

**ON THE ORIGIN OF Li ISOTOPIC VARIATIONS IN Ca-AL-RICH INCLUSIONS (CAIs).** D. S. Burnett<sup>1</sup>, J. M. Paque, J. R. Beckett and Y. Guan, California Institute of Technology, Pasadena, CA 91125, <sup>1</sup>burnett@gps.caltech.edu.

**Introduction:** A relatively large literature exists on Li isotopic variations in planetary materials with variations relative to the LSVEC standard of  $\pm 30\text{-}40\%$ , except for CAIs, where  ${}^6\text{Li}$  enrichments predominate [1, 2] with variations up to 100%. For CAIs a variety of possible origins for Li isotope variations exist: (a) in-situ decay of  ${}^7\text{Be}$  ([1]=CRM); (b) spallation nuclear reactions by accelerated solar particles [2]; (c) inherited pre-solar unknown nuclear (UN) anomalies; (d) evaporation during CAI formation (e.g., [3]); (e) isotope mixing accompanying alteration events/processes; and (f) isotope fractionation associated with diffusion.

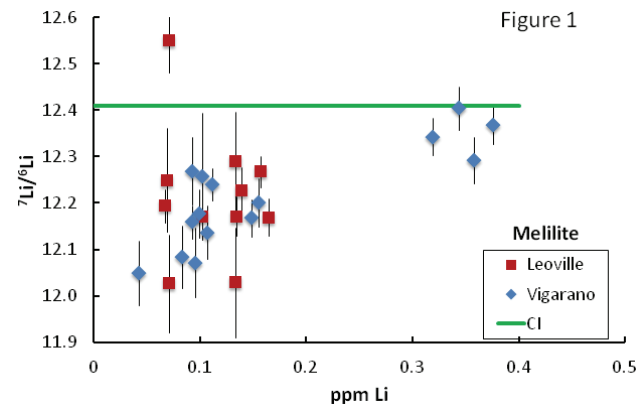
**Sample Selection:** As a moderately volatile element, Li should be depleted in primary CAI material; however, alteration processes potentially add Li from external reservoirs. We therefore selected CAIs with minimal secondary alteration: Leoville 3537-2 (here LV), a type B1 CAI lacking the pervasive Allende type alteration and Vigarano 3138 F6 (here F6), a compact type A CAI that is highly unusual in having  ${}^{16}\text{O}$ -rich melilite [4], i.e., potentially free of any Li associated with the melilite (mel) O isotope exchange observed in most CAIs.

**Experimental:** Analyses were made of mel and clinopyroxene (cpx) in both CAIs using the Caltech Cameca ims-7f Geo. To minimize fractionations from charging, automatic secondary ion energy scans were made every 50 cycles and  $\text{Mg}\pm\text{Ca}$  were analyzed. Secondary ion signals were collected from areas  $\sim 35$  microns in diameter, whereas the primary  $\text{O}^-$  was rastered over  $50\ \mu\text{m}$ , slightly larger than the field aperture, to minimize the effects of surface contamination but without introducing large deadtime corrections. This procedure, plus cleaning and recoating of the LV section, essentially eliminated Li surface contamination.

Standards were custom synthesized to minimize errors due to compositional variations in isotopic mass fractionation and elemental sensitivities (“matrix effects”) as well as to be able to directly relate our measured  ${}^7\text{Li}/{}^6\text{Li}$  to the LSVEC standard. Samples of a type B CAI composition glass (for mel) and a Ti-rich CAI cpx composition glass were spiked with a solution of LSVEC  $\text{Li}_2(\text{CO}_3)$  to levels dominating background Li concentrations, then fused in a piston-cylinder press to minimize Li volatilization losses.

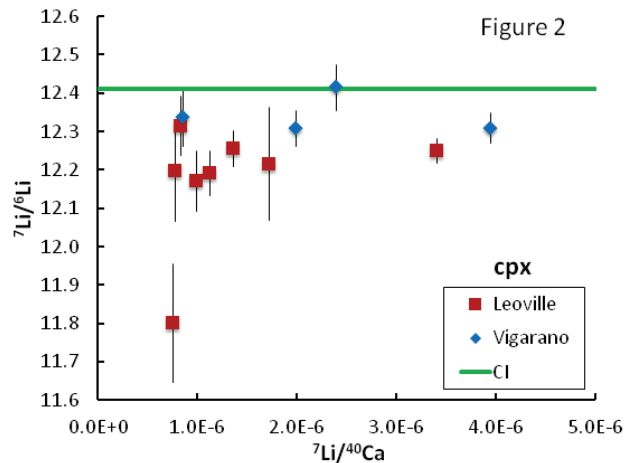
**Results:** CAI Li isotopic variations potentially occur on all spatial scales, so depth profiles for each analysis spot were carefully examined for  ${}^7\text{Li}/{}^6\text{Li}$  vari-

ations exceeding counting statistics (cts) limits. A separate constraint comes from standard reproducibility. For each mel standard profile, 20-50 cycle blocks agree within  $2\sigma$  cts. The measured sigma of the data is only slightly larger than the sigma cts. Replicate analyses agree to within 3%. Reproducibility of the cpx standard is not as good (8%,  $2\sigma$  for replicate analyses), probably because a wider range of primary ion currents was used.



