

BORON ISOTOPIC COMPOSITION OF IGNEOUS MINERALS AND SECONDARY ALTERATION PRODUCTS IN NAKHLA. L. J. Spivak-Birndorf¹, M. Wadhwa¹ and L. B. Williams¹, ¹School of Earth and Space Exploration, Arizona State University, Tempe, AZ 85287-1404. Lev.Spivak-Birndorf@asu.edu

Introduction: Understanding the role of water in the evolution of the crust of Mars is an important problem in planetary science. Large deposits of aqueous alteration minerals, including phyllosilicates, have recently been detected on the martian surface using remote sensing techniques [1-3]. Martian meteorites also host a variety of secondary minerals that can provide insights into aqueous alteration processes in the martian crust ([4]; and references therein). The nakhlites are among the most aqueously altered martian meteorites and contain relatively abundant (~1-3 vol.%) secondary mineral assemblages known as iddingsite [5]. Constraints on the timing, temperatures and chemical composition of near-surface martian fluids that formed iddingsite in the nakhlites have previously been determined from petrologic and geochemical studies of these secondary phases [4-13].

Boron is relatively soluble and can be readily mobilized in aqueous fluids [14]. The utility of B isotopes for tracing fluid-rock interactions has been demonstrated by several recent studies [15-19]. Boron can adsorb to reactive clay surfaces, including those in the interlayers, during interaction with fluids and the in early stages of diagenesis [16, 17]. Boron is also incorporated into the tetrahedral sites in clay minerals during diagenesis [20]. Clay minerals can therefore preserve information about the chemistry of fluids from which they formed [19]. Boron isotope fractionation during these processes is thought to be controlled by the preference of each B isotope for a different coordination state [21]. The heavier isotope, ¹¹B, prefers to be in trigonal coordination, while the lighter isotope, ¹⁰B, prefers tetrahedral coordination [21]. The fractionation of B isotopes during incorporation into and adsorption onto clay minerals is strongly temperature dependent [19]. As such, if the temperature of the altering fluids and the ¹¹B/¹⁰B ratio of the secondary phases are known, the B isotopic composition of these fluids can be estimated.

There are currently very limited data on the B isotopic compositions of the martian meteorites [22,23]. Furthermore, there are no reported B isotopic measurements of igneous minerals in the nakhlites. In an effort to better constrain the B isotopic compositions of the various (silicate and aqueous fluid) reservoirs on Mars, we present ¹¹B/¹⁰B measurements of iddingsite, pyroxene, and a magmatic inclusion in an olivine grain in Nakhla. Quantifying the various B isotopic reservoirs of Mars is an important step toward understanding the martian geochemical cycle of B and what it can

tell us about the aqueous alteration of the martian crust.

Samples and Analytical Methods: A description of our analytical methods is provided in [23]. Most of the B isotopic measurements of iddingsite were made on a thick section of Nakhla, including all of the post-NH₄Cl exchange analyses [23]. Subsequent to these analyses, the Nakhla thick section was re-polished and two additional thin sections were prepared from it. One of these thin sections was characterized by optical microscopy to identify iddingsite and various igneous minerals. This thin section was ultrasonicated in 1.82% mannitol solution to remove surface contaminant B as previously described [23] and was then gold-coated immediately following this cleaning procedure. The B isotopic compositions of igneous phases (augites and a glassy melt inclusion in olivine) and several areas of iddingsite were measured in the polished gold-coated thin section using the Cameca IMS 6f ion microprobe at Arizona State University (ASU).

Results: The $\delta^{11}\text{B}$ values measured in various mineral phases in Nakhla are shown in Fig. 1. No significant differences in the ¹¹B/¹⁰B ratio were found between different areas of iddingsite analyzed by us in the thick section and the thin section. As such, our previously reported iddingsite data obtained on the Nakhla thick section [23] are presented together with the results of the new measurements of iddingsite on the thin section (solid red symbols in Fig. 1). For comparison, the $\delta^{11}\text{B}$ values measured in iddingsite after the NH₄Cl exchange procedure to remove interlayer B [23] are also shown (open red symbols in Fig. 1). The average $\delta^{11}\text{B}$ of Nakhla iddingsite before ($-5.4 \pm 1.0\text{‰}$) and after ($-5.7 \pm 2.8\text{‰}$) the NH₄Cl exchange are identical within errors ($\pm 1\sigma_{\text{mean}}$). The large errors and considerable scatter in the B isotopic compositions of pyroxene are the result of the low B concentrations ($< \sim 1\text{ppm}$) in this phase. However, the average $\delta^{11}\text{B}$ value for Nakhla pyroxene ($-4.5 \pm 3.0\text{‰}$) is also indistinguishable from that of iddingsite within errors. The magmatic inclusion has a higher B content than the pyroxene, but an identical $\delta^{11}\text{B}$ value within error ($-4.4 \pm 2.5\text{‰}$).

