

BORON AND LITHIUM CONTENTS AND ISOTOPIC COMPOSITIONS OF THE LUNAR VOLCANIC GLASSES. Alberto E. Saal¹, Marc Chaussidon², Aandrey A. Gurenko³ & Malcolm J. Rutherford¹. ¹DEEPS, Brown University, 324 Brook St., Box 1846, Providence, RI, 02912, USA (*asaal@brown.edu*). ²IPGP, Univ Paris Diderot, UMR 7154 CNRS, F-75005 Paris, France. ³CRPG-CNRS, BP20, 54501 Vandoeuvre les Nancy, Cedex, France.

Introduction: Boron and Lithium are moderately volatile elements and their abundance, isotopic composition and spatial distribution could provide important constraints on models for the thermal and chemical evolution of the Moon's interior. Most of the geochemical inferences about the deepest section of the Moon have been based on studies of the lunar volcanic glasses, representing the most primitive melts recovered by the Apollo mission. Here, following previous work on lunar mare basalts [1, 2, and ref therein], we report new in-situ measurements of Boron and Lithium (B, Li) abundances and isotopic compositions on individual beads of lunar volcanic glasses from the Apollo 15 and 17 landing sites. The new data provide us with a new perspective, not only on the sources and processes that affected the volcanic glasses during and after eruption, but also offer greater insights into the possible Li and B isotope composition of the primitive mantle of the Earth, which has proven problematic due to the large effects on the isotope fractionation associated to the hydrosphere.

Samples and Analytical Techniques: We investigated three main compositional groups of glasses: very low-Ti and low-Ti glasses (sample 15427,41; 15426,138; 15426,32), and high-Ti glasses (sample 74220,864). The glassy spherules range in size from 100 to 300 μm for 74220,864 and from 200 to 400 μm with two outliers of ~ 700 μm for 15427,41. Not all of the glass beads are completely glassy; some of them, show extremely fine crystallization of either olivine (15427,41) or olivine and ilmenite (74220,864). Also, we were able to recognize five compositional subgroups (A, B, C, D and E) of Delano's very-low-Ti glasses [3]. The major, trace and volatile (H, C, F, S, Cl) elements contents of the lunar volcanic glasses studied have been previously reported [4-7]. Lunar volcanic glass beads were individually handpicked, mounted into indium metal contained in an aluminum metal disc, and then polished in such a way as to attempt to expose the precise geometric center of as many beads as possible. The sample mount was polished to 1 μm quality with diamond paste, cleaned with distilled water, dried in a vacuum oven and then gold coated. The abundances of B and Li and $^{11}\text{B}/^{10}\text{B}$ and $^7\text{Li}/^6\text{Li}$ ratios dissolved in the interior of the lunar volcanic glasses were measured by SIMS using a Cameca IMS 1280 at the Centre de Recherches Pétrographiques et Géochimiques (CRPG-CNRS, Nancy, France), employing methods previously developed for chondrules,

CAIs, glasses and minerals [8]. Li and B were measured independently in subsequent analytical sessions. Standards and samples were sputtered with an $^{16}\text{O}^-$ primary beam of 15 nA intensity for Li, and 20-40 nA for B. Secondary positive ions of Li and B were accelerated at 10 kV and analyzed at a mass resolution of ~ 2000 . We used a $\approx 25\mu\text{m}$ primary beam rastered at $5\times 5\mu\text{m}$, which results in a ≈ 35 μm crater. Counting times were 10s for ^6Li and 5s for ^7Li , 16s for ^{10}B , 4s for ^{11}B and 4s for $^{28}\text{Si}^{++}$ and the secondary ions were collected by ion counting. Each analysis consisted of 80 cycles (~ 30 min) for Li and 300 cycles (~ 3 hs) for B with 1 and 5 min of pre-sputtering, respectively. Concentrations of Li and B were calculated using MPI-DING glass standards [9] with errors $< 5\%$ (2σ). The Li and B isotopic ratios are expressed as $\delta^7\text{Li}$ and $\delta^{11}\text{B}$ values relative to NBS-LSVEC (12.0192) and NBS 951 (4.04558). The instrumental mass fractionation factors (IMF) used to calculate $^7\text{Li}/^6\text{Li}$ and $^{11}\text{B}/^{10}\text{B}$ ratios were determined from repeat analyses of GOR132G and GOR128G reference glasses, with typical a values of 1.040 and 0.970; and the average error in the isotope ratios were $< 1\%$ and $< 1.5\%$ (1σ) respectively.

