



Boron isotope systematics of a fossil hydrothermal system from the Troodos ophiolite, Cyprus: Water–rock interactions in the oceanic crust and subseafloor ore deposits

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ABSTRACT

We determined concentrations and isotopic compositions of boron in a complete section of the hydrothermally altered Cretaceous oceanic crust of the Troodos ophiolite. The boron content and $\delta^{11}\text{B}$ value for each lithological section are: pillow lava (3.8–206.8 $\mu\text{g/g}$, 63 $\mu\text{g/g}$ average; $\delta^{11}\text{B} = +0.17\%$ to $+15.6\%$, $+8.1\%$ average), sheeted dike complex (0.6–18.0 $\mu\text{g/g}$, 4.0 $\mu\text{g/g}$ average; $\delta^{11}\text{B} = +3.3\%$ to $+10.6\%$, $+6.0\%$ average), and plutonic complex (0.3–8.4 $\mu\text{g/g}$, 1.7 $\mu\text{g/g}$ average; $\delta^{11}\text{B} = -1.7\%$ to $+18.5\%$, $+4.5\%$ average). These boron contents are higher than the estimated original igneous values throughout the oceanic crust, indicating uptake of boron from seawater and hydrothermal fluid at temperatures ranging from ≤ 50 °C to >300 °C. Although our boron data for the Troodos ophiolite are generally consistent with those for the Oman ophiolite of similar age, the distinctly low $\delta^{11}\text{B}$ values of the lower gabbro section in the Troodos ophiolite ($<+3\%$) suggest reaction with ^{11}B -depleted fluid at a very small water/rock ratio. The boron content of the bulk oceanic crust (12.3 $\mu\text{g/g}$) estimated for the Troodos ophiolite is relatively high as a result of strong boron enrichment in the pillow lava section, which underwent prolonged seafloor weathering. Despite these differences, the weighted average $\delta^{11}\text{B}$ value of the bulk oceanic crust ($+7.6\%$) is similar to that of the Oman ophiolite ($+7.9\%$). We also analyzed the boron isotope geochemistry of a subseafloor hydrothermal stockwork sulfide deposit in the Troodos ophiolite to investigate its formation processes. In contrast to the normal upper oceanic crust, the $\delta^{11}\text{B}$ values of the rocks below the ore body decrease with increasing depth and have large negative values (-6%) in the highly altered uppermost dike section. These low $\delta^{11}\text{B}$ values are coupled with high boron contents (2.5–17 $\mu\text{g/g}$) and high and uniform $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (0.7064 average), and are unlikely to have resulted from interactions with fluids at a small water/rock ratio. These characteristics are better explained by interaction of ore-forming hydrothermal fluids with oceanic crust that had previously been enriched in boron through hydrothermal alteration at low temperatures. These observations demonstrate that boron and boron isotopes are useful for quantitative evaluation of fluid-related processes with multiple stages, including petrogenesis of hydrothermal ore deposits.

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1. Introduction

Boron is a powerful tracer for understanding various igneous and fluid-related geochemical processes. Because of its high incompatibility in magmatic systems and its high mobility in fluids, boron is strongly concentrated in surface reservoirs (5 to 500 $\mu\text{g/g}$) compared to the upper mantle (<1 $\mu\text{g/g}$; Chaussidon and Jambon, 1994). The boron

isotope ratio ($^{11}\text{B}/^{10}\text{B}$) varies widely in natural systems, and each geochemical reservoir has its particular boron isotopic composition: for example, $\delta^{11}\text{B}_{\text{seawater}} = +39.5\%$, $\delta^{11}\text{B}_{\text{upper mantle}} = -7\%$, and $\delta^{11}\text{B}_{\text{mean continental crust}} = -10.5\%$ (Spivack and Edmond, 1987; Chaussidon and Albarède, 1992; Chaussidon and Jambon, 1994).

