fluid fluxes and lithospheric heterogeneity. *Chemical Geology*, 254, 19–35. https://doi.org/10.1016/j.chemgeo.2008.05.015

Deniel, C., & Pin, C. (2001). Single-stage method for the simultaneous isolation of lead and strontium from silicate samples for isotopic measurements. *Analytica Chemic Acta*, 426, 95–103. https://doi.org/10.1016/s0003-2670(00)00118-5

Deschamps, F., Godard, M., Guillot, S., Chauvel, C., Andreani, M., Hattori, K., et al. (2012). Behavior of fluid-mobile elements in serpentines from abyssal to subduction environments: Examples from Cuba and Dominican Republic. *Chemical Geology*, 312–313, 93–117. https://doi.org/10.1016/j.chemgeo.2012.04.009

de Souza, G. F., Reynolds, B. C., Kiczka, M., & Bourdon, B. (2010). Evidence for mass-dependent isotopic fractionation of strontium in a glaciated granitic watershed. *Geochimica et Cosmochimica Acta*, 74, 2596–2614. https://doi.org/10.1016/j.gca.2010.02.012

Escarit, J., Hirth, G., & Evans, B. (1997). Effects of serpentinization on the lithospheric strength and the style of normal faulting at slow spreading ridges. *Earth and Planetary Science Letters*, 151, 181–189. https://doi.org/10.1016/0012-821X(97)81847-x

Friedman, I., & O’Neil, J. R. (1977). Compilation of stable isotope fractionation factors of geochemical interest. In *Proceeding of Lunar Science Conference*, 2031–2050. https://doi.org/10.1016/0009-2541(86)90053-7

Früh-Green, G. L. (2008). Multiple fluid history recorded in Alpine ophiolites. *Journal of the Geological Society*, 174, 959–970. https://doi.org/10.1144/jgs147.6.0959

Garuti, G., Bartoli, O., Scacchetti, M., & Zaccarini, F. (2008). Geological setting and structural styles of volcanic massive sulfide deposits in the Northern Apennines (Italy): Evidence for seafloor and sub-seafloor hydrothermal activity in unconventional ophiolites of the Mesozoic Tethys. *Boletin de la Sociedad Geologica Mexicana*, 60, 121–145. https://doi.org/10.18268/bsgm2008v60n1a9

Groza, N. V., Klein, F., Seewald, J. S., & Syva, S. P. (2017). Experimental study of carbonate formation in oceanic peridotite. *Geochimica et Cosmochimica Acta*, 199, 264–286. https://doi.org/10.1016/j.gca.2016.10.052

Guillon, M., Meier, D. L., Allan, M. M., Heinrich, C. A., & Yardley, B. (2008). A MATLAB-based program for the reduction of laser ablation ICP-MS data of homogeneous materials and inclusions. *Mineralogical Association of Canada Short Course*, 40, 328–333.

Hart, S. R., & Zindler, A. (1986). In search of a bulk-Earth composition. *Chemical Geology*, 57, 247–267. https://doi.org/10.1016/0009-2541(86)90053-7

Jagoutz, E., Palme, H., Baddinghauser, H., Blum, C., Cendales, M., Dreibus, G., et al. (1979). The abundances of major, minor and trace elements in the Earth’s mantle as derived from primitive ultramafic nodules. *Proceeding of Lunar Science Conference*, 10, 2031–2035.

John, B. E., & Chessad, M. J. (2010). Deformation and alteration associated with oceanic and continental detachment fault systems; Are they similar? In *Geophysical monograph*.

Jones, C. E., Jenkyns, H. C., Coe, A. L., & Stephen, H. P. (1994). Strontium isotopic variations in Jurassic and Cretaceous seawater. *Geochimica et Cosmochimica Acta*, 58, 3061–3074. https://doi.org/10.1016/0016-7037(94)90179-1

Karson, J. A., Früh-Green, G. L., Kelley, D. S., Williams, E. A., Yoerg, D. R., & Jakuba, M. (2006). Detachment shear zone of the Atlantis Massif core complex, Mid-Atlantic Ridge 30°N. *Geochemistry, Geophysics, Geosystems*, 7. https://doi.org/10.1029/2005GC000199

