

LI-ISOTOPE STUDIES OF OLIVINE IN MANTLE XENOLITHS BY SIMS. D. R. Bell^{1,2}, R.L. Hervig¹ and P. R. Buseck^{1,2}, ¹Department of Geological Sciences, ²Department of Chemistry and Biochemistry, Arizona State University, Tempe, AZ 85287-1404. David.R.Bell@asu.edu, Richard.Hervig@asu.edu, Pbuseck@asu.edu.

Introduction: Variations in the ratio of the stable isotopes of Li are a potentially powerful tracer of processes in planetary and nebular environments [1]. Large differences in the ⁷Li/⁶Li ratio between the terrestrial upper mantle and various crustal materials make Li isotope composition a potentially powerful tracer of crustal recycling processes on Earth [2].

Recent SIMS studies of terrestrial mantle and Martian meteorite samples report intra-mineral Li isotope zoning [3-5]. Substantial Li isotope heterogeneity also exists within and between the components of chondritic meteorites [6,7]. Experimental studies of Li diffusion suggest the potential for rapid isotope exchange at elevated temperatures [8]. Large variations in $\delta^7\text{Li}$, exceeding the range of unaltered basalts, occur in terrestrial mantle-derived xenoliths from individual localities [9]. The origins of these variations are not fully understood.

Determining the origins and potential effects of small-scale heterogeneities is an important aspect of Li isotope applications to both terrestrial and extra-terrestrial samples. We set out to study variations in $\delta^7\text{Li}$ on a range of scales in minerals (mostly olivine) in mantle-derived xenoliths from selected petrological settings. The goal was to determine the relative roles of magmatic, metasomatic, and post-magmatic processes in affecting the Li isotope ratios. We anticipate that the combination of these phenomenological observations with experimental data on Li isotope diffusion and partitioning will allow a better basis for interpretation of Li isotope signatures in a variety of planetary and meteoritic environments.

Samples: Basalt-hosted xenoliths from the SW USA and kimberlite-hosted xenoliths from southern Africa were investigated. The samples included low- and high-temperature garnet peridotites, olivine megacrysts and dunites, and spinel lherzolites. Olivine grains were separated from xenoliths by crushing and handpicking, and mounted in epoxy discs together with grains of an internal olivine standard from a fertile spinel lherzolite xenolith KBH-1, from Kilbourne Hole.

Analytical technique: Li isotope microanalyses were obtained on the Cameca ims 3f SIMS at ASU. The primary beam was ¹⁶O⁻ (5-20 nA, 30-50 μm diameter). Positive secondary ions were detected in pulse counting mode. The mass spectrometer was operated at a mass resolving power of ~ 1200 ($M/\Delta M$) to

resolve ⁶LiH from ⁷Li (but no hydride was observed). Counting times were 10s for ⁶Li and 1s for ⁷Li in each cycle, with 50 to 200 cycles per analysis. The Li isotopic composition of the KBH-1 olivine was calibrated against a similar olivine SC-1 ol from San Carlos, analyzed by TIMS with $\delta^7\text{Li}$ of $3.4 \pm 1\text{‰}$ [10]. Variations in ⁷Li/⁶Li are expressed as $\delta^7\text{Li} = 1000\{[(^7\text{Li}/^6\text{Li})_{\text{sample}}/(^7\text{Li}/^6\text{Li})_{\text{std}}]-1\}$, where std refers to the L-SVEC standard reference material. Analytical errors for each point were within 0.1 to 0.3‰ of that expected from counting statistics. Errors decreased with increasing Li concentration in the analyzed phase, determined qualitatively from the ⁷Li count rate. Count rates varied by a factor of six, reflecting to first order the variation in Li concentration, with lower count rates requiring more cycles to achieve the desired standard error of $\pm 1\text{‰}$ (1 σ) or better. Other studies have not observed a significant matrix effect in Li isotope analysis by SIMS [e.g., 11]. During the course of this study small differences in the instrumental fractionation of ⁷Li/⁶Li between basaltic glass, clinopyroxene, and olivine were observed [12]. Further characterization of these instrumental analytical effects is in progress.

Intra-granular heterogeneity in $\delta^7\text{Li}$: Traverses of 4 – 10 analytical spots at 50 – 200 μm intervals were performed across selected grains in order to investigate the degree of homogeneity. Both homogeneous and heterogeneous grains were encountered, with $\delta^7\text{Li}$ variations up to 15 ‰ occurring within individual grains. In some cases the $\delta^7\text{Li}$ heterogeneity was correlated to heterogeneity in Li abundance. Most olivines from low-temperature garnet peridotites and fertile spinel lherzolites were homogeneous, with occasional 1-3 ‰ depletion or enrichment of grain margins. More striking heterogeneity (up to 15 ‰) is present in depleted spinel lherzolite olivines from San Carlos. Zoning to high- $\delta^7\text{Li}$ and low- $\delta^7\text{Li}$ grain margins occurs. $\delta^7\text{Li}$ variability related to cracks with higher Li content was also observed. Multiple causes are probable, including contamination by Li-rich secondary phases on crack surfaces, exchange with a high- $\delta^7\text{Li}$ fluid phase, and preferential diffusive loss of ⁶Li during extraction of Li into an external fluid phase. The heterogeneity indicates that bulk analysis of mineral separates from xenoliths for Li isotopes is risky. More detailed study is planned in order to evaluate the relative importance of each effect for individual samples.

