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Tectonic origin of serpentinites on Syros, Greece: Geochemical signatures of abyssal origin preserved in a HP/LT subduction complex

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ABSTRACT

This study combines whole rock trace and major element geochemistry, and stable isotope (δD and $\delta^{18}O$) analyses with petrographic observations to deduce the origin and tectonic setting of serpentinization of ultramafic blocks from the exhumed HP/LT Aegean subduction complex on Syros, Greece. Samples are completely serpentinized and are characterized by mineral assemblages that consist of variable amounts of serpentine, talc, chlorite, and magnetite. δD and $\delta^{18}O$ values of bulk rock serpentinite powders and chips ($\delta D = -64$ to $-33‰$ and $\delta^{18}O = +5.2$ to $+9.0‰$) reflect hydration by seawater at temperatures <250 °C in an oceanic setting pre-subduction, or by fluids derived from dehydrating altered oceanic crust during subduction. Fluid-mobile elements corroborate the possibility of initial serpentinization by seawater, followed by secondary fluid-rock interactions with a sedimentary source pre- or syn-subduction. Whole rock major element, trace element, and REE analyses record limited melt extraction, exhibit flat REE patterns, and do not show pronounced Eu anomalies. The geochemical signatures preserved in these serpentinites argue against a mantle wedge source, as has been previously speculated for ultramafic rocks on Syros. Rather, the data are consistent with derivation from abyssal peridotites in a hyper-extended margin setting or mid-ocean ridge and fracture zone environment. In either case, the data suggest an extensional and/or oceanic origin associated with the Cretaceous opening of the Pindos Ocean and not a subduction-related derivation from the mantle wedge.

1. Introduction

Serpentinized ultramafic rocks are found in most subduction-related metamorphic complexes as massive bodies, exotic blocks, or fine-grained matrix within shear zones. Often, field relationships alone are not sufficient to determine the tectonic origin of serpentinites captured in exhumed subduction complexes and orogenic shear zones. The history of serpentinites can be further obscured by complete replacement of primary minerals or textures, making it difficult to distinguish between serpentinites originating from seafloor-altered peridotite (i.e., mid-ocean ridges and fracture zones or hyper-extended margins) and hydrated mantle wedge (fore-arc) peridotite. However, recent compilations of global serpentinite data demonstrate that whole rock major and trace element geochemistry can be used to fingerprint different tectonic settings due to unique signatures of immobile and fluid-mobile elements created during melt-rock interaction and serpentinization (Deschamps et al., 2013; Kodolanyi et al., 2012). In particular, serpentinized mantle from an abyssal origin is distinguishable from a mantle wedge origin based on variable enrichments in trace and major element chemistry and stable isotope signatures (e.g., Barnes et al., 2009, 2014; Dai et al., 2011; Deschamps et al., 2013; Hattori and Guillot, 2007; Kodolanyi et al., 2012; Li and Lee, 2006; Savov et al., 2005). This distinction is critical for studies that use ultramafic rocks in exhumed subduction complexes as a window into geochemical and geodynamic processes at the slab-mantle interface, as it has direct implications for modeling elemental fluxes and rheology during subduction, and a wide range of ramifications for tectonic reconstructions.

Geochemical signatures recorded in serpentinites are a complex combination of protolith partial melting, melt-rock interaction history, and serpentinization conditions. In general, serpentinization is isochemical with respect to most major elements, high field strength elements (HFSE; Nb, Ta, Zr, Hf), medium and heavy rare earth elements (M-HREE), and transition metals (Sc, V, Cr, Co, Ni, Cu, Zn, Ga), all of which show limited mobility on a hand specimen scale (Deschamps et al., 2013; Mével, 2003). Therefore, the abundances of these elements may serve as a proxy for melt history prior to serpentinization, indicating the tectonic setting of the protolith peridotite. Some major elements (CaO, SiO_2, MgO), and light REE (LREE) can be mobilized during serpentinization or melt-rock interaction and should be interpreted

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with caution (Malvoisin, 2015; Milliken et al., 1996; Paulick et al., 2006; Snow and Dick, 1995).

