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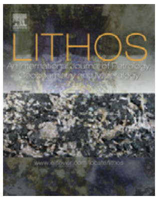

The process of serpentinization in dunite from New Caledonia

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ABSTRACT

Dunite from New Caledonia displays three types of serpentine-dominated veins. The earliest, type 1 veins are narrow (50–100 μm wide) and rarely extend across more than a single olivine grain. They are lizardite, contain abundant brucite and never contain magnetite. Type 2 veins are 0.01 to 0.1 mm wide, extend across several olivine grains and cut across the type 1 veins. They are lizardite, contain magnetite, often in vein interiors, and contain less brucite than type 1 veins. Type 3 veins are dominantly chrysotile, cm-scale, have a magnetite-rich core, and extend for meters or more. Analyses of two representative samples indicate that the type 1 veins have relatively Fe-rich serpentine ($X_{Mg} = 0.92$) and brucite ($X_{Mg} = 0.82$). These minerals are less magnesian than those in the type 2 veins; serpentine has $X_{Mg} = 0.93–0.94$ and brucite has $X_{Mg} = 0.84$. In the magnetite-rich core to the type 3 vein both serpentine ($X_{Mg} = 0.94–0.97$) and one of the two brucite populations ($X_{Mg} = 0.94$) are Mg-rich. Opx in harzburgite layers in these samples is cut by serpentine veins that are on the order of 0.05 mm wide. The serpentine veins after Opx lack talc or magnetite and, as with veins cutting olivine, the older veins are more Fe rich ($X_{Mg} = 0.84$) than the younger veins ($X_{Mg} = 0.90$). We conclude that the formation of magnetite was accompanied by the extraction of iron from the early-formed serpentine and brucite.

Thermodynamic calculations suggest that the type 1 veins formed in a rock-dominated system where the activities of FeO, MgO, and SiO_2 were dictated by the compositions of olivine and orthopyroxene. In contrast the type 2 veins were formed in a more fluid-dominated system where the infiltrating fluid was relatively oxidizing and out of equilibrium with the original brucite–serpentine assemblage. Reduction of this fluid was accompanied by reaction of brucite and serpentine to magnetite and hydrogen. By producing magnetite, this reaction extracted iron from brucite and serpentine, making them both more magnesian. This would drive the brucite–serpentine–magnetite assemblage to higher oxygen fugacity, progressively decreasing the efficiency of the magnetite-forming reactions.

1. Introduction

Serpentinization is an important geochemical process accompanying the formation of the ocean floor. The hydration of peridotites not only induces huge rheological changes in the oceanic crust (Escartin et al., 2001), but also produces reduced fluids emanating from seafloor vents (Beard and Hopkinson, 2000; Charlou et al., 2002; Kelley, et al., 2001) that recently have been postulated to be an ideal environment for the origin of life (Russell and Arndt, 2005; Russell and Hall, 1997; Sleep et al., 2004). Additionally, partially serpentinized ultramafic rocks have been proposed as potential hosts for sequestration of anthropogenically-produced carbon (e.g. Kelemen and Matter, 2009).

Peridotites and their metamorphic equivalents are chemically relatively rather simple. They can, for most purposes, be described by the system $CaO–MgO–FeO–SiO_2–H_2O–O$. However, the processes that transform olivine and pyroxene to serpentine and other products are still a matter of considerable debate (Evans, 2008; Frost and Beard, 2007). Frost and Beard (2007) proposed that low water and/or silica activities stabilize magnetite- and Fe-alloy-bearing assemblages relative to brucite and serpentine respectively. Evans (2008), on the other hand, proposes that magnetite and iron alloys form via the reaction olivine + water = serpentine + magnetite/iron alloys because the X_{Mg} of serpentine in equilibrium with olivine or orthopyroxene is higher than that of the bulk rock.

