# SM-ND AGE AND REE SYSTEMATICS OF LARKMAN NUNATEK 06319: CLOSED SYSTEM FRACTIONAL CRYSTALLIZATION OF A SHERGOTTITE MAGMA.

J.T. Shafer[1], A.D. Brandon[2], T.J. Lapen[2], M. Righter[2], and A.H. Peslier[3,4], [1]Lunar and Planetary Institute, Houston, TX 77058 (shafer@lpi.usra.edu), [2]Department of Geosciences, University of Houston, Houston, TX 77204, [3]NASA-JSC, Houston, TX 77058, [4]Jacobs Technology, E.S.C.G., Mail Code JE23, 2224 Bay Area Blvd, Houston, TX 77058.

Sm-Nd isotopic data were collected on mineral separates and bulk rock powders of LAR 06319, yielding an age of 180±13 Ma (2σ). This age is concordant with the Lu-Hf age (197±29 Ma, [1]) determined in conjunction with these data and the Sm-Nd age (190±26 Ma) of Shih et al., 2009 [2]. The Sm-Nd data form at statistically significant isochron (Fig. 1) that is controlled largely by leachate-residue pairs (samples with the R suffix are residues after leaching in cold 2N HCl for 10 minutes).

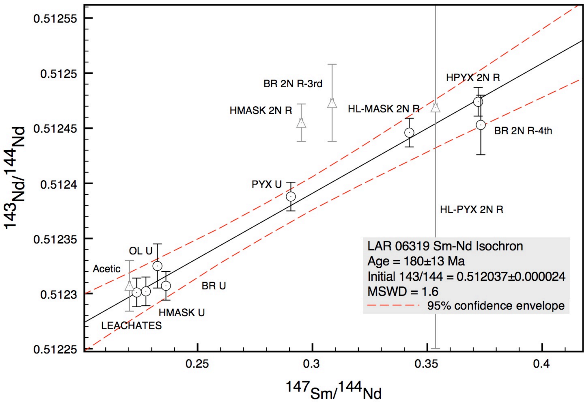

**Figure 1:** Sm-Nd isochron for LAR 06319. Mineral separates in light gray where not used to calculate the isochron. Isochron slope calculated using Isoplot v.3.0 (Model 1 fit). Multiple leachate samples were averaged into a single plot as all leachates were identical within error.

Unleached bulk rock and bulk rock leachates have nearly identical $^{143}$Nd/$^{144}$Nd and $^{147}$Sm/$^{144}$Nd isotopic compositions, indicating the the leached phase largely controlled the REE budget in LAR 06319. Laser ablation ICP-MS results indicate that phosphates are the major hosts of the REE in LAR 06319 [4] and are likely the main contributors to the isotopic composition of the leachate. The strong control the phosphate has on the slope of the isochron (Fig. 2) means that the isochron has age significance only if 1) the phosphate is magmatic in origin, 2) formed concurrently with the rest of the phases, and 3) remained a closed system to Nd and Sm. Petrographic studies [3,4] indicate that the phosphate is a primary phase that crystallized late in the crystallization sequence generally interstitial with maskelynite (shock devitrified plagioclase) and occasionally as inclusions primarily in pyroxene. While phosphate is easily leachable in weakly acidic solutions and is therefore susceptible to aqueous alteration, the phosphate in LAR 06319 appears to have remained closed to REE.

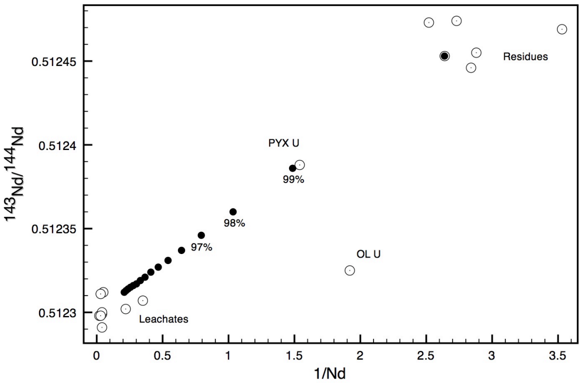

**Figure 2:** Measured $^{143}$Nd/$^{144}$Nd vs 1/Nd for bulk rock and mineral separates of LAR 06319. A linear array between leached residues and their leachates indicates that mixing between two reservoirs, one relatively unradiogenic and high in Nd (phosphate) and one relatively radiogenic but low in Nd (bulk rock minus phosphate) largely controls the slope of the isochron. Black dots are 1% increment additions of phosphate to an average bulk rock residue. Note that OL U does not plot on this line but plots on the isochron, indicating that the phosphate is in equilibrium with the early formed olivine.

Purified olivine separates (olivine in LAR 06319 is an early phenocryst phase and was off the liquidus before commencement of phosphate crystallization [3]) plots on the isochron yet off the linear array in Figure 2, indicating that the phosphate, while controlling the slope of the isochron, appears to be in isotopic equilibrium with olivine and therefore has remained closed to Nd and Sm. In addition, the 180 Ma age is very similar to other Sm-Nd ages generated for shergottites, suggesting that this age is recording a common igneous crystallization age.

The initial $\varepsilon Nd_I$ of LAR 06319 is -6.88±0.33, which is identical within error to Zagami [5], Shergotty [6], RBT 04262 [2], NWA 1068 [7], and NWA 856 [5]. These shergottites are slightly more enriched than Los Angeles [6]. Near identical source $^{147}$Sm/$^{144}$Nd ratios of these samples indicates a probable origin from the same source. This strongly LREE enriched source must have differentiated early in Mars history, as evidence by the 50+ epsilon unit difference between the enriched and depleted shergottites.

