

ION MICROPROBE ANALYSES OF TRACE ELEMENTS IN LUNAR APATITES. K.L. Robinson^{1*}, J.J. Barnes^{1,2}, J. Villeneuve³, D. Johnson¹, E. Deloule³, I.A. Franchi¹, and M. Anand^{1,4}. ¹School of Physical Sciences, The Open University, Walton Hall, Milton Keynes, UK MK7 6AA. ²ARES, NASA Johnson Space Center, Houston, TX 77058 ³CRPG/CNRS-Université de Lorraine, Vandoeuvre les Nancy, France. ⁴Dept. of Earth Sciences, Natural History Museum, London, SW7 5BD, UK. *katie.robinson@open.ac.uk

Introduction: Lunar samples contain varying amounts of a chemical component known as KREEP (named for its enrichment in K, Rare Earth Elements, and P), which is related to the incompatible element-rich final fractionates of the Lunar Magma Ocean (LMO) [1]. Measurements of Cl isotopes in apatite from a variety of lunar rocks appear to show a positive correlation between a proxy for KREEP involvement in a sample's petrogenesis (e.g., bulk-rock La/Sm or ϵNd) and $\delta^{37}\text{Cl}$ signature of apatite [2,3]. The heavy ^{37}Cl isotope seems to be most elevated in KREEP-rich samples. Previous work used published bulk-rock REE data for specific lunar samples. However, a comprehensive study of REEs, trace elements, and volatile elements in the same apatite grains has not yet been done.

To further assess the observed correlation described above, we have measured *in situ* REE and trace elements in apatite from multiple samples previously measured for Cl isotopes. If apatite $\delta^{37}\text{Cl}$ is related to the KREEP content of the rock, samples with the highest apatite $\delta^{37}\text{Cl}$ should have similarly elevated KREEP-like REE signatures. If there is a petrogenetic connection between volatile content and KREEP evolution on the Moon, a systematic study of these same apatite grains in lunar samples may reveal useful information.

Samples and Methods: Seven samples were selected for trace element analysis from among samples containing apatite previously analyzed for volatiles [2-6]. We selected a compositionally diverse set of samples, with a range of bulk compositions including high Ti (10044,645), low Ti (12039,44; 15058,15; Miller Range 05035,30), and KREEP (15386,46) basalts, and more evolved lithologies (granulite 79215,50; quartz monzodiorite 15403,71), as well as a wide range of reported $\delta^{37}\text{Cl}$ values [2-6].

Trace elements were measured in apatite grains from the selected samples with the Cameca ims 1270 at the Centre de Recherches Pétrographiques et Géochimiques in Nancy, France using secondary ion mass spectrometry (SIMS) at high spatial resolution (~10 μm). We measured ^{45}Sc , ^{51}V , ^{52}Cr , ^{60}Ni , ^{85}Rb , ^{88}Sr , ^{89}Y , ^{90}Zr , ^{138}Ba , ^{139}La , ^{140}Ce , ^{141}Pr , ^{142}Nd , ^{147}Sm , ^{153}Eu , ^{155}Gd , ^{159}Tb , ^{161}Dy , ^{165}Ho , ^{166}Er , ^{169}Tm , ^{174}Yb , ^{175}Lu (all referenced to ^{44}Ca), following an established

protocol for measuring trace elements in volcanic glasses. A 12 nA O⁻ 13 kV primary beam was focused on a 10 μm diameter area, and the positive secondary ions were measured by ion counting at a high mass resolution of 14000 (M/ Δ M) to separate the isobaric oxide interferences without energy filtering. Standardization was performed using Durango apatite [13] and well-characterized glass standards.