Discussion: The identical B isotopic compositions measured in pyroxenes and a magmatic inclusion in olivine of Nakhla are consistent with a lack of isotopic fractionation between crystals and melt during the formation of igneous rocks [15]. The enrichment of B in the magmatic inclusion relative to pyroxene is also consistent with the incompatible behavior of B in igneous systems [14]. The $\delta^{11}\text{B}$ value of igneous miner-

als in Nakhla is somewhat higher than that reported for igneous minerals in other martian meteorites [22] and may indicate heterogeneity in the B isotopic compositions of martian magmas.

In our previous report, we suggested that the similarity of the $^{11}\text{B}/^{10}\text{B}$ ratios of exchangeable interlayer and tetrahedrally bound B in Nakhla iddingsite could be the result of similar coordination of B in the fluid and minerals (i.e., both tetrahedral) [23]. The speciation and coordination of B in aqueous fluids is pH dependent, with predominately tetrahedrally coordinated B (i.e., present in the fluid as $\text{B}(\text{OH})_4^-$ species) at higher pH [21]. Therefore, it is likely that the pH of the fluids that formed nakhlite iddingsite was somewhat alkaline.

The similarity of B isotopic compositions in primary igneous and secondary alteration phases in Nakhla can also provide insight into the aqueous processing of the crust of Mars. This similarity suggests that the B in iddingsite is derived primarily from the dissolution of the igneous phases, as has been suggested for other trace elements [10]. The similarity of the B isotopic compositions of the igneous minerals, trapped interlayer fluids and iddingsite in Nakhla suggests that no resolvable isotopic fractionation of B occurred during the alteration of this meteorite. If the relatively low-temperature ($<150^\circ\text{C}$; [4-7]) fluids that altered Nakhla had a low pH, fractionation of B isotopes would be expected between these various phases due to the isotopic preference of different aqueous B species. The lack of such fractionation effects suggests that the fluids that altered Nakhla (1) had a relatively high pH and (2) derived their B predominantly from dissolution of the local igneous mineral assemblage.

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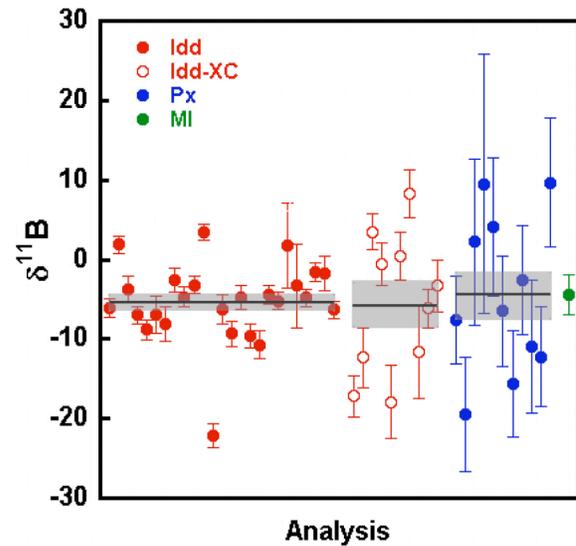


Figure 1. B isotope compositions measured in Nakhla iddingsite (Idd and Idd-XC), pyroxene (Px) and a magmatic inclusion (MI). For iddingsite, closed symbols are pre- NH_4Cl exchange and open symbols are post-exchange. Each data point represents an analysis on a single spot and errors are in-run $\pm 1\sigma_{\text{mean}}$. Solid horizontal lines are averages of all analyses on a particular phase and grey boxes are $\pm 1\sigma_{\text{mean}}$ errors for each of these average values.