Li CONCENTRATION AND ISOTOPE RATIO IN LUNAR ZIRCONS: Li-ENRICHED AND -DEPLETED MAGMAS ON THE MOON. Michael J. Spicuzza, John W. Valley, and Takayuki Ushikubo, Department of Geoscience, University of Wisconsin-Madison, Madison, WI 53706-1692 (spicuzza@geology.wisc.edu).

Introduction: The lunar magma ocean (LMO) hypothesis postulates the early formation of stratified lunar mantle, an anorthositic crust, and late stage Fe- and Ti-rich differentiates. The most evolved and differentiated liquids in the LMO model are known as KREEP and contain high concentrations of K, REE's, P as well as other incompatible elements including Zr. As a mildly incompatible element, Li should also be enriched in (KREEP). Lunar samples identified as "KREEP-rich" have higher whole-rock lithium concentrations than other lithologies. Slightly higher [Li] in high-Ti mare basalts compared to low-Ti mare basalts [1-3] is consistent with interpretations that the genesis of high-Ti mare basalts requires more involvement of late stage differentiates of the LMO.

Zircons are found in a wide variety of lunar lithologies and as individual crystals in soil [4,5]. Zircon-producing magmas on the Moon are thought to require a KREEP component since magmas derived from a KREEP-free mantle source would not contain enough zirconium, even after significant fractional crystallization, to crystallize zircon. Here, we present the first measurements of Li concentration and δ^7Li values for a suite of lunar zircons. We correlate these new data with trace element data previously reported [5,6] for the same zircons in order to assess the potential for the trace element concentrations in zircon to constrain the petrogenesis of zircon-producing lunar magmas.

Background: The retention of original igneous Li in terrestrial zircons has been demonstrated in studies by SIMS [7-9]. Lithium can be incorporated into igneous zircon through a number of charge-balanced substitutions [7,8,10]. Diffusion experiments suggest a relatively rapid diffusion rate for Li in zircon [11], however in situ measurements of natural terrestrial zircons [7,8] suggest much slower diffusion consistent with the interpretation that Li diffusion rates are controlled by the diffusion of charge-balancing cations (e.g. REE's). Thus the [Li] in many igneous zircons is retained and can constrain the petrogenesis of out-of-context zircons.

On Earth, Li concentrations in zircon are bimodal: zircons from continental crustal settings are high (~1- 200 ppm Li) compared with zircons from oceanic crust and kimberlites (< 50 ppb, most <10 ppb) [7-9]. The extremely low [Li] in oceanic zircons reflects the incompatible trace element depleted MORB source regions; accurate δ^7Li measurements are not possible on these zircons. The δ^7Li values of continental igneous terrestrial zircon range widely from -20‰ to +15‰ [7, 8]. Negative values likely reflect the incorporation of supracrustal materials as weathering causes large fractionation of Li isotopes.

Samples: Lunar zircons were separated from 12023 and 14240 lunar soils, and from lunar rocks 15405 (quartz monzodiorite lithology), and 15455 (breccia with shocked norite). Textural and geochemical evidence suggests subsolidus modification of trace element concentrations for 2 regolith grains and three zircons from 15455 (likely via shock or incorporation into high-temperature impact melts). These samples are classified as "disturbed" and discussed separately.

Methods: Analyses of [Li] and δ^7Li in lunar zircon were measured in-situ (~10 µm spot) by SIMS at the University of Wisconsin (WiscSIMS) following the methodology outlined in [7]. Individual zircons were analyzed 1 to 3 times. The δ^7Li uncertainty in this study is estimated at ≤ ± 2.6 ‰ (2SD). Undisturbed lunar zircons show <10% intragrain variability in [Li]. All other trace element data are from [5].

Results: *Li contents*: [Li] is bimodal in lunar zircon. Four Li-poor lunar regolith zircons contain 0.01 to 0.05 ppm, 4 Li-rich regolith zircons are homogeneous and have 50-150 ppm Li, and 3 zircons from quartz monzodiorite 15405 have 70-150 ppm Li. Five "disturbed" zircons are contain 4 to 33 ppm Li.

Li isotope ratios in lunar zircons: The average δ^7Li value for individual Li-rich zircons from lunar

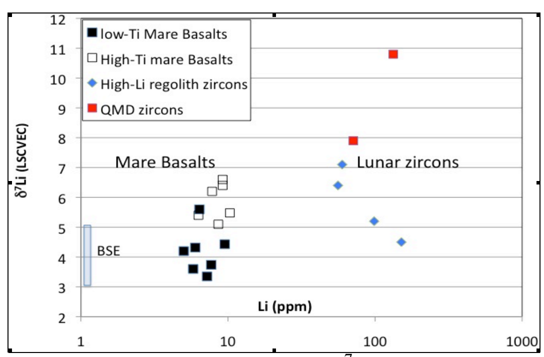

Figure 1: Li concentration vs. δ^7Li for lunar zircons. Mare basalt whole-rock values from [1-3]. Bulk-silicate Earth (BSE) from [15].

regolith ranges from 4.1 to 7.1‰ (LSVEC) (average = 5.8‰ ± 2.4 2SD, n=4). Two individual zircons from 15405 (Quartz monzodiorite) yield average values of 7.9 and 10.8 ‰. Zircons interpreted to be disturbed include: 1) three zircons analyzed from a single ~ 500 µm chip of breccia 15455 (individual measurements range from -6 to +9‰). 2) an otherwise Li-poor A12 regolith zircon contains a crosscutting CL-dark Li-rich zone that yields values of -39 and -9‰; and 3) a single A14 regolith zircon (~20 ppm Li) that is rimmed by badelleyite yields δ^7Li values of -2 and -17‰.