Fluid-mobile elements (FME; e.g., B, Li, As, Sb, Pb, U, Cs, Sr, Ba) and stable isotopes (O, H) record chemical exchanges between rock and fluid during serpentinization. Serpentinites act as "sponges" for these elements through the incorporation of up to ~13 wt% H_2O (Deschamps et al., 2011; Kendrick et al., 2013; Scambelluri et al., 2004b; Vils et al., 2008). Although all serpentinites show enrichments in FME, the magnitude and range of enrichment differs between tectonic settings depending on the composition of the serpentinizing fluid (Bebout, 2013; Deschamps et al., 2011, 2012; Lafay et al., 2013; Plank, 2014; Scambelluri et al., 2004a, 2004b; Yuan-Hui, 1991). In mid-ocean ridge and hyper-extended margin settings, seawater serves as the primary serpentinizing fluid and contributes enrichments in Eu, B, Cl, U, Sr, and Li (Kodolanyi et al., 2012). Slab-derived fluids are produced during the dehydration of sediments and altered oceanic lithosphere in the subduction channel and can contribute As, Sb, Ti, Cs, Sr, Rb, Li, and LREE to the serpentinized mantle wedge (Deschamps et al., 2010, 2013; Hattori and Guillot, 2007; Savov et al., 2005, 2007).

Seawater, meteoric water, and slab-derived serpentinizing fluids impart diagnostic stable isotopic signatures (O and H) and may serve as indicators of the tectonic setting of serpentinization, namely seafloor, continental, or subduction-related (Alt and Shanks, 2006; Barnes et al., 2013, 2014; Burkhard and O'Neil, 1988; Cannaò et al., 2016; Cartwright and Barnicoat, 1999; Früh-Green et al., 1990, 1996, 2001; Kyser et al., 1999; Sakai et al., 1990; Skelton and Valley, 2000; Tzen-Fu et al., 1990). Unaltered peridotite has average bulk $\delta^{18}O$ and δD values of ~ +5.5‰ and ~ −80‰, respectively (Eiler, 2001; Kyser and O'Neil, 1984; Mattey et al., 1994). Serpentinites exhibit deviations from peridotite values based on the isotopic composition of the serpentinizing fluid and the temperature of the interaction. The oxygen isotope composition can distinguish between the contribution of seawater or subduction-related metamorphic fluids during serpentinization. Hydrogen isotope compositions are more easily reset by subsequent fluid overprinting, and can be useful to measure the extent of interaction with meteoric water once the serpentinites have been exposed at the surface. Hence, stable isotopes may be used in conjunction with FME to constrain the tectonic setting of serpentinization and the degree of post-exhumation overprinting (Barnes et al., 2009, 2013, 2014; Burkhard and O'Neil, 1988; Cartwright and Barnicoat, 1999; Deschamps et al., 2010; Früh-Green et al., 2001).

In this study, we investigate the tectonic origin of the serpentinites found on the island of Syros, Greece. Syros is famous for its preservation of eclogite- and blueschist-facies rocks associated with serpentinites in multiple meta-ophiolitic outcrops (Katzir et al., 2007; Keiter et al., 2011; Ridley and Dixon, 1984). Well-known as an analogue for subduction zone processes, Syros has been used as a natural laboratory to investigate geochemical fluxes across the slab-mantle interface (Ague, 2007; Breeding et al., 2004; Miller et al., 2009), the formation of blackwall reaction rims between mafic and ultramafic rocks in subduction zones (Marschall et al., 2006; Miller et al., 2009; Pogge von Strandmann et al., 2015), as well as to understand the dynamics of subduction and exhumation of high pressure - low temperature (HP/LT) terranes (Keiter et al., 2004; Trotet et al., 2001a). Although many studies have investigated the mechanisms of element transfer between the subducting oceanic crust and the overlying mantle wedge using the lithologies found on Syros, there has been no systematic study to address the tectonic origin of the serpentinites.

