LITHIUM ISOTOPE MEASUREMENTS OF PYROXENES AND EVALUATION OF MATRIX EFFECTS IN SIMS ANALYSES: APPLICATION TO MARTIAN METEORITES.

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Introduction: In recent years, several studies have attempted to quantify the original magmatic water content of parental melts from which the martian meteorites crystallized. While numerous techniques have been employed to measure "water" in its various forms (e.g., OH, H_2O) in both the hydrous and anhydrous phases hosted within the martian meteorites, the analytical challenges involved often make the results ambiguous.

Most recently, researchers have attempted to quantify the volatile content of these melts through indirect methods involving measurements of the abundances and distributions (and, in some cases, isotopic ratios) of elements that have strong affinities for volatile phases (e.g., B, Li)[1-6]. However, such studies have been complicated by the fact that the magmatic signatures for these elements may be altered by diffusive re-equilibration during post-crystallization cooling of the rock. They may also be hindered by incomplete understanding of the magnitude of matrix effects associated with the analysis of isotopic (e.g., $^7Li/^6Li$) ratios by in situ analytical techniques such as secondary ion mass spectrometry (SIMS). For instance, variations in major element compositions substantially affect the $^7Li/^6Li$ ratios measured in olivine by SIMS (1.3‰ / mol% Fo) [7]. Such effects, if found to be present in pyroxenes, could potentially account for a significant portion of previously observed $^7Li/^6Li$ variations in martian meteorite pyroxenes. Although the magnitude of such effects in pyroxenes is believed to be small [1], these remain to be evaluated quantitatively.

Therefore, we have initiated a systematic study of $^7Li/^6Li$ ratios in well-characterized homogeneous terrestrial clinopyroxene megacrysts with Mg# ranging from 60 to 93. We performed SIMS measurements on polished fragments of these megacrysts. For evaluating matrix effects associated with major element compositional variations, we additionally performed solution-based multicollector inductively coupled plasma mass spectrometer (MC-ICPMS) analyses on fractions from the same megacrysts. These results were then applied to $^7Li/^6Li$ ratios obtained on martian meteorite pyroxenes by SIMS analyses.

Samples and Methodology: Clinopyroxene samples consisted of cm-sized compositionally homogeneous aluminous augite megacrysts from Dish Hill, California (Mg# 64-83) and subcalcic diopside megacrysts from the Premier and Jagersfontein kimberlites, South Africa (Mg# 86-94). Martian meteorite polished thin sections were obtained from Smithsonian Museum of

Natural History (Shergotty and Zagami) and NIPR (Yamato 000593). Major element zonations in the meteorite pyroxene grains were mapped by backscattered electron (BSE) imaging on a JEOL 845 scanning electron microscope at Arizona State University (ASU) and were used to locate suitable areas for SIMS analyses.
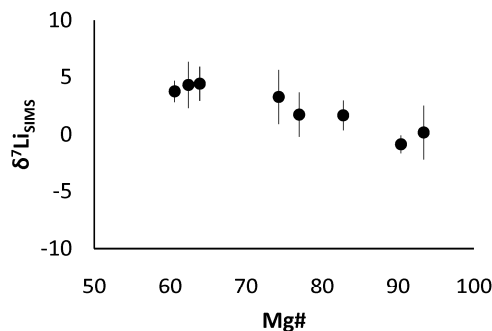

Fig. 1. $^7Li/^6Li$ ratios (expressed in per mil relative to the L-SVEC Li standard, i.e., δ^7Li) measured by SIMS versus Mg# of clinopyroxene megacrysts. Error bars are 2SD uncertainties from multiple analyses on each individual clinopyroxene megacryst.
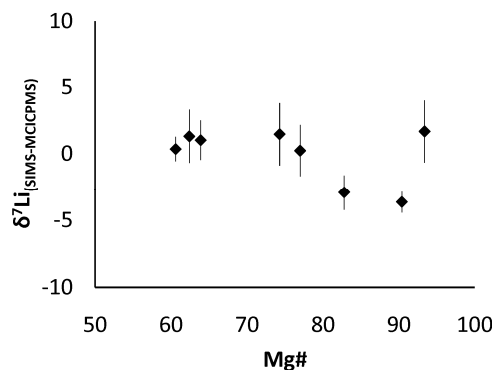

Fig. 2. δ^7Li values from SIMS analyses subtracted from δ^7Li values from solution MC-ICPMS versus Mg# of clinopyroxene megacrysts. Error bars are propagated from the 2SD uncertainties associated with the analyses performed by each technique.

Secondary Ion Mass Spectrometry. Lithium isotope ratios were measured on the Cameca IMS-6f ion microprobe at ASU using methods similar to those described previously [7]. SIMS analyses were conducted with a 5-20 nA O⁻ beam with a spot diameter of 20 to 100 micrometers. After a 6 minute pre-sputter, the counts at the masses of interest ($^6Li^+$, $^7Li^+$) were integrated for 10 and 1 seconds, respectively, for each

cycle, and each measurement consisted of 100 cycles. Interfering $^6LiH^+$ was separated from $^7Li^+$ using high mass resolution (~1200 MRP) and the energy window completely open. The $^7Li^+/^6Li^+$ ratios determined by SIMS were standardized relative to a basaltic glass standard (BCR-2g) [8] and the measured $^7Li/^6Li$ ratios were then renormalized and expressed relative to the NIST L-SVEC standard [9].

