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Petrogenesis of serpentinites from the Franciscan Complex, western California, USA

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ABSTRACT

Serpentinites from the Franciscan Complex of California, USA, were analyzed for their bulk major and trace element compositions, relict mineral (spinel and pyroxene) compositions, and stable isotope (O, H, Cl) compositions with the goal of determining protolith origin and subsequent serpentinizing fluid sources in order to decipher the tectonic setting of serpentinization. We focused on serpentinite bodies found in the Franciscan Complex (west of Cuesta Ridge; south of San Francisco; Tiburon Peninsula; Healdsburg) ($n=12$). Three samples from Cuesta Ridge (part of the Coast Range ophiolite) were also analyzed for comparison. Serpentinites from Cuesta Ridge have flat to U-shaped chondrite-normalized REE patterns and spinels with Cr# values >0.60 implying a supra-subduction zone origin. In contrast, Franciscan serpentinites west of Cuesta Ridge and Tiburon Peninsula have positive-sloped REE patterns. This depletion in LREE is typical of abyssal peridotites. Most relict spinels have low Cr# values (<0.3) and relict clinopyroxenes from Tiburon Peninsula have high HREE concentrations, also supporting an abyssal origin. Franciscan serpentinite samples from south of San Francisco and near Healdsburg have U-shaped REE patterns and spinel compositions that lie within the forearc peridotite field with some overlap into the abyssal field and are of more ambiguous origin. All samples are high in fluid-mobile elements with remarkable positive Ce and Y anomalies. We speculate that these anomalies may be due to involvement of highly oxidizing fluids resulting in the preferential scavenging of Ce and Y by ferromanganese oxyhydroxides during serpentinization. All samples (except those south of San Francisco) have $\delta^{18}O$ values of +5.4 to +7.9‰, typical values for oceanic serpentinites formed via low-T seawater hydration on the seafloor. δD values of all samples are extremely low (−107 to −90‰), likely the result of post-serpentinization, post-emplacement interaction with meteoric water at low temperature. Samples south of San Francisco lie on the San Andreas fault and have high $\delta^{18}O$ values (+7.2 to +9.5‰) likely due to low-T interaction with meteoric water at high fluid–rock ratios. Most of the serpentinites have $\delta^{37}Cl$ values between +0.2 and +0.9‰, typical values for serpentinites formed by interaction with seawater. Exceptions are those from the San Andreas fault and one sample from Cuesta Ridge with a high $\delta^{37}Cl$ value (+1.7‰) possibly from interaction with a slab-derived fluid.

1. Introduction

Serpentinites are formed in many different geologic settings, such as off-axis fractures and faults associated with seafloor spreading ridges, hydrated mantle wedge above a subducting slab (supra-subduction zone, SSZ), within the subduction channel, and along flexural faults associated with plate bending during subduction (e.g., Dilek, 2003; Ranero et al., 2003). In many cases, obducted serpentinites (and associated ophiolitic units) are highly dismembered and deformed making tectonic interpretation of the origin of these rocks difficult. Determining the geologic setting of serpentinization is critical to addressing tectonic questions and quantifying geochemical fluxes.

Due to the preferential partitioning of H_2O and fluid mobile elements (FME, e.g., Cl, F, B, S, As, Sb, Pb, Ni, Cr) into serpentinites, serpentinites act as a record of fluid history. Different modes of hydration and sources of serpentinizing fluids (e.g., seawater vs. slab-derived) reflect different tectonic settings of serpentinization and create variations in the resulting serpentinite geochemistry (Kodolánya et al., 2012). In general, serpentinization is isochemical with respect to the major elements, with the exception of CaO loss; however, the behavior of trace elements is not as well constrained (Mével, 2003). MgO can be lost due to low-temperature (<150 °C) marine weathering on the seafloor (Snow and Dick, 1995) and interaction with high temperature fluids from hydrothermal systems can also result in mobility of some LREE (Eu and Ce), as