Discussion: The δ^7Li values measured by SIMS in 4 Li-rich (>50 ppm) regolith zircons are similar to values from whole-rock mare basalts [1-3] (Fig. 1). Zircons from the quartz monzodiorite, a highly evolved composition for the Moon have higher δ^7Li values, suggesting the possibility of limited igneous isotopic fractionation of Li.

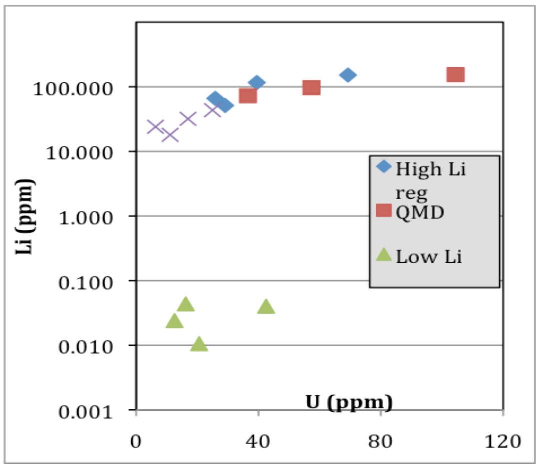

Fig. 2. Li concentration in lunar zircons vs Uranium. Disturbed zircons shown as crosses.

The measured [Li] in lunar zircons is bimodal and correlates well with incompatible trace elements such as U (Fig. 2). [Li] in lunar zircons also varies inversely with [Ti] and therefore with temperature [12]. Low [Li] zircons (with higher Ti) likely reflect zircon crystallization at higher temperatures than high-Li zircons. Zircons from the highly evolved quartz monzodiorite (15405) have among the highest Li and the lowest Ti in our dataset, and suggest that high-Li zircon-producing magmas may be more silicic.

The [Li] data set for lunar zircons is small to date, but it appears to mimic the bimodal nature of the terrestrial zircon dataset (Fig. 3). On Earth the bimodality is related to depleted (oceanic) and enriched (continental) sources. Lunar zircons, when plotted on the trace element discrimination diagrams of Grimes et al. (Figs. 2A-C in [13]) straddle the lower boundary of the continental field. Although the variability in trace element concentrations in lunar zircon is small compared to terrestrial zircon, Li-rich lunar zircons, especially those from the highly evolved QMD lithology, plot toward the continental field and Li-poor zircons towards the oceanic field.

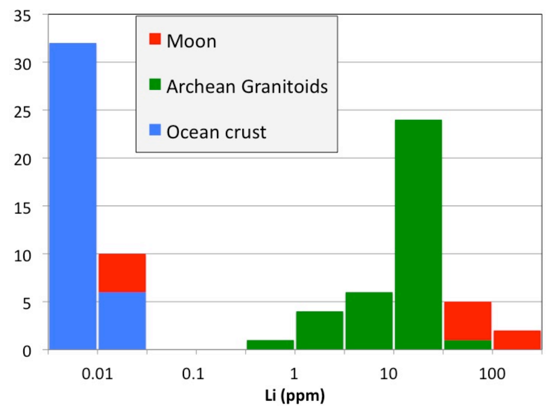

Fig. 3. [Li] in lunar zircons vs. terrestrial samples. Terrestrial data from [8,9].

The bimodality of [Li] may indicate the presence of enriched and depleted magmas on the Moon, as it does on Earth. If lunar magmas lacking a KREEP component crystallize zircons, then [Li] would be low.

If all lunar zircon-producing magmas contain a KREEP component and KREEP is Li-rich, then it is difficult to explain the bimodal [Li] in lunar zircons. One possibility is if silicate liquid immiscibility during the latest stages of the LMO differentiated KREEP magmas into a K-rich "feldspathic" fraction and a more mafic REEP-rich fraction enriched with Zr (14). It is reasonable to assume that Li is enriched in the K-fraction, leaving the REEP-fraction depeleted in Li (but still Zr-rich). The extent of the enrichment / depletion is uncertain. The REEP-fraction, or magmas incorporating the REEP fraction could have elevated Zr concentrations without significant enrichment of Li, allowing for the crystallization of low-Li lunar zircon.

References: [1] Seitz H-M. *et al.* (2006) *EPSL* **245**,6-18. Magna T *et al.* (2006) *EPSL* **243**, 336-353. [3] Day JMD et al. (2008) LPSC **XXXIX**, 1072. [4] Meyer C et al. (1991) *LPSC **XXII*** 895-896. [5] Spicuzza MJ et al. (2011) *LPSC **XLII***, 2445. [6] Valley JW et al. (2011) *Goldschmidt Conf.* #2058. [7] Ushikubo T et al. (2008) *EPSL* **272**, 666-676. [8] Bouvier A-S (2011) *CMP* [9] Grimes CB et al. (2011) *CMP* **161**, 13-33. [10] Hoskin PWO and Schaltegger U (2003) *RIMS* **53**, 27-55. [11] Cherniak DJ and & Watson EB (2010) *CMP* **160**, 383-390. [12] Ferry J and Watson EB (2007) *CMP* **154**, 429-437. [13] Grimes CB et al. (2007) *Geology* **35**, 643-646. [14] Neal CR and Taylor LA (1989) *GCA* **53**, 529-541. [15] Seitz H-M et al. (2004) *Chem. Geol.* **212**, 163-177.