



# Fingerprinting fluid sources in Troodos ophiolite complex orbicular glasses using high spatial resolution isotope and trace element geochemistry

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## Abstract

The Troodos igneous complex (Cyprus) is a ca. 90 Ma old, well preserved supra-subduction zone ophiolite. Troodos is unique in that it shows evidence of fluid-saturation throughout the complex, from its base (i.e. podiform chromitites) to its uppermost units – the upper pillow lavas (UPL). However, it is unclear what the source of dissolved water in UPL tholeiites is, with possibilities including shallow seawater infiltration, assimilation of altered Troodos oceanic crust, recycled serpentinized oceanic crust, or subducted pelagic sediments. In order to identify and characterize these components we have carried out a detailed high-resolution study on tholeiitic lavas on orbicular structures and glasses from the UPL in Troodos. Basaltic orbicules were measured for their Sr–Nd–Hf–Pb isotope compositions, and *in situ* for their B isotopes using LA-MC-ICP-MS. UPL orbicules display a very narrow range in  $\epsilon\text{Nd}$  and  $\epsilon\text{Hf}$  (+7 to +8 and +13 to +15, respectively) indicating melting of a depleted mantle source. Lead isotopes, specifically  $^{207}\text{Pb}/^{204}\text{Pb}$  vs.  $^{206}\text{Pb}/^{204}\text{Pb}$ , form a mixing array with pelagic sediments. Furthermore, high-resolution characterization of individual orbicules revealed that UPL tholeiites display strong variability in  $^{87}\text{Sr}/^{86}\text{Sr}$  (0.7039–0.7060) at the outcrop scale. Samples display  $\delta^{11}\text{B}$  between  $-8.2 (\pm 0.5)\text{‰}$  and  $+5.9 (\pm 1.1)\text{‰}$  with an average B content of ca. 5  $\mu\text{g/g}$ . Contrary to expectation, altered orbicules and their associated hyaloclastite matrixes display lower  $\delta^{11}\text{B}$  (down to  $-10\text{‰}$ ) and higher B contents (max. 200  $\mu\text{g/g}$ ) when compared to fresh glass. Furthermore, the orbicules studied here show little or no evidence of interaction with seawater, which is supported by their trace element contents and isotope compositions. When all isotope systems are taken into account, UPL lavas reflect melting of a depleted mantle source that was overprinted by hydrous sediment melts, and potentially, fluid-like subduction components that in part originate from serpentinized oceanic crust. Subsequent low-temperature alteration then drove  $\delta^{11}\text{B}$  to lower values coupled with increased B uptake due to its adsorption into palagonite.

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## 1. INTRODUCTION

The Troodos massif in Cyprus is a late-Cretaceous Supra-Subduction zone ophiolite (Pearce et al., 1984; Osozawa et al., 2012) – i.e. it exhibits field relationships consistent with oceanic crust, yet it displays calc-alkaline lithologies in addition to tholeiitic basalts (Myashiro, 1973). Despite some initial controversy (e.g. Myashiro, 1973 vs. Moores, 1975), there is now a general consensus that Troodos is a supra-subduction zone ophiolite and not a classical mid-ocean ridge ophiolite. One important line of evidence supporting a supra-subduction zone origin for the Troodos ophiolite complex (TOC) is the fact that fresh volcanic glasses found therein have high water contents (2–3 wt.% – Muenow et al., 1990; Cameron, 1985) when compared to mid-ocean-ridge basalts (MORB). This carries interesting implications, as water solubility of MORB at pressures present on the seafloor (e.g. 2000 m or 200 MPa) is only around 1.4 wt.% (Dixon et al., 1995). As such, the high water content in the extrusive lithologies found in the uppermost portions of the Troodos ophiolite suggests that during melting at the mantle source, melts were likely water saturated, and might have lost some of their water on their ascent to the surface. For example, Ballhaus et al. (2015) concluded that fluid saturation in the Troodos ophiolite complex must have occurred at a minimum pressure 150 MPa, based on field observations of outcrops over the entire Troodos crustal sequence. Samples found throughout the Troodos ophiolite show textural evidence of fluid exsolution in the form of ubiquitous orbicular textures (see discussion in Ballhaus et al., 2015). The resulting exsolved fluid is also thought to have played an important role, for example, in the formation of orbicular-shaped pods of chromitite ore at the base of the Troodos sequence (Matveev and Ballhaus, 2002). Selective large ion lithophile element (LILE) enrichment (e.g. Rautenschlein et al., 1985), coupled with the observation that W and Sb are enriched in basalts and boninites from Troodos (König et al., 2008), is suggestive of fluid overprint of their mantle source, and provide additional evidence that fluid-mediated processes were widespread in both Troodos' source regions and in the sections of the ophiolite above them.