If we are to predict the conditions under which the various serpentinite assemblages form and understand the environments that form serpentinites then it is essential that we distinguish between these possibilities, as each has distinctly different implications for the parameters that control the serpentinizing environment. The formation of magnetite, and the behavior of iron generally, are particularly critical, because it is the iron-bearing reaction that drives serpentinizing environments to extremely low fO_2 values via the production of ferric iron accompanied by the reduction of water to hydrogen. Because of these reducing conditions Russell and Arndt (2005), Russell and Hall

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(1997) and Sleep et al. (2004) have suggested serpentinizing environments as the cradle for early life. Thus the chemical influences on these environments must be understood if the initiation of life is to be successfully modeled or simulated.

Additionally, the process of serpentinization offers an opportunity to study metamorphic environments in which equilibrium is only reached, if it is reached at all, on very limited length-scales. Such environments are of increasing interest as the scope of metamorphic studies extends to lower temperatures, and to situations where bulk composition may not be fixed on the length-scale of interest (i.e. metasomatic systems). Equilibrium thermodynamics have provided valuable insights into metamorphism at greenschist grade and higher, but application of equilibrium techniques to lower temperature environments requires careful assessment of the existence, or otherwise, of thermodynamic equilibrium, and the length-scales on which it is attained. The chemical simplicity of serpentinizing environments facilitates this task.

In this paper we make a detailed study of serpentine veins in dunite from New Caledonia. Results are used to constrain the reactions involved in the formation of iron-bearing phases, drivers of low oxygen fugacity conditions, and the length-scales and extent of thermodynamic equilibrium during serpentinization.

2. Regional geology

The island of New Caledonia represents the exposed portion of Norfolk Ridge, a microcontinent that rifted from the eastern Gondwanaland margin during the late Cretaceous. The oldest rocks on the island consist of a series of accretionary terranes that include a suite of Permian to Jurassic island arc-derived strata, schistose rocks that were locally metamorphosed to blueschist facies in the Jurassic, fragments of a Triassic ophiolite, and a suite of volcanic rocks and sediments of island arc affinity that extends into the Jurassic (Aitchison et al., 1995). These rocks are unconformably overlain by a transgressive Upper Cretaceous sequence that ranges from conglomerates and coal measures upwards to shallow marine sandstones. For the sake of this paper we refer to this whole sequence as the basement. Overlying the basement are three westward-directed thrust sheets. Lying on the northwestern portion of the island is a sheet composed mostly of basalt and minor ocean-floor sediments that is called the Poya terrane (Cluzel et al., 2001). On the northeastern portion of the island is a sheet of high-pressure rocks known as the Pouébo terrane (Cluzel et al, 2001) that are mostly in blueschist facies but locally have been metamorphosed up to eclogite facies (Clarke et al., 1997). U–Pb zircon ages indicate that the peak metamorphism in the Pouébo terrane occurred around 44 Ma (Spandler et al., 2005). Lying structurally above the other two is a thrust sheet of ophiolite that is most extensively exposed as the Massif du Sud in the southern part of the island, but which occurs as klippes along the whole island. The southern parts of the ophiolite are highly depleted and thought to have experienced hydrous melting after a previous depletion episode (Ulrich et al., 2010). Subduction is thought to have begun near the Loyalty Islands 56 Ma (Cluzel et al., 2012). Obduction is constrained to have occurred in the Eocene. Stratigraphic relations constrain the Poya terrane to have been emplaced between 33.7 and 35 Ma (Cluzel et al., 2001) and apatite fission track dating implies that the Pouébo terrane was emplaced at 34 Ma (Baldwin et al., 2007). The ophiolite was emplaced between 34 Ma, the age of the youngest sediment beneath the nappe, and 27 Ma, the age of stitching plutons that intrude the nappe (Cluzel et al., 2006). After the emplacement of the nappes, New Caledonia was subjected to extension that began in the Miocene and has extended to the Neogene (Cluzel et al, 2001; Lagabrielle et al., 2005; Rawling and Lister, 2002).