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well as, Si, Fe, Cr, and Ni (e.g., Augustin et al., 2012; Douville et al., 2002; Janecky and Seyfried, 1986; Paulick et al., 2006). Despite original geochemical heterogeneities in the protolith, major- and trace-element chemistry has been used to identify the tectonic setting of serpentinization (e.g., Dai et al., 2011; Deschamps et al., 2010; Hattori and Guillot, 2007; John et al., 2010b; Li and Lee, 2006). For example, SSZ serpentinites are characterized by low Al/Si weight ratios (<0.03), enrichments in FME compared to abyssal peridotites, U-shaped REE patterns, and slight enrichments in LREE relative to HFSE. In contrast, abyssal peridotites have moderate Al/Si ratios (>0.03) and low LREE concentrations (Agranier et al., 2007; Deschamps et al., 2010, 2011; Hattori and Guillot, 2007; John et al., 2010b; Kodolánya et al., 2012; Li and Lee, 2006; Niu, 2004; Savov et al., 2005, 2007). However, melt refertilization in a MOR setting can also result in LREE enrichments in abyssal peridotites creating U-shaped REE patterns (Niu, 2004; Paulick et al., 2006).

In addition, stable isotopes (O, H, Cl, Li, B) are effective tracers of serpentinizing fluid sources and post-serpentinite fluid interaction (Alt and Shanks, 2006; Barnes and Sharp, 2006; Barnes et al., 2006, 2009; Benton et al., 2001, 2004; Burkhard and O'Neil, 1988; Cartwright and Barnicoat, 1999; Früh-Green et al., 1990, 1996, 2001; Kyser et al., 1999; Sakai et al., 1990; Skelton and Valley, 2000; Tonarini and Scambelluri, 2010; Vils et al., 2009; Yui et al., 1990). The final isotopic composition of the serpentinite will be determined by the isotopic composition of the serpentinizing fluid, the temperature of interaction, and the water/rock ratio. For example, high $\delta^{18}O$ values may be the result of low-temperature serpentinization by seawater (large $\Delta^{18}O_{serp\text{-}water}$) or interaction with an ^{18}O-enriched slab derived fluid. More recent work has used Cl and B stable isotope geochemistry to trace serpentinizing fluid sources and infer tectonic setting of serpentinization (Barnes and Sharp, 2006; Barnes et al., 2006, 2009; Benton et al., 2001). For example, isotopic work (O, H, Sr, Li, and B isotopes) on Mariana forearc serpentinites indicates slab-derived fluids as the serpentinizing fluid source (Alt and Shanks, 2006; Benton et al., 2001, 2004; Sakai et al., 1990; Savov et al., 2005, 2007), supporting previous conclusions based on trace element geochemistry.

The purpose of this study is to use stable isotope (O, H, Cl) and major- and trace-element geochemistry to identify serpentinizing fluid sources and unravel the serpentinization history of metasomatized ultramafic rocks from several localities within the Franciscan Complex and Coast Range ophiolite (CRO). The primary focus of this work is the serpentinites within the Franciscan Complex with only a few samples from the CRO included for comparison. The Franciscan Complex has been the location of decades of research, yet little work, particularly geochemistry, has focused on the Franciscan serpentinites. However, these serpentinites may play a critical role in understanding the tectonic history of the Franciscan Complex. For example, several models have been proposed to explain the rapid exhumation rates necessary to explain the lack of complete retrogression observed in high-grade blocks of the Central Belt. One of those group of models invokes exhumation of the high-grade block in a buoyant serpentinite diapir/channel (e.g., Ernst, 1970; Horodyskyj et al., 2009; Moore, 1984). Identifying serpentinizing fluid sources and the location of serpentinization may aid in evaluating these models.