Results and Discussion: $\delta^7\text{Li}$ and $\delta^{11}\text{B}$ values measured in ~ 50 beads (25 very low-Ti, 8 low-Ti and 17 high-Ti glasses) range from 2 to 9‰ and -4 to -12‰, respectively. The Li and B concentrations range from 3 to 17 ppm and 0.3 to 4 ppm, respectively. The largest variation in isotopic composition is defined by the very low-Ti glasses, which have the lowest Li and B contents of all the compositional groups. Part of these variation seems to be related to the major element contents of the five compositional subgroups (A, B, C, D and E) of Delano's very-low-Ti glasses. The low- and high-Ti glasses show more restricted isotopic composition and significantly higher Li and B contents (a factor of 4 for Li and 10 for B) consistent with their higher incompatible trace and volatile element contents [4-7]. Within each group, there is no clear correlation between the Li and B concentration and their isotopic compositions, only a subtle inverse correlation is observed for Li content and $\delta^7\text{Li}$ in the low-Ti glasses. Interestingly, we noticed a positive, although noisy, correlation between $\delta^7\text{Li}$ and $\delta^{11}\text{B}$ defined by the glass bead analyses for each compositional group.

The average $\delta^{11}\text{B}$ for each one of the three compositional groups is -9 ‰, value significantly lower than the -5‰ presented by Zhai et al. [2] in mare basalts.

The $\delta^{11}\text{B}$ of the lunar glasses are consistent with the Earth's primitive mantle value proposed by Chaussidon and Marty [10], and slightly lower than those proposed by Marschall et al. [11]. The average $\delta^7\text{Li}$ values for the very low- and low-Ti glasses are 7‰, but the high-Ti glasses have an average $\delta^7\text{Li}$ of 4 ‰. There is no positive correlation between $\delta^7\text{Li}$ and Li concentrations as previously observed for the low- and high-Ti mare basalts [1]. Furthermore, the high-Ti glasses is the only group with $\delta^7\text{Li}$ consistent with the values proposed for the Earth's mantle [11].

In order to unravel the observed intra-group variations, we did several profiles for $\delta^7\text{Li}$, $\delta^{11}\text{B}$, Li and B contents in two large glass beads ($\sim 700\mu\text{m}$) of very-low and low-Ti compositions. We observed significant variation in concentration and isotopic composition within each grain. Although the variations are more significant in the very low-Ti glass due to the lower Li and B concentrations, both beads define two components characterized by the presence of rims with extreme isotopic compositions in $\delta^7\text{Li}$ of 11 to 8‰ and $\delta^{11}\text{B}$ of -14 to -9 ‰, and high Li and B contents; and cores with $\delta^7\text{Li}$ of 5 to 6.5‰ and $\delta^{11}\text{B}$ -3 to -5‰, and lower Li and B concentrations.

The isotopic composition defined by the profiles in single beads reproduce the total variation defined by single spot analyses for the very-low and low Ti glasses analyzed. Interestingly, the data for the profile in the low-Ti glass, once the analysis with high $\delta^7\text{Li}$ and low $\delta^{11}\text{B}$ measured on the rim is excluded, define a nice trend of decreasing $\delta^7\text{Li}$ and $\delta^{11}\text{B}$ with increasing distance from the core; a trend suggestive of kinetic magmatic degassing. Furthermore, the values from this single profile define a similar positive trend in the $\delta^7\text{Li}$ versus $\delta^{11}\text{B}$ outlined by the single spot analyses of the individual glasses. In contrast, the data for the profile in the very low-Ti glass do not define a kinetic degassing trend in $\delta^7\text{Li}$ versus $\delta^{11}\text{B}$, but a relatively flat, or even, negative trend. We believe that the lack of a degassing trend in the profile of the very low-Ti glass is due to its lower Li and B concentrations, a factor of 4 and 10, than those in the low-Ti glass, respectively. These lower concentrations make the very low-Ti glass more susceptible to modifications by the enriched Li and B surface component during kinetic interaction.

Although the core compositions of both beads are consistent with values previously presented for Luna mare basalts, the extreme $\delta^7\text{Li}$ and $\delta^{11}\text{B}$ and high Li and B concentration of the rims define a component that, because of its high Li and B concentrations, cannot be produced by either solar wind implantation or cosmic ray spallation [12]. This unusual rim composition might be produced by the generation of magmatic gas enriched in highly and moderately volatile elements

during fire-fountain eruption, with the gas interacting back with the melt or hot glass during cooling and formation of the surface correlated elements observed in the lunar volcanic glasses [13].

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