**Melilite.** Fig. 1 shows  ${}^7\text{Li}/{}^6\text{Li}$  for LV and F6 plotted vs. Li concentration. Error bars are 2 sigma. Whenever statistically significant intraprofile variations were found, the different regions are plotted as separate points on the figures. For LV, 4 of 6 profiles are uniform in  ${}^7\text{Li}/{}^6\text{Li}$  to within  $2\sigma$  cts (3%). One anomalous LV point shows intraprofile variations in  ${}^7\text{Li}/{}^6\text{Li}$  of 43%. The other nonuniform profile shows a smaller variation of 22%. For F6 mel, based on secondary ion images, it was not possible to find a  $30\ \mu\text{m}$  spot free of inclusions rich in Ti (cpx?), Mg (spinel?) or, less commonly, Na (alteration?). The cpx inclusions are Li rich compared to mel, thus a potential source of  ${}^7\text{Li}/{}^6\text{Li}$  variations. For F6, 6 out of 9 spots are uniform in  ${}^7\text{Li}/{}^6\text{Li}$  to within  $2\sigma$  cts (3-5%). The other three profiles have variations of 10-15%. The four F6 points around 0.35 ppm Li on Fig. 1 are from one profile. In summary, mel  ${}^7\text{Li}/{}^6\text{Li}$  is mostly uniform on the  $3 \times 35\ \mu\text{m}$  scale of a given depth profile, but even if the one anomalous LV point (highest  ${}^7\text{Li}/{}^6\text{Li}$  on Fig. 1) is excluded, real microscale variations up to 20‰ are present. The points on Fig. 1 show roughly 30‰ variations with no obvious difference between LV and F6. However, the center of gravity of the data overall is  ${}^6\text{Li}$  enriched by 15-20‰ relative to CI chondrites.

**Clinopyroxene.** Fig. 2 shows cpx  ${}^7\text{Li}/{}^6\text{Li}$  for LV and F6 vs. the  ${}^7\text{Li}/{}^{40}\text{Ca}$  counting rate ratio (proportion-



al to Li concentration; cpx elemental standard calibrations are yet to be done). For LV, 5 of 6 profiles are uniform; the 6th has variations of 43%. As a compact type A, cpx in F6 is rare and small, thus hard to analyze. For four grains, the intraprofile  $^7\text{Li}/^6\text{Li}$  are uniform to within  $2\sigma$  cts, but up to 15‰ variations could be present.  $^7\text{Li}/^6\text{Li}$  appears slightly higher in F6. The Li concentrations in F6 cpx are higher than LV, in contrast to mel, where the Li concentrations are similar (Fig. 1).

**Discussion:** Constraints on fractionation mechanisms: (A) *Evaporation.* Our cleanest, and potentially most interesting, conclusion is that we see clear, albeit relatively small,  $^6\text{Li}$  enrichments whereas evaporation (e.g., [3]) should produce relatively large  $^6\text{Li}$  depletions. This suggests that Li is added subsequent to any evaporation event. (B) *Alteration.* Ignoring one anomalous LV point, the data on Fig. 1 are suggestive of mixing of more typical solar system (CI) Li into primary CAI material with excess  $^6\text{Li}$ . The high ppm Li F6 points are from a single high Na melilite spot. (C) *Spallation and UN anomalies.* These are suggested by the overall  $^6\text{Li}$  enrichments (compare [2], [1], and [5]). From any source, non-stellar processes, presumably high energy particle reactions, are required for these nuclei, but quantitative estimates are wildly model dependent. (D)  $^7\text{Be}$ . [1] proposed the presence of  $^7\text{Be}$ , a radioactive nucleus with a 75 day lifetime, during CAI formation. Our relatively low Be/Li samples are not optimum for testing  $^7\text{Be}$  but Figs. 3 and 4 show no evidence for the required increase in  $^7\text{Li}/^6\text{Li}$  with  $^9\text{Be}/^6\text{Li}$ . Data from [6] provide tighter constraints. (E) *Isotope fractionation during diffusion.* This could be important, particularly for the small scale isotopic variations.

*Decoupling of moderately volatile elements and O isotopes.* F6 is a rare CAI in having  $^{16}\text{O}$ -rich mel [4], yet it has relatively high mel Li concentrations (Figs. 1 and 2) and low Be/Li in cpx (Fig. 4). The overall lack

of  $^7\text{Li}/^6\text{Li}$  enrichments means that Li, and possibly other moderately volatile elements, were added subsequent to any major evaporation event; however, this appears to be a separate event/process from that of O-isotope exchange in CAI mel (and anorthite). The number of required separate events/processes in nominally simple materials such as CAIs continues to grow.

**References:** [1] Chaussidon M. et al. (2006) *GCA*, 70, 224–245. [2] Liu M.-C. et al. (2011) *Proc. Sci., 11th Symp. Nuclei in the Cosmos., in press*. [3] Grossman L. et al. (2000) *GCA*, 64, 2879–2894. [4] MacPherson G. J. (2010) *LPS XXXXI*, Abstract #2356. [5] McKeegan K. D. et al. (2000) *Science*, 289,1334–1337. [6] Marhas K. K. et al. (2009) *MAPS Supp.*, 5271.

**Acknowledgements:** We thank G. MacPherson for the loan of Vigarano F6, and the NASA Cosmochemistry Program for support for this work.