In order to determine if the zonation seen in pyroxene phenocrysts [3,4] is consistent with progressive crystallization of a single magma, REE abundances were modeled. Parent magma REE abundances were calculated by determining the REE content of the liquid in equlibrium with the most magnesian/primitive pyroxene. Using the partition coefficients of [8], the chondrite normalized REE profile in the parent magma is approximately flat at 10x chondritic and subparallel to the measured REE content of a melt inclusion in the core of a large olivine phenocryst and the whole rock composition. Due to the close agreement of these data, for all trace element modeling the parent magma REE concentrations are assumed to be identical to that of the melt inclusion. Fractional and equilibrium crystallization of the parent magma was modeled using partition coefficients from [8], [9], and [10]. Other model parameters (phase proportions, fraction of liquid remaining) are from the detailed MELTS modeling of [3]. Crystallization was modeled using a 7-stage crystallization sequence that closely matches the observed petrography of LAR 06319.

Since pyroxene (ortho- and clinopyroxene) crystallizes nearly throughout the crystallization sequence and the pyroxenes have measureable REE contents (as opposed to olivine which generally was at or below the LA-ICP-MS detection limits), calculated pyroxene compositions in equilibrium with modeled liquids were compared to the measured pyroxene REE abundances (Fig. 4). Early crystallized orthopyroxene LA-ICP-MS results are nearly identical with those generated from both the fractional and equilibrium crystallization models, indicating that using the melt inclusion composition as equivalent to the parent magma is consistent with the orthopyroxene data. Later stage clinopyroxene also closely matches the model results. However, one highly REE enriched clinopyroxene crystals (La ~ 10x chondritic with low phosphorous concentrations indicating that the high REE contents are unlikely due to hitting a micro-phosphate inclusion) has REE concentrations higher than any pyroxene crystallized with the equilibrium crystallization model, suggesting that fractional crystallization was the dominant crystallization process. However, many measured pyroxene compositions fall in the gap between the calculated orthopyroxene and clinopyroxene compositions on Fig. 4, suggesting clinopyroxene began crystallization earlier in the sequence than assumed in the model. Additionally, the measured LREE abundances in the clinopyroxene crystals are slightly more enriched than the modeled abundances. This discrepancy is likely due to slightly inaccurate partition coefficients.

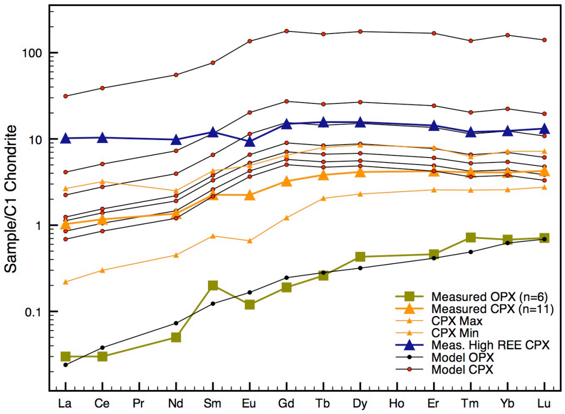

**Figure 3:** C1 Chondrite normalized REE profiles of in-situ pyroxene in LAR 06319. Traces with small round dots are calculated pyroxene compositions generated by the fractional crystallization model. The calculated orthopyroxene compostion matches nearly identically to measure orthopyroxene from LAR 06319 (average of 6 spot analyses). The average clinopyroxene (11 spot analyses) is also very close to the calculated clinopyroxene composition at the beginning of clinopyroxene crystallization. CPX Max and CPX Min show the range of moderate REE clinopyroxene. The fact that some clinopyroxene compositions extend below the model compositions may indicate that clinopyroxene crystallization commenced earlier than assumed in the model. A single, very high REE content pyroxene was analyzed. HREE contents of this sample are similar to late stage pyroxene calculated in the model, although LREE contents are significantly higher than in the model.

**Summary:** The Sm-Nd age of LAR 06319 is 180±13 Ma, which corresponds well to other measured radiogenic ages on this rock and with the ages of other shergottites that it appears to be genetically related to. Measured LA-ICP-MS REE element abundances of pyroxenes are in good agreement with modeled compositions derived from fractional crystallization of a parent magma with whole-rock REE contents equivalent to a melt inclusion in the core of a large olivine phenocryst. These trace element results are consistent with progressive closed-system fractional crystallization of a single magma, which implies that the isotopic results are indeed reflecting the true crystallization age of LAR 06319 and that the enriched shergottite source was producing magmas late in Martian history.

**References:** [1] Shafer J.T. et al. (2009) *LPS XXXX*, Abstract #1803. [2] Shih C.-Y. et al. (2009) *LPS XXXX*, Abstract #1360. [3] Peslier A.H. et al. (2009) submitted. [4] Sarbadhikari A.B. et al. (2009) *GCA*, 73, 2190-2214. [5] Debaille V. et al. (2008) *EPSL*, 269, 186-189. [6] Bouvier A. et al. (2008) *EPSL*, 266, 105-124. [7] Shih C.-Y. et al. (2003) *LPS XXXIV*, Abstract #1439. [8] Borg L.E. and Draper D.S. (2003) *MAPS*, 38, 1713-11731. [9] Bindeman I.N. et al. *GCA*, 62, 1175-1193. [10] Lofgren G. et al. (2006) *Amer. Min.*, 91, 1596-1606.