Kelemen, P. B., Matter, J. M., Teagle, D. A. H., Coggon, J. A., & Team, a. t. O. D. P. S. (2020). *Oman Drilling Project, Scientific Drilling in the Samail Ophiolite, Sultanate of Oman, International Ocean Discovery Program*. https://doi.org/10.14379/OmanDP.proc.2020
Kelley, D. S., Karson, J. A., Frith-Green, G. L., Yoeger, D. R., Shank, T. M., Butterfield, D. A., et al. (2005). A serpentinite-hosted ecosystem: The lost city hydrothermal field. *Science*, 307, 1428–1434. https://doi.org/10.1126/science.1102556

Kelley, D. S., Karson, J. A., Karson, J. A., Blackman, D. K., Frith-Green, G. L., Butterfield, D. A., et al. (2001). An off-axis hydrothermal vent field near the Mid-Atlantic ridge at 30°N. *Nature*, 412, 145–149. https://doi.org/10.1038/35084000

Klein, F., Bach, W., Humphris, S. E., Kahl, W.-A., Jöns, N., Moskowitz, B., & Berquo, T. S. (2014). Magnetite in seafloor serpentinite—Some like it hot. *Geology*, 42, 135–138.2014. https://doi.org/10.1130/G35068.1

Kyser, T. K., O’Hanley, D. S., & Wicks, F. I. (1999). The origin of fluids associated with serpentinization processes: Evidence from stable-isotope compositions. *The Canadian Mineralogist*, 37, 23–237.

Lagabrielle, Y., & Lemoine, M. (1997). Alpine, Corsican and Apennine ophiolites: The spreading-wide ridge model. *Comptes Rendus de l’Académie des Sciences—Series II*, 325, 909–920. https://doi.org/10.1016/s1251-8050(97)83269-5

Le Breton, E., Bruné, S., Ustaszewski, K., Zahiriovic, S., Seton, M., & Müller, R. D. (2021). Kinematics and extent of the Piemont-Liguria Basin—implications for subduction processes in the Alps. *Solid Earth Discuss*. [preprint] accepted, 2021. accepted. https://doi.org/10.5194/se-2020-161

Li, J.-L., Schwarzenbach, E. M., John, T., Ague, J. J., Huang, F., Gao, J., et al. (2020). Uncovering and quantifying the subduction zone sulfur cycle from the slab perspective. *Nature Communications*, 11, 514. https://doi.org/10.1038/s41467-019-14100-4

Ludwig, K. A., Kelley, D. S., Butterfield, D. A., Nelson, B. E., & Früh-Green, G. L. (2006). Formation of carbonate chimneys at the Lost City hydrothermal field. *Geochimica et Cosmochimica Acta*, 70, 3625–3645. https://doi.org/10.1016/j.gca.2006.04.016

Malvouis, B. (2015). Mass transfer in the oceanic lithosphere: Serpentinization is not isochemical. *Earth and Planetary Science Letters*, 430, 75–85. https://doi.org/10.1016/j.epsl.2015.07.043

Manatschal, G., & Müntener, O. (2009). A type sequence across an ancient magma-poor ocean-continent transition: The example of the western Alpine Tethys ophiolites. *Tectonophysics*, 473, 4–19. https://doi.org/10.1016/j.tecto.2008.07.021

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

Marroni, M., Molli, G., Montanini, A., & Tribuzio, R. (1998). The association of continental crust rocks with ophiolites in the North-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

McCarty, V. A. Chelle-Michou, C., Müntener, O., Arculus, R., & Blundy, J. (2018). Subduction initiation without magmatism: The case of the missing Alpine magmatic arc. *Geology*, 46, 1059–1062. https://doi.org/10.1130/g45366.1

McDonough, W. F., & Sun, S.-S. (1995). The composition of the Earth. *Chemical Geology*, 120, 223–253. https://doi.org/10.1016/0009-2541(94)00140-4

Mével, C. (2003). Serpentinization of abyssal peridotites at mid-ocean ridges. *Comptes Rendus Geoscience*, 335, 825–852. https://doi.org/10.1016/j.crte.2003.08.006

Miller, D. J., & Christensen, N. J. (1997). Seismic velocities of lower crustal and upper mantle rocks from the slow spreading Mid-Atlantic Ridge, south of the Kane transform fault. *Proceedings of the ocean drilling program, scientific results*, 153, 437–454.