The southern exposures of the New Caledonian ophiolite consist mainly of harzburgite and dunite (Titus et al., 2011), with minor gabbro. The peridotite has been extensively weathered to laterite and ferricrete over much of the island, but spectacular exposures are present in areas of active erosion. The samples we studied came from downstream of Yaté dam, where the Yaté River has exposed an extensive area of fresh outcrops. The Yaté dam lies in the depleted, southern portion of the ophiolite.

3. Sample description

The peridotite exposed along the Yaté River is mostly harzburgite containing 10 cm- to 1 meter-wide bands of dunite that lie parallel to a foliation defined by flattened elongate Opx grains. Also present are 1 cm- to 10 cm-wide orthopyroxenite veins that cut the foliation. Serpentinization ranges from 20% to more than 60% and becomes more intense adjacent to widely spaced serpentinized fault zones that are from meters to tens of meters wide.

We studied two olivine-rich samples in detail, NC09-05, and NC09-11. NC09-05 comes from the riverbed about 500 m downstream of Yaté Dam; NC09-11 comes from approximately 250 m further downstream. NC09-05 was collected because it displayed the contact between harzburgite and dunite (Fig. 1a) whereas NC09-11 was collected because it contained a cm-wide serpentinite vein (Fig. 1b) cutting dunite. Sample NC09-05 is from 58K 0694325 mE 7549876 mN, and NC09-11 is from 58K 0694449 mE 7550113 mN (WGS84/UTM/UPS).

Both samples consist mainly of olivine with minor chromite rimmed by Cr-magnetite; the harzburgite portions of NC09-05 also contain about 10–15% Opx with fine Cpx lamellae. The patches of Opx seen in Fig. 1a are individual grains. NC09-05 contains about 30% serpentine that is uniformly distributed throughout. Sample NC09-11 contains 50% serpentine in regions distal to the large vein. The serpentine abundance increases to 100% within about 0.5 cm from the vein.

To determine the geochemical processes attendant on vein formation, we analyzed in detail five types of serpentine veins that we recognized in these two samples. As with rocks described by Beard et al. (2009), the initial stage of serpentinization in the New Caledonia rocks involves two types of serpentine veins. Type 1 veins are narrow (about 50–100 μm wide) and are rarely longer than a single olivine grain (Fig. 1c). These veins never contain magnetite and contain brucite that is generally more abundant adjacent to the olivine. These veins often show a medial line and undeformed wall-perpendicular fibers; the presence of brucite at the margins of the vein suggests that these veins are syntaxial. Type 2 veins are 0.01 to 0.1 mm wide and cut across the type 1 veins (Fig. 1d, e). They rarely extend for more than 2 mm before being terminated by an en-echelon manner or being cut by another type 2 vein. Magnetite is commonly found in the cores of the type 2 veins and brucite may be present on the margins. It is relatively rare to see the wall-parallel serpentine fibers observed in the type 1 veins; serpentine in the type 2 veins is finer-grained and less well oriented. Type 2 veins are often composed of several generations of type 1 and small type 2 veins, with complex cross-cutting relationships. Later veins are often wholly enclosed by earlier veins, suggesting that growth was syntaxial on existing vein margins. Type 1 and Type 2 veins exhibit the typical mesh textures seen in serpentinization of olivine, and are likely to be dominantly replacive (see Section 5 for discussion).

Further serpentinization results in formation of type 3 veins. The type 3 veins are cm-scale veins that extend for meters or more through an outcrop. We studied a type 3 vein in NC09-11 that is slightly less than 1 cm across (Fig. 1b) and contains a distinct magnetite-rich core. In thin section, these large veins lack the fibers seen in type 1 veins and appear almost amorphous in plane polarized light, with very little variation in color as the stage is rotated. The vein studied is composed of multiple generations of parallel veins, with the zoning pattern indicating that the exterior of the veins is the oldest, and the central vein the youngest, consistent with syntaxial vein formation. The greatest proportion of magnetite occurs close to the core of this vein (Fig. 1b), although the central vein is magnetite-free, and also in magnetite-bearing stringers that cut across the vein at a high angle to the vein walls, cutting the