Solution-based MC-ICPMS. All chemical procedures were conducted under clean laboratory conditions in the Isotope Cosmochemistry and Geochronology Laboratory (ICGL) at ASU. Fractions of the same terrestrial clinopyroxenes that were analyzed by SIMS were digested in concentrated $HF:HNO_3$ (1:3), dried down and then dissolved completely in concentrated HNO_3. Li was separated from these solutions following the procedures of [10]. Aliquots of dissolved samples were dried and finally brought into solution in 1 mL 5M HNO_3:MeOH (1:4), loaded on a column with BioRad AG50W-X8 (200–400 mesh) resin and Li was eluted with 5M HNO_3:MeOH (1:4). The $^7Li/^6Li$ ratios were measured in the purified Li solutions on the Thermo Neptune MC-ICPMS housed in the ICGL at ASU. Instrumental mass bias was corrected with the sample-standard bracketing technique, using the L-SVEC Li standard. Each analysis run consisted of 20 cycles, with an acquisition time of 8 s for each Li isotope. Isotopic compositions of the samples are given in delta values relative to the NIST L-SVEC standard.

Results and Discussion: Figure 1 shows the $^7Li/^6Li$ ratios (expressed relative to the L-SVEC standard as δ^7Li values) measured by SIMS for each individual megacryst plotted against its Mg#. Subtracting the δ^7Li value obtained by SIMS from that obtained by MC-ICPMS and plotting against Mg# (Fig. 2), it is evident that there do not appear to be any systematic matrix effects in the SIMS analyses that are unambiguously resolvable outside of the typical analytical uncertainties (i.e., ±2-3‰, 2SD). Therefore, such effects are negligible for SIMS analyses of martian meteorite pyroxenes that have major elements compositions well within those evaluated here, but it is possible that corrections may be warranted for more extreme compositional variations.

Figure 3 is a BSE image of Shergotty showing a large zoned pyroxene. We performed a SIMS traverse across the grain, which shows variable δ^7Li values that are atypical for high-temperature magmatic processes. Identical "W" shaped trends, with similar δ^7Li values, were also measured in Zagami. These observed variations are consistent with those reported previously [1, 2,11] and are interpreted to be due to subsolidus diffusive re-equilibration. A SIMS traverse across a large

augite crystal from the Yamato 000593 nakhlite (Fig. 4) displays even larger deviations in δ^7Li values (>30‰ lighter in the core relative to the rim). These results confirm the work of [1,10], where the authors also noted "U" (and "W") shaped trends in δ^7Li values across crystals in several nakhlites suggestive of intra-crystalline post-crystallization mobilization of Li, rather than growth in equilibrium with a degassing melt.
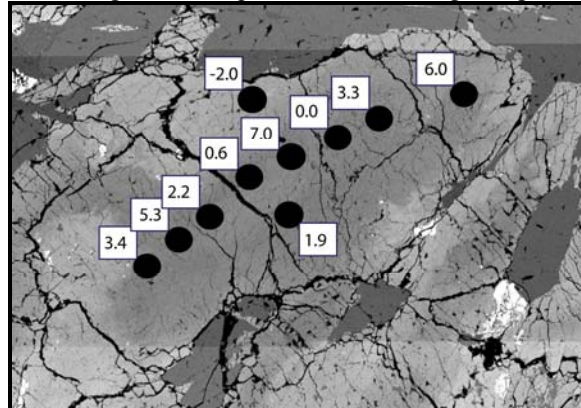

Fig. 3. Typical δ^7Li values for traverses across a Shergotty pyroxene grain (shown here in a BSE image). Typical errors (2SD) are ±2‰. Field of view is 2 mm.
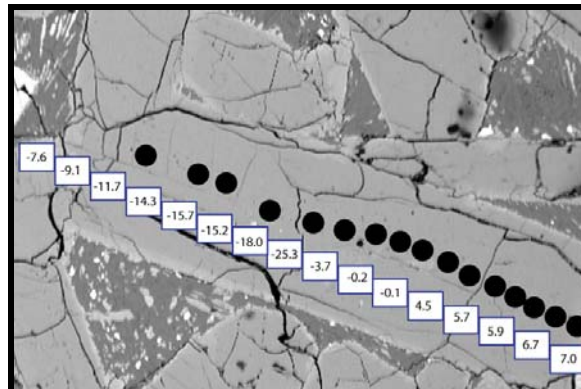

Fig. 4. Typical δ^7Li values for a traverse across a Yamato 000593 pyroxene (shown here in a BSE image). Typical errors (2SD) are ±2‰. Field of view is 2 mm.

This study, along with previous investigations [3-6,12], confirms the interpretations of [1,2] regarding the susceptibility of light elements to mobilization and isotopic fractionation by secondary processes.

References: [1] Beck et al. (2006) *GCA 70*, 4813-4825. [2] Beck et al. (2004) *GCA 68*, 2925-2933. [3] Herd et al. (2004) *GCA 69*, 2431-2440. [4] Lentz et al. (2001) *GCA 65*, 4551-4565. [5] McSween et al. (2001) *Nature 409*, 487-490. [6] Treiman et al. (2006) *GCA 70*, 2919-2934. [7] Bell et al. (2009) *Chem. Geology 258*, 5-16. [8] Kasemann et al. (2005) *Anal. Chem. 77*, 5251-5257. [9] Qi et al. (1997) *Int. J. Mass Spectr. Ion Process 171*, 263-268. [10] Seitz et al. (2004) *Chem. Geol. 212*, 163–177. [11] Anand and Parkinson (2010) *LPS XVI*, 2362. [12] Williams et al. (2010) *LPS XVI*, 2641.