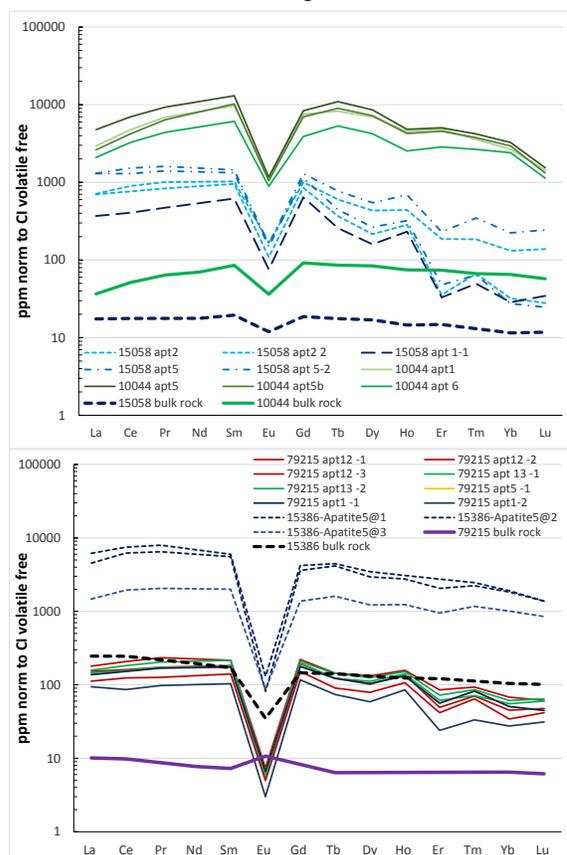


Figure 1. Representative spider diagrams of REE elements in lunar apatites, normalized to volatile-free chondrites [7]. Heavy lines represent bulk rock REE for each sample [3 and references therein, 8-13]. (top) REE in apatites in low Ti basalt 15058 (dashed) and high Ti basalt 10044 (solid). (bottom) REE in apatite in granulite 79215 (solid) and KREEP basalt 15386 (dashed).

Discussion: Figure 1 shows apatite REE abundances for four of the samples measured in this study: 10044, 15058, 15386, and 79215, compared with their bulk rock REE abundances [3 and references therein, 8-13]. Apatite in all of the samples is highly enriched (~10 to ~100x CI) in REEs relative to the bulk rock

values (Fig 1). Using partition coefficients for apatite and basaltic melt [15], the calculated REE content of the instantaneous equilibrium melts are highly enriched in REEs compared to the bulk rock, which is consistent with apatite crystallization from a late-stage fractionated melt.

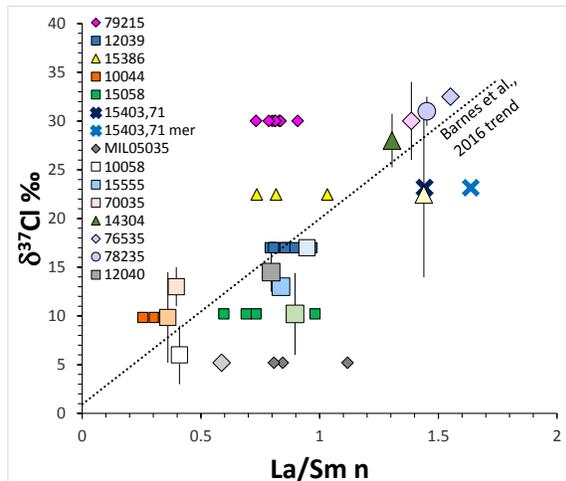


Figure 2. Average $\delta^{37}\text{Cl}$ of apatite [2-6] vs CI chondrite normalized bulk La/Sm for lunar samples [3 and references therein,7-13]. Large pale points represent literature bulk rock data for a sample, while small darker points are individual trace element analyses from this study [3 and references therein,7-13]. The 15403,71 merrillite point uses the $\delta^{37}\text{Cl}$ value from coexisting apatite [5].

Figure 2 shows average $\delta^{37}\text{Cl}$ versus CI normalized La/Sm for lunar samples, after Barnes et al.,[3]. It combines the literature bulk rock data used in Barnes et al.[3] to establish the apparent correlation between $\delta^{37}\text{Cl}$ of apatite and a proxy for KREEP (represented by La/Sm), with our measurements of REE in apatite. The broad trend is still apparent, but there is more spread than was observed for the bulk data. The spread in La/Sm ratios within apatite in individual samples is interesting. Apatite in some samples plots to the right (higher La/Sm ratio) of the bulk rock value, while in others, apatite La/Sm falls to the left (lower La/Sm ratio) of its bulk rock value. Meanwhile, the bulk and apatite La/Sm values for 12039 largely agree.

