

LITHIUM ISOTOPIC ANALYSES OF CHONDRITES AND CHONDRULES. W.F. McDonough¹, F-Z. Teng¹, R.L. Rudnick¹, and R.D. Ash¹. ¹Department of Geology, University of Maryland, College Park, MD 20742 (mcdonough@geol.umd.edu)

Introduction: Light stable isotopes provide insights and constraints on nebular and parent body processes. Lithium isotope studies of chondrites offer such potential, with some specifically unique aspects. Lithium is monovalent, the lightest of non-gaseous elements, it has a 15% mass difference between its 2 isotopes (⁶Li and ⁷Li), it is fluid mobile, and it is one of the fastest diffusing elements (after H, He). In this study we consider two goals. First, the extent of Li isotopic fractionation in chondrules and bulk chondrite as a proxy of nebular and parent body processes, and second, accuracy and precision in Li isotopic analyses. We find that the lithium isotopic composition of chondrites and their chondrules are relatively homogeneous and reflect limited mass fractionation during condensation, accretion and post-accretion evolution.

Analytical Methods: For the chondrite analyses, bulk rock and chondrule fragments were ground to a fine powder with an agate mortar, dissolved in high pressure bombs fluxed with a mixture of HF-HNO₃ followed by a HClO₄ fusion. All samples were monitored for complete dissolution of solids. Chromatographic separation of Li was accomplished using a modified published procedure, the details of the method and our modifications are reported in [1-2]. Total procedural blanks were analyzed for concentration and isotopic composition and determined to be negligible relative to the mass of sample (1-25 mg) analyzed. The Li isotopic measurements were performed on a Nu Plasma multi-collector ICP-MS at the University of Maryland. The $\delta^7\text{Li}$ values for all samples are determined by comparison to the standard L-SVEC, measured before and after each sample analysis [1-2]. The time-dependent monitoring of the absolute variation in ⁷Li/⁶Li values of L-SVEC throughout the analysis session provides a further check on precision and accuracy of analyses, which are better than $\pm 1\%$ (2-sigma). During all analytical sessions we measured the $\delta^7\text{Li}$ values of 2 or more reference materials (this includes processed rock standards) before each batch of samples and, where possible, after each suite of samples.

Purified metals of isotopically enriched ⁷Li (>99% pure) and enriched ⁶Li (>99% pure) were prepared as solutions and mixed to produce solutions with an appropriate range of $\delta^7\text{Li}$ values to calibrate the range of compositions encountered. These spikes were also added to selected in-house standard materi-

als and these mixtures were analyzed and compared with their predicted compositions.

Results: In total, 19 chondrites were analyzed in this study; all but 2 (CV3 Efremovka and the EH3 Kota-Kota) are falls. The falls were selected to minimize earth-derived contamination. In addition, samples selected were chosen to obtain a representative spectrum of chondrites. The average $\delta^7\text{Li}$ value for all of the chondrites is 1.3 ± 1.3 (1 σ). Twelve carbonaceous chondrites, including the groups CI, CM, CO, CV and CK, have an average $\delta^7\text{Li}$ value of 1.7 ± 1.3 . Six Allende chondrule fragments were analyzed and have an average $\delta^7\text{Li}$ value of 1.1 ± 0.9 , which is identical to the bulk Allende composition ($\delta^7\text{Li} = 1.6$). The 6 ordinary chondrites, including LL, H/L and H groups, have an average $\delta^7\text{Li}$ value of 0.4 ± 2.0 .

Discussion: There is a unimodal distribution of $\delta^7\text{Li}$ values for all of the chondrites with considerable overlap in compositions for the carbonaceous and ordinary chondrites, although the ordinary chondrite Krymka has a markedly lower $\delta^7\text{Li}$ value (Fig. 1). The 3 samples plotting at a $\delta^7\text{Li}$ value of +4 include the CI chondrites Ivuna and Orgueil and the CK4 chondrite Karoonda. The higher $\delta^7\text{Li}$ values for the CI chondrites are unlikely to be a pristine nebular signature, but is suggested to be the result of parent body aqueous alteration processes. It is also likely that the higher $\delta^7\text{Li}$ value of Karoonda is due to aqueous alteration processes on its parent body.

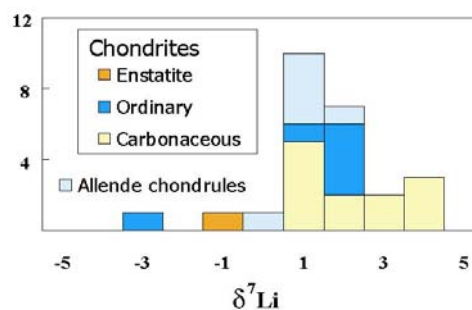


Fig. 1. A histogram plot of the $\delta^7\text{Li}$ values of carbonaceous chondrites, ordinary chondrites and an enstatite chondrite. Also shown are data for 6 Allende chondrule fragments. The average $\delta^7\text{Li}$ value for the chondrites is 1.3 ± 1.3 (1 σ) and that for the chondrules is 1.1 ± 0.9 , which is identical to the bulk Allende ($\delta^7\text{Li} = 1.6$).