Molli, G. (1995). Pre-orogenic high temperature shear zones in an ophiolite complex (Bracco massif, Northern Apennines, Italy). In R. L. M. Vissers, & A. Nicolas (Eds.), *Mantle and lower crust exposed in oceanic ridges and in ophiolites*. Dordrecht: Kluwer Academic Publishers.

Moody, J. B. (1976). Serpentinization: A review. *Lithos*, 9, 125–138. https://doi.org/10.1016/0024-4977(76)90030-x

Niu, Y. (2004). Bulk-rock major and trace element compositions of abyssal peridotites: Implications for mantle melting, melt extraction and post-melting processes beneath mid-ocean ridges. *Journal of Petrology*, 45, 2423–2458. https://doi.org/10.1093/petrology/egh068

O’Hanley, D. S. (1996). *Serpentinites: Records of tectonic and petrological history*. New York; Oxford: Oxford university press.

Paulick, H., Bach, W., Godard, M., De Hoog, J. C. M., Sühr, G., & Harvey, J. (2006). Geochemistry of abyssal peridotites (Mid-Atlantic Ridge, 15°20′N, ODP Leg 209): Implications for fluid/rock interaction in slow spreading environments. *Chemical Geology*, 234, 179–210. https://doi.org/10.1016/j.chemgeo.2006.04.011

Peters, D., Bretsch, A., John, T., Scambelluri, M., & Pettke, T. (2017). Fluid-mobile elements in serpentinites: Constraints on serpentinization environments and element cycling in subduction zones. *Chemical Geology*, 466, 654–666. https://doi.org/10.1016/j.chemgeo.2017.07.017

Piccardo, G. B., Piccardo, M., & Guarnieri, L. (2014). The Ligurian Tethys: Mantle processes and geochemistry. *Earth-Science Reviews*, 138, 409–434. https://doi.org/10.1016/j.earscirev.2014.07.002

Rampone, E., Hofmann, A. W., Piccardo, G. B., Vannucci, R., Bottazzi, P., & Ottolini, L. (1996). Trace element and isotopic geochemistry of depleted peridotites from an N-MORB type ophiolite (Internal Liguride, N. Italy). *Contributions to Mineralogy and Petrology*, 123, 61–76. https://doi.org/10.1007/bf00310745

Rehkämper, M., & Hofmann, A. W. (1997). Recycled ocean crust and sediment in Indian Ocean MORB. *Earth and Planetary Science Letters*, 147, 93–106.

Rouméjon, S., Frith-Green, G. L., Orcutt, B. N., & Party, I. E. S. (2018). Alteration heterogeneities in peridotites exhumed on the southern wall of the Atlantis Massif (IODP Expedition 357). *Journal of Petrology*, 59, 1329–1358. https://doi.org/10.1093/petrology/egy065

Sakai, R., Kusakabe, M., Ito, M., & Ishii, T. (1997). Origin of waters responsible for serpentinization of the Izu-Ogasawara-Mariana forearc seamounts in view of hydrogen and oxygen isotope ratios. *Earth and Planetary Science Letters*, 100, 291–303. https://doi.org/10.1016/0012-821x(90)90192-2

Salters, V. J. M., & Stracke, W. C. (1983). Composition of the depleted mantle. *Chemistry, Geophysics, Geosystems*, 5, 1–27. https://doi.org/10.1029/2001gc000597

Scambelluri, M., Müntener, O., Ottolini, L., Pettke, T. T., & Vannucci, R. (2004). The fate of Bi, Ce and Li in the subducted oceanic mantle and in the antigorite breakdown fluids. *Earth and Planetary Science Letters*, 222, 217–234. https://doi.org/10.1016/j.epsl.2004.02.012

Schmidt, M. W. (1992). Amphibole composition in tonalite as a function of pressure: An experimental calibration of the Al-in-hornblende partitioning process. *Journal of Geophysical Research: Solid Earth*, 107, 304–310. https://doi.org/10.1029/97jb0310745
Schwarzenbach, E. M., Caddick, M. J., Beard, J. S., & Bednar, R. J. (2016). Serpentinization, element transfer, and the progressive development of zoning in veins: Evidence from a partially serpentinized harzburgite. *Contributions to Mineralogy and Petrology*, 171, 1–22. https://doi.org/10.1007/s00410-015-1219-3

