

**THE CHLORINE ISOTOPIC COMPOSITION OF LUNAR URKREEP.** J. J. Barnes<sup>1,\*</sup>, R. Tartèse<sup>1,2</sup>, M. Anand<sup>1,3</sup>, F. M. McCubbin<sup>4</sup>, C. R. Neal<sup>5</sup>, and I. A. Franchi<sup>1</sup>, <sup>1</sup> Planetary and Space Sciences, The Open University, Milton Keynes, MK7 6AA, UK, \*Jessica.barnes@open.ac.uk, <sup>2</sup>IMPMC, Muséum National d'Histoire Naturelle, Paris, 75005, France, <sup>3</sup>Department of Earth Sciences, Natural History Museum, London, SW7 5BD, UK, <sup>4</sup>NASA Johnson Space Center, Mailcode XI2, 2101 NASA Parkway, Houston, Texas 77058, USA, <sup>5</sup>Department of Civil & Environmental Engineering & Earth Science, University of Notre Dame, IN, 46