Three major fluid-related processes that affect the oceanic crust are hydration by hydrothermal alteration at mid-ocean ridges, seafloor weathering, and dehydration during subduction at convergent margins. Boron isotope data have been applied to elucidate these processes. The strong boron enrichment and high $\delta^{11}\text{B}$ generally observed in the upper oceanic crust reflect uptake of seawater-derived boron during seafloor weathering and hydrothermal alteration at various temperatures (e.g., Spivack and Edmond, 1987). Boron enrichment and high $\delta^{11}\text{B}$ in

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arc magmas are interpreted as the contribution of boron-rich fluids or melts liberated from the subducting oceanic slab to the mantle wedge (e.g., Morris et al., 1990; Palmer, 1991a; Ishikawa and Nakamura, 1994; Tonarini et al., 2001).

For quantitative understanding of these fluid-related processes, the spatial distribution of boron content and boron isotopes in the altered oceanic crust is essential information. However, boron data from ocean drilling in the intact oceanic crust is restricted to lava and sheeted dike sections of the upper crust (Spivack and Edmond, 1987; Ishikawa and Nakamura, 1992; Smith et al., 1995). Recently, vertical profiles of boron content and $\delta^{11}\text{B}$ value in an oceanic crustal section from the uppermost pillow lava to the lowermost gabbro were reported for the Oman ophiolite, which represents Cretaceous oceanic lithosphere formed at a fast-spreading ridge system (Yamaoka et al., 2012). These results showed that the hydrothermally altered gabbro section is considerably enriched in ^{11}B , and the $\delta^{11}\text{B}$ value estimated for the bulk oceanic crust (+7.9‰) is much higher than a previous estimate (+3.7‰) that was based on composite data from oceanic crust in different settings (Smith et al., 1995). Profiles of boron concentration and $\delta^{11}\text{B}$ have the potential to vary in different oceanic crusts because the mode of hydrothermal alteration reflects the influences of tectonic structure associated with different spreading rates. Therefore, studies of the boron isotopes in oceanic crustal sections require examples from varied tectonic settings.

Seafloor hydrothermal systems also produce sulfide ore deposits. Most massive sulfide deposits form a mound on the seafloor immediately adjacent to the stockwork zone, indicating precipitation of metal from vent fluids emitted from the seafloor. The TAG active hydrothermal mound on the Mid-Atlantic Ridge is an example of such exhalative-type ore deposits (Humphris et al., 1995; Hannington et al., 1998). Cyprus-type massive sulfide deposits, found in many ophiolites, are regarded as fossil examples of ore-forming processes in modern hydrothermal systems. However, some of the largest deposits in ophiolites consist only of stockwork ore, with little or no massive sulfide. These stockwork-type ore deposits are thought to have formed below the seafloor from the subsurface mixing of cold seawater with upwelling hydrothermal fluids (Cann et al., 1987; Herzig and Friedrich, 1987). Difficulties in observing this setting have hampered studies of stockwork-type ore deposits in the modern ocean (Alt et al., 1986; Alt, 1995). Although boron isotopes have been studied in hydrothermal vent fluids (Palmer, 1991b; You et al., 1994; James et al., 1995), no boron isotope data are available for the underlying altered oceanic crust associated with ore solution. Boron isotope studies of ore deposits will improve our knowledge of the ore-forming processes associated with seafloor/subseafloor hydrothermal activity.

The Troodos ophiolite is a fragment of oceanic lithosphere that formed during the Cretaceous. Although most ophiolites have critical differences from modern oceanic crust, they offer unique opportunities to investigate a complete sequence of the oceanic crust. In the Cyprus Crustal Study Project in the 1980s, the International Crustal Research Drilling Group recovered several cores from the Troodos ophiolite (Cyprus Crustal Study Project Initial Report, 1987, 1989, 1991). The whole vertical sequence of the oceanic crust, from extrusive rocks to the basal plutonic complex, was recovered from holes CY1 and CY4. Samples from hole CY2A, which penetrated a mineralized stockwork-type ore deposit (Agrokippia B) within pillow lava and underlying sheeted dikes, have led to many detailed mineralogical and geochemical studies (e.g., Herzig and Friedrich, 1987; Thy, 1987; Baragar et al., 1989; Bednarz and Schmincke, 1989; Alt, 1994).

In this study, we determined concentrations and isotope compositions of boron in rock samples from these drill cores and from well-characterized outcrops in the Troodos ophiolite. The objectives of this paper are (1) to describe the distribution of boron and boron isotopes in the hydrothermally altered Troodos oceanic crust and (2) to elucidate the origin of subseafloor stockwork-type ore deposits from boron isotope systematics.