Li isotope heterogeneity in SW USA mantle. The $\delta^7\text{Li}$ values of fertile spinel lherzolites from San Carlos and Kilbourne Hole fall within the range of $\delta^7\text{Li}$ recorded for MORB. $\delta^7\text{Li}$ of refractory spinel lherzolites are more variable, extending as high as 25 ‰. Olivine grains within the refractory samples are commonly heterogeneous, with heavy $\delta^7\text{Li}$ occurring in both cores and rims of grains. $^{87}\text{Sr}/^{86}\text{Sr}$ and $\delta^7\text{Li}$ are both correlated with indices of melt depletion, suggesting metasomatism during open-system melting and local increase of lithospheric mantle $\delta^7\text{Li}$ by cryptic metasomatism. High Li content and $\delta^7\text{Li}$ was recorded in olivine from the Phalaborwa carbonatite (South Africa) suggesting the potential of carbonatite melt as an effective mantle metasomatic agent.

Li isotope heterogeneity in southern African mantle: Megacrysts, high-temperature deformed peridotites, and low-temperature granular peridotites were analyzed. Minor intragranular heterogeneity was recorded by low-T garnet peridotites, whereas high-T garnet lherzolites and Mg-rich megacrysts displayed inter- and intra-granular $\delta^7\text{Li}$ heterogeneity. The heterogeneity is most likely to derive from metasomatic processes occurring shortly before kimberlite entrainment [13]. Li and $\delta^7\text{Li}$ increase from low-temperature, refractory peridotites through high-temperature peridotites, to megacrysts. Clinopyroxenes mimic the trend displayed by olivine. The trend is interpreted to represent mixing and reaction between Li- and ^7Li -depleted Archean mantle lithosphere (avg. ~ 1 ppm, -1 ± 2 ‰) and a megacryst magma component from the deeper mantle with $\delta^7\text{Li} \sim +14$ ‰.

Low Li concentrations in refractory, LIL-enriched peridotites suggest extraction during Archean partial melting. The average $\delta^7\text{Li}$ of Archean refractory peridotites is lower than the MORB range, suggesting modification by metasomatic fluids [e.g., 9]. Together, these systematics suggest that Li was extracted during flux-melting by hydrous metasomatizing fluids. An alternative is that the mantle $\delta^7\text{Li}$ has undergone secular evolution as a result of the recycling of high- $\delta^7\text{Li}$ altered oceanic crust [2, 14].

$\delta^7\text{Li}$ of kimberlite megacrysts is higher than typical mantle-derived materials and suggests a source containing Li from recycled oceanic crust. The agent transporting this deeper component is a volatile- and incompatible element-rich magma parental to the megacrysts. The magma is assumed to form by segregation of small melt fractions from lithologically heterogeneous mantle upwelling during dispersal of the Gondwana supercontinent in the Mesozoic. Combined $\delta^7\text{Li}$ and radiogenic isotope data on kimberlites and megacrysts [15,16] suggest that the Li-rich, high- $\delta^7\text{Li}$

component may indicate deeply recycled oceanic crust and associated mantle in a widespread global reservoir.

Summary: Li isotope heterogeneity occurs on intra-granular, inter-granular, inter-sample, and regional scales in mantle-derived xenolith samples. Processes responsible for Li isotope heterogeneity include bulk recycling of surface materials into the mantle, metasomatism of mantle rocks by silicate and carbonatite melts and hydrous fluids, and emplacement-related alteration and isotopic exchange. A similarly complex array of processes may be expected in meteorite samples. If the resulting signatures can be isolated by high-spatial resolution analysis, the Li isotope compositions recorded will permit tracing of a rich complexity of processes in terrestrial and meteoritic materials.

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References: [1] Tomascak, P.B. 2004 *Rev. Min. Geoch.* 55, 153-195, [2] Elliott, T. et al. 2004 *EPSL* 220, 231-245. [3] Beck, P. et al. 2004 *GCA* 68, 2925-2933, [4] Jeffcoate, A. B. et al. 2004 *GCA* 68 (11S), A52, [5] Wagner, C. and Deloule, E. 2004 *GCA* 68 (11S), A49, [6] Chaussidon, M. and Robert, F. 1998 *EPSL* 164, 577-589, [7] Sephton, M.A. et al. *Astrophys. J.* 612, 588-591, [8] Richter, F.M. et al. 2003 *GCA* 67, 3905-3923, [9] Nishio, Y. et al. 2004 *EPSL* 217, 245-261, [10] Seitz, H.-M. et al. 2004 *Chem. Geol.* 212, 163-177, [11] Decitre, S. et al. 2002 *G3*, [12] Hervig, R.L. et al. 2004 *Eos* 85(47), Abstr. V51C-0593, [13] Smith, D. and Boyd, F. R. 1987, in P.H. Nixon (ed.) *Mantle Xenoliths*, Wiley, pp. 551-561, [14] Bouman, C. et al. 2000 *J. Conf. Abstr.* 5, 239, [15] Janney, P.E. et al. 2002 *J. Petrol.* 43, 2339-2370, [16] Nowell, G.M. et al. 2004 *J. Petrol.* 45, 1583-1612.