The purported fluid immiscibility taking place in the TOC is likely to result in significant geochemical fractionation. As stated by Roedder (2003), all chemical species present – i.e. the elements, their isotopes, and the compounds they form – will become distributed between the two immiscible phases, and the compositional divergence between the two can be extreme. However, the extent to which fluid exsolution will lead to substantial elemental and isotopic fractionation is not well understood. In this regard it is important to pinpoint the source of the water feeding into the TOC, as this provides basic information about the depth where fluid immiscibility occurred, i.e. shallow (interaction with seawater) or at magmatic depth (dehydration of subducted lithologies like MORB and sediments).

Here we present combined *in situ* major and trace element data, as well as Sr–Nd–Hf–Pb and B isotope data

on fresh glass samples of primitive lavas from the upper pillow lava (UPL – 1) unit of the TOC. We aim to utilize these geochemical tracers to constrain the principal source of water present in the UPL. Boron isotope systematics of UPL phases are then used to assess whether this stable isotope system may be used to trace the putative fluid exsolution taking place at the Troodos as suggested by Ballhaus et al. (2015). Moreover, the isotope information presented here will help to narrow down the exact source of water feeding into the lithologies present in Troodos (eg. sediment melts, assimilation, seawater infiltration, etc.).

## 2. GEOLOGICAL SETTING AND SAMPLING

The TOC extends over an area of ca. 3000 km<sup>2</sup> forming the core of the island of Cyprus (Fig. 1A). It represents an extremely well preserved and complete section of oceanic crust, comprising all lithologies between the upper mantle and Cretaceous marine sediments (Fig. 1B Gass, 1968; Regelous et al., 2014). The TOC comprises a lower sequence of ultramafic lithologies (e.g. harzburgites, dunites, chromitites) that have been extensively serpentinized, overlain by gabbro and a sheeted dyke complex, and evolved tholeiitic arc andesites and dacites (Fig. 1B). The latter are topped by a series of more primitive lavas (UPL) that include picrites and boninites (Cameron, 1985; Rautenschlein et al., 1985). Unlike a lower sequence of pillow lavas, the UPL are not overprinted by hydrothermal alteration, which had ceased by the time the UPL were emplaced.

Even though the bulk of the unit is heavily altered, with the widespread presence of zeolites, calcite and smectite, there are sections which are very well preserved (e.g. Cameron, 1985, König et al., 2008). In some localities of the UPL (i.e. Kapilio, Kalavassos, and Klirou/Akaki river Canyon – Fig. 1) millimetric- to decimetric-sized orbicules of fresh basaltic or bonitic glass are found in the midst of friable material or within a 'hyaloclastite' like matrix (Fig. 2A). Based on their trace element chemistry, UPL lithologies are thought to have been emplaced in a subduction zone setting (Cameron, 1985; Rautenschlein et al., 1985), where subducted sediments were a significant component (e.g. König et al., 2008, and references therein).

This study is focused on 18 fresh basaltic glass samples from UPL localities at Kalavassos, Klirou bridge along the Akaki river canyon, and Kapilio. Basaltic samples are typically glassy or with spinifex-like quench textures, and have a small modal fraction of olivine phenocrysts rich in melt inclusions, accessory Cr-spinel and rare clinopyroxene. Two differentiated samples from Akaki River canyon were also studied. The latter are typically classified as hyaloclastites and can be found in direct contact with basaltic orbicules. Exact sample locations are listed in [Supplementary Table S1](#). For more on the geological and geochemical characteristics of the Troodos ophiolite complex, please refer to the review by Pearce and Robinson (2010) and recent contributions by Regelous et al. (2014) and Ballhaus et al. (2015).

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