There may be some compositional heterogeneity in the apatites, as suggested by the spread in the REE plots in Fig. 1 and 2. Some of these apatites have been reported heterogeneous (e.g.[16]) and we observed zoning in some of the cathodoluminescence images of the measured apatites (Fig. 3). However, apatite is not necessarily the sole carrier of trace elements in these rocks. REE-merrillite has been reported in all the samples discussed here except 10044, 12039, and 79215 [3 and refs. therein,17]. Our measurements of apatite and coexisting merrillite in 15403,71 show that merrillite has a higher La/Sm ratio than apatite (Fig. 2). REE measurements of merrillite and apatite in La Paz

Icefield 02205 and phosphate-rich Apollo 14 samples show similar characteristics [18,19]. The presence of merrillite would thus cause the bulk rock La/Sm to be shifted higher relative to apatite La/Sm for that rock. This may explain the differences between bulk and apatite La/Sm ratios for 15386. Bulk rock La/Sm for 79215 is consistent with the trend, but the apatite La/Sm is much lower. As merrillite is not observed in 79215, this indicates that another phase(s) with high La/Sm may be affecting the bulk ratio.

In summary, our preliminary findings are in broad agreement with previous work suggesting a link between Cl isotopes and KREEP in lunar rocks [2,3]. However, a more detailed comparison of the Cl isotope dataset against other proxies for KREEP (e.g., Th) and consideration of other petrogenetic processes are required to fully understand the Cl isotope signatures of lunar samples.

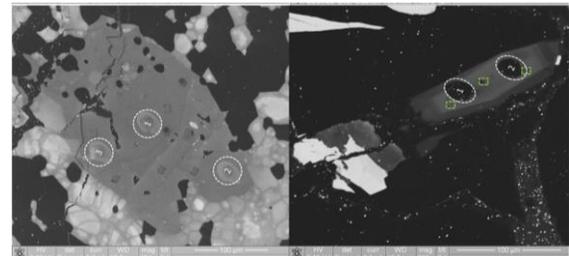


Figure 3. Cathodoluminescence images of two apatites measured in this study. Dashed circles indicate trace element SIMS pits, while smaller squares are nanoSIMS pits. (L) Apatite 12 in granulite 79215. Apatite in this sample is largely homogenous in CL. (R) Meanwhile, apatite 9 in low Ti basalt 12039 is clearly zoned in CL.

References: [1]Warren P.H, Wasson J.T.(1979) *Rev. Geo. Space Phys.* 17, 73-85. [2]Boyce J.W. et al. (2015) *Sci. Adv.*, 1 (8), 1-8. [3]Barnes J.J.et al. (2016) *EPSL* 447, 84-94. [4]Barnes J.J. et al. (2017) *LPSC XLVIII abstr.# 1724*, this volume. [5]Robinson K.L. et al. (2016) 47th LPSC, abstr.# 2199. [6]Treiman A. H. et al. (2014) *Am. Min.*, 99, 1860-1870. [7]Anders E.,Grevesse N. (1989) *GCA* 53, 197-214. [8]Joy K.H. et al. (2008) *GCA* 72, 3822-3844. [9]Liu Y. et al. (2007) *MaPS* 44, 261-284 [10] Helmke P.A. et al. (1973) *The Moon* 8, 129-148. [11]Hallis L.J et al. (2014) *GCA* 134, 289-316. [12]Hudgins J.A. et al. (2008) *GCA* 72, 5781-5798. [13]Neal C.R.(2001) *JGR* 106, 27,865-885. [14] Chew D.M.et al.(2016) *Chem. Geo.* 435,35-48. [15]Prowatke S., Klemme S.(2006) *GCA* 70, 4513-4527. [16]Greenwood, J. P. et al.(2011) *Nat. Geosci.*, 4, 79-82. [17]McCubbin F.M. et al.(2010) *Am. Min.* 95, 1141-1150.[18]Jolliff B.L.et al. (1993) *GCA* 57, 4069-4094. [19]Anand M. et al. (2006) *GCA*70,246-264.

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