2. Geological settings

The Troodos ophiolite, on the island of Cyprus in the eastern Mediterranean Sea, is a fragment of Cretaceous oceanic lithosphere (Fig. 1). The ophiolite formed around 90–92 Ma according to U–Pb ages from zircon in plagiogranites (Mukasa and Ludden, 1987). Although the various ophiolites in the eastern Mediterranean region formed in different tectonic settings (Robertson, 2002), geochemical studies on fresh volcanic glasses have concluded that the Troodos ophiolite was formed by seafloor spreading above a supra-subduction zone (Robinson et al., 1983; Rautenschlein et al., 1985). Some structural features suggest that the Troodos oceanic crust formed at a slow-spreading center (Varga and Moores, 1985; Dilek et al., 1990), whereas the paleomagnetic studies suggest that it formed at an intermediate- to fast-spreading center (Allerton and Vine, 1987). It preserves a complete sequence of the oceanic crust, consisting of pillow basalts, sheeted dike complex, and gabbroic and ultramafic cumulates, overlying depleted and tectonized mantle harzburgites. On the basis of glass compositions, two distinct lava suites have been recognized on the northern flank of the Troodos: lower tholeiite lavas (high-Ti series) and upper depleted tholeiite lavas (low-Ti series) (Robinson et al., 1983; Schmincke et al., 1983). The plutonic rocks were formed from multiple magma chambers (Malpas et al., 1989). Although it is suggested that low-Ti lower gabbroic and websteritic cumulates formed from an intrusive magma chamber during an off-axis event, the relations between magma systems of cumulate and volcanic rocks are still unclear (Baragar et al., 1989; Browning et al., 1989; Thy et al., 1989).

The sampling area of this study was not affected by late-stage boninitic magmatic activity that occurs along the east–west trending Arakapas fault zone in southern Cyprus, which is interpreted as a fossil transform fault (Simonian and Gass, 1978; Flower and Levine, 1987). Emplacement of the ophiolite began with a 90° anticlockwise rotation between Maastrichtian and early Eocene time, and episodic uplift has continued from the early Miocene to the present (Robertson and Woodcock, 1979; Moores et al., 1984). Emplacement-related metamorphism is limited to late-stage filling of fractures and faults (Gillis and Robinson, 1990).

3. Samples

The samples used in this study are core samples from holes CY1 (35°02'54"N, 33°10'46"E, 475 m core length), CY2A (35°02'40"N, 33°08'55"E, 689 m core length), and CY4 (34°54'06"N, 33°05'38"E, 2263 m core length) as well as samples from well-characterized outcrops along the Akaki River (Fig. 1). Samples from holes CY1 and CY4 and the Akaki River represent oceanic crust that underwent typical hydrothermal alteration near the spreading axis, whereas samples from hole CY2A represent a mineralized stockwork sulfide deposit (Agrokippia B) developed in the lower pillow lava section and the underlying hydrothermal upflow zone.

Hole CY1 penetrated an upper series of low-Ti pillow lava (Fig. 1). It is divided into two of the alteration zones defined by Gillis and Robinson (1988): (1) the Seafloor Weathering Zone (SWZ, 0–275 m) characterized by pervasive alteration ($\leq 50^\circ\text{C}$, high water/rock ratio > 100) and abundant smectite, calcite, Fe-hydroxides, and K-feldspar, and (2) the Low-Temperature Zone (LTZ, 275–475 m) characterized by large variations in the pervasiveness of alteration ($\leq 100^\circ\text{C}$, water/rock ratio > 20) and abundant smectite, celadonite, zeolite, and calcite. The development of secondary minerals tends to be controlled by the porosity of the rock (Gillis and Robinson, 1991).

Hole CY4 penetrated the lower sheeted dike complex (0–675 m), the upper gabbro and sporadic dikes (675–1330 m), and the layered lower gabbro and ultramafic (websteritic) cumulates (1330–2263 m; Fig. 1). Geophysical data suggest that the petrologic Moho is about 500 m deeper than the bottom of CY-4 (Robinson, 1989). The dikes consist of interfingering low-Ti and high-Ti series rocks altered to greenschist-facies mineral assemblages containing albite, chlorite, actinolite, quartz,

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