Schwarzenbach, E. M., Früh-Green, G. L., Bernasconi, S. M., Alt, J. C., & Plas, A. (2013). Serpentinization and carbon sequestration: A study of two ancient peridotite-hosted hydrothermal systems. *Chemical Geology*, 351, 115–133. https://doi.org/10.1016/j.chemgeo.2013.05.016

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. *Geochemistry and Cosmochimica Acta*, 91, 283–305. https://doi.org/10.1016/j.gca.2012.05.021

Schwarzenbach, E. M., Gill, B. C., & Johnston, D. T. (2018). Unraveling multiple phases of sulfur cycling during the alteration of ancient ultramafic oceanic lithosphere. *Geochemistry and Cosmochimica Acta*, 223, 279–299. https://doi.org/10.1016/j.gca.2017.12.006

Shanks, W. C, Böhlke, J. K, & Seal, R. R (1995). Stable isotopes in mid-ocean ridge hydrothermal systems. *Interactions between fluids, minerals, and organisms*. Washington D.C.: American Geophysical Union.

Sun, S.-S., & McDonough, W. F. (1989). Chemical and isotopic systematics of oceanic basalts: Implications for mantle composition and processes. *Earth and Planetary Science Letters*, 96, 149–186. https://doi.org/10.1016/0012-821X(89)90006-8

Tribuzio, R., Renna, M. R., Dallai, L., & Zanetti, A. (2014). The magmatic-hydrothermal transition in the lower oceanic crust: Clues from the Ligurian ophiolites, Italy. *Contributions to Mineralogy and Petrology*, 168, 21. https://doi.org/10.1007/s00410-014-1109-8

Tribuzio, R., Thirlwall, M. F., Vannucci, R. (2004). Origin of the Gabbro-Peridotite association from the Northern Apennine ophiolites. *Geological Society, London, Special Publications*, 20, 1–22. https://doi.org/10.1191/0305871405sp0993oa

Vogel, M. (2016). Peridotite-hosted hydrothermal systems past and present: Serpentinization, metasomatism and carbonate precipitation in modern and Jurassic ultramafic seafloor, Dr. Sc., Department of Earth Sciences, ETH Zurich, Zurich, Switzerland, 142 pp.

Vilas, F., Tonarini, S., Kalt, A., & Seitz, H.-M. (2009). Boron, lithium and strontium isotopes as tracers of seawater-serpentinite interaction at the Mid-Atlantic ridge, ODP Leg 209. *Earth and Planetary Science Letters*, 266, 414–425. https://doi.org/10.1016/j.epsl.2009.07.005

Vogel, M. (2016). Boron and lithium in modern and Jurassic ultramafic seafloor. *Earth and Planetary Science Letters*, 466, 59–88. https://doi.org/10.1016/j.epsl.2017.01.015

von Damm, K. L. (1990). Seafloor hydrothermal activity: Black smoker chemistry and chimneys. *Chemical Geology*, 81, 1–22. https://doi.org/10.1016/0009-2541(90)90046-4

Wenner, D. B., & Taylor, H. P. (1973). Oxygen and hydrogen isotope studies of the serpentinization of ultramafic rocks in oceanic environments and continental ophiolite complexes. *American Journal of Science*, 273, 207–239. https://doi.org/10.2475/ajs.s273.3.207

Wenner, D. B., & Taylor, H. P. (1974). D/H and δ18O studies of serpentinization of ultramafic rocks. *Geochemistry and Cosmochimica Acta*, 38, 1255–1268. https://doi.org/10.1016/0016-7037(74)90120-3

Whitemarsh, R. B., Manatschal, G., & Minshull, T. A. (2001). Evolution of magma-poor continental margins from rifting to seafloor spreading. *Nature*, 413, 103–104. https://doi.org/10.1038/35091503

Wierzchoslawski, H., Anczkiewicz, R., Pawlik, I., Rogov, M. A., & Kuznetsov, A. B. (2017). Revised middle-upper Jurassic strontium isotope stratigraphy. *Chemical Geology*, 466, 239–255. https://doi.org/10.1016/j.chemgeo.2017.06.015

Zaccarini, F., & Garuti, G. (2008). Mineralogy and chemical composition of VMS deposits of northern Apennine ophiolites, Italy: Evidence for the influence of country rock type on ore composition. *Mineralogy and Petrology*, 94, 61–83. https://doi.org/10.1007/s00710-008-0109-9