We have also run a series of tests that involved column chemistry of mixed solutions, doping of pure Li solution with known concentrations of “added contaminants” (specifically, alkali metals and alkaline earths) and the spiking of samples and standards with isotopically enriched ^7Li and ^6Li solutions. This extensive series of tests have provided us with documentation of what controls the accuracy and precision of the mass spectrometric analyses. It has also given us considerable insight into other factors that influence the fractionation process in the mass spectrometer. We have also analyzed experiments involving spiking of solutions (as well as geological standards (e.g., BHVO-2) and column chemistry) with isotopically enriched ^7Li or ^6Li spikes; these experiments provide an important control on the accuracy of our analyses. One of these experiments is highlighted in Figure 2. These and other experiments are used to establish the accuracy of our method over a range of $\delta^7\text{Li}$ values between -50 to $+50$.

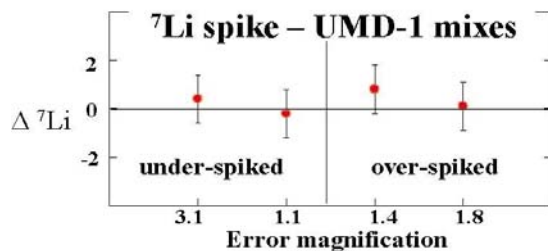


Fig. 2. $\Delta^7\text{Li}$ values versus error magnification value for multiple spiking experiments. These and other experiments demonstrate the accuracy over the scale of the observed variation of Li isotopic compositions. The over and under spiked runs were generated using mixtures of both enriched ^6Li and enriched ^7Li spikes added separately to different aliquots of UMD-1, an in-house reference Li solution. Error bars are 2 sigma.

We have conducted tests documenting our limits of accuracy and precision down to 10 ppb solutions. Importantly, we have analyzed repeatedly the international Belgium SRM – standard reference material. During this time we matched the accepted $\delta^7\text{Li}$ value [3] and found a factor of 6, or more, improvement in the precision for this SRM than that reported in [3]. In addition, we have analyzed our in-house standard (UMD-1) more than 100 times, with a 2-sigma precision of $\pm 1.0\%$. Some of these analyses were performed on the solution that was processed through column chemistry in order to establish confidence in our column yields and as an additional check on column blanks envision. An example of these data is given in Figure 3.

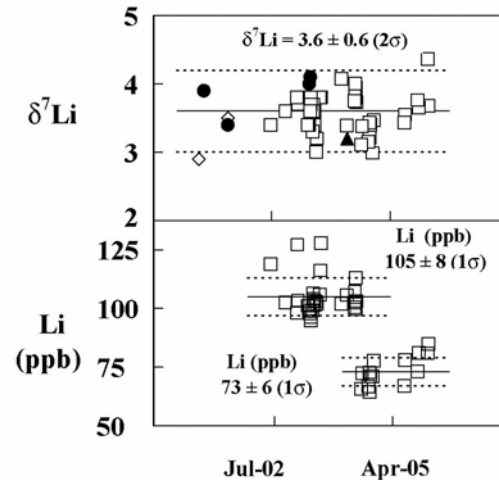


Fig. 3. Compilation of analyses of four preparations of shale standard AO-12, from the Amadeus Basin. Different symbols denote analyses of separate digestion and preparation with Li concentrations ranging from 50 ppb to 150 ppb. Filled-squares represent samples taken through column chemistry procedure described in [1] and all other samples were taken through column chemistry procedure described in [2]. The overall mean $\delta^7\text{Li} = 3.6 \pm 0.6$ (2σ). The uncertainty for Li concentration measurement of the solutions is $< 10\%$, based on two dilutions of the same AO-12 solution.

The homogeneous composition of chondrule fragments from Allende can be compared with data reported for chondrules from Semarkona, which were obtained by SIMS analyses [4]. These 2 data sets compare favorably for their average $\delta^7\text{Li}$ values, although the chondrule data from Semarkona show a 40% spread in values.

References: [1] F-Z. Teng *et al.* (2004) *GCA* 68, 4167-4178 [2] R.L. Rudnick *et al.* (2005) *Chemical Geology* 212, 45-57 [3] H.P. Qi *et al.* (1998) *Fresenius J. Anal. Chem.*, 361, 767-773 [4] M. Chaussidon and F. Robert (1998) *EPSL* 164, 577-589

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