2. Geologic setting and sample locality descriptions

2.1. Overview of the Franciscan Complex and Coast Range ophiolite

The Franciscan Complex of western California and southern Oregon is primarily a shale mélange containing rare low-T, high-P blocks of blueschist, eclogite, and amphibolites, as well as serpentinite blocks, and massive serpentinite slivers (e.g., Bailey et al., 1964; Cloos, 1983, 1986; Ernst, 1970). The Franciscan Complex is a type example of an accretionary wedge that formed during subduction (Bailey and Blake, 1969; Ernst, 1970). The Complex is divided into three north-south trending belts called the Coastal, Central, and Eastern Belts and is overlain by the Coast Range ophiolite and the Great Valley Group (e.g., Bailey and Blake, 1969; Blake et al., 1988; Cloos, 1986; Ernst, 1970; Terabayashi and Maruyama, 1998).

The Middle Jurassic Coast Range ophiolite (CRO; 161–168 Ma) is a >700 km long section of 4–5 km stratigraphically thick dismembered ophiolitic remnants consisting of serpentinized peridotite, pyroxenite, gabbro, diorite, sheeted dike and sill complexes, and submarine lavas overlain by radiolarian chert. In most places the CRO is dismembered and tectonically thinned, representing an incomplete section. The CRO is considered to be basement for the overlying Great Valley Sequence (forearc sedimentary rocks) and in fault contact (Coast Range Fault) with the underlying Franciscan Complex (e.g., Bailey et al., 1970; Coleman, 2000; Hopson et al., 1981, 2008; Shervais et al., 2004, 2005).

2.2. Serpentinites of the Franciscan Complex and Coast Range ophiolite

The best-known and well-studied serpentinites are part of the California Coast Ranges (e.g., CRO, Josephine ophiolite, Trinity ophiolite); however, more poorly studied serpentinites are common within the Franciscan Complex (Coleman, 2000; Wakabayashi, 2004). The CRO stretches from Elder Creek in the north to Point Sal in the south. The CRO is generally thought to have formed in a supra-subduction zone environment (Saleeby, 1982; Shervais, 2001; Shervais and Kimbrough, 1985; Stern and Bloomer, 1992); however, other hypotheses have been proposed such as backarc spreading (e.g., Dickinson et al., 1996) and mid-ocean ridge spreading (e.g., Dickinson et al., 1996; Hopson et al., 1981, 2008). Recent geochemical work suggests that the CRO had a complex history and that a simple supra-subduction model cannot explain all the characteristics (Shervais et al., 2004).

Serpentinite bodies in the Franciscan Complex occur as long slivers (up to 4 km in length and 1 km thick), as smaller blocks, and possibly as sedimentary mélange units (Bailey et al., 1964; King et al., 2003; Loney et al., 1971; Page, 1972; Wakabayashi, 2011a,b). The mechanism for incorporation of the Franciscan serpentinites into the metasedimentary mélange is unclear. One possibility is that the serpentinites were offscraped from metamorphic core complexes as part of the subducting oceanic plate (Coleman, 2000; Wakabayashi, 2004). Alternatively, the serpentinites may be derived from tectonic erosion of the overriding mantle wedge (i.e., blocks from the basal section of the CRO) (Cloos and Shreve, 1988; King et al., 2003; Wakabayashi, 2004) or be sedimentary serpentinites similar to serpentine mud volcanoes found in the forearc (Fryer et al., 2000; Wakabayashi, 2011b). Most of these interpretations are based on possibilities presented from tectonic models and field relationships. Overall, there has been very little work done focusing on the geochemistry of Franciscan serpentinites (Coleman and Keith, 1971; Hirauchi et al., 2008; King et al., 2003; Loney et al., 1971; Page, 1967).

2.3. Sample localities

For the purposes of this study we have concentrated on serpentinite bodies found in the Franciscan Complex. Three samples from/near Cuesta Ridge in the Coast Range ophiolite were also analyzed for comparison (Fig. 1, Table 1). All samples are serpentinized >~95% and consist of lizardite with trace amounts of chrysotile (mineralogy determined by XRD using the Bruker D8 Advance X-Ray Diffractometer at the University of Texas at Austin). Relict pyroxenes are preserved only in sample RM11-4. Relict chromium-rich spinels are present in all samples