Previous studies have speculated that serpentinization occurred at a late stage of the subduction-exhumation history of Syros based on two reported mantle-like oxygen isotope values and preserved serpentine mesh texture from one location on the island (Pogge von Strandmann et al., 2015). We expand upon this work using a combination of major element, trace element, and stable isotope geochemistry from serpentinite samples that cover all major occurrences on the island of Syros. We determine whether these serpentinites represent remnants of the mantle wedge, portions of the down-going oceanic slab, or a mixture of both, and whether they support the notion of one ophiolite on Syros, as has been suggested (Keiter et al., 2011), or are derived from multiple, unrelated ophiolitic slices. Moreover, we are able to address whether serpentinization took place on the seafloor by seawater during Cretaceous rifting and seafloor spreading (likely associated with the Pindos Ocean), during subduction and/or exhumation by slab-derived fluids, or post-obduction via meteoric water.

2. Geologic background

2.1. Tectonic history

Syros is part of the greater Aegean subduction complex, which represents the continuous subduction of the African plate below the Turkish-Aegean plate (Jolivet and Brun, 2010; Keiter et al., 2011; Le Pichon and Angelier, 1979; McKenzie, 1970; Papanikolaou, 2013; Reilinger et al., 2006). From as far north as the Balkans, systematic age variations in arc magmatic intrusions and volcanic rocks in the Aegean record the consistent southward migration of the subduction trench since the late Cretaceous to its present position south of Crete (Fytikas et al., 1984; Pe-Piper and Piper, 2002).

Though long-lived and undoubtedly nuanced, the history of the Aegean subduction complex is well constrained due to the unique preservation of lithologies that record different portions of the subduction and exhumation history. Specifically, the Cycladic Blueschist Unit (CBU) hosts spectacularly preserved blueschist and eclogite outcrops, which place peak temperatures for HP-LT subduction of the unit at ~500–550 °C and pressures at ~18–20 kbar in the Eocene (Okrusch and Bröcker, 1990; Ridley, 1984; Ridley and Dixon, 1984; Trotet et al., 2001b). Likewise, limited greenschist metamorphic overprinting from Miocene-age exhumation via back-arc extension and metamorphic core complex formation has allowed for the determination of additional P-T-t constraints (Bröcker and Keasling, 2006; Keiter et al., 2011; Miller et al., 2009; Ring and Layer, 2003; Soukis and Stockli, 2013; Trotet et al., 2001b).

The majority of Syros is composed of the CBU, belonging to the lower unit of the Attic-Cycladic Crystalline Complex (Okrusch and Bröcker, 1990). The CBU on Syros is a series of stacked tectonic units that include Variscan basement gneiss, Triassic and Jurassic continental margin metasediments, and Cretaceous ophiolite slices (Bulle et al., 2010; Dürr et al., 1978; Keay, 1998; Keiter et al., 2011; Okrusch and Bröcker, 1990; Tomaschek et al., 2003). The ophiolite slices, often referred to as the 'metabasite unit' (Keiter et al., 2011; Seck et al., 1996; Tomaschek et al., 2003; Trotet et al., 2001a), include meta-mafic and meta-sedimentary fragments of oceanic crust in association with serpentinized ultramafic rocks (Bonneau, 1984; Bröcker and Enders, 2001; Broecker and Enders, 1999; Hopfer and Schumacher, 1997). Petrology and geochemical analyses of individual blocks within these ophiolite slices have identified them as the high-pressure equivalents of basalt, tuff, plagiogranite, gabbro, serpentinized mantle, and marine sediments, suggesting an oceanic lithosphere precursor (Katzir et al., 2007; Keiter et al., 2011; Seck et al., 1996). This interpretation is supported by well-preserved pillow and cumulate textures in larger blocks (Keiter et al., 2011).

Though these lithologies clearly indicate that the subducted package derived from an oceanic precursor, the tectonic setting of this oceanic slab has remained enigmatic. Researchers have speculated both a confined back-arc basin setting on the northern edge of the Tethys Ocean, or a mid-ocean ridge setting based on geochemistry (Lagos et al., 2002; Mocek, 2001; Seck et al., 1996). The CBU's interlayered schists and marbles have been interpreted as remnants of a Mesozoic passive margin sequence, dated by Triassic neritic fossils (Okrusch and Bröcker, 1990) and zircon U-Pb ages (Tomaschek et al., 2001), whereas the meta-igneous blocks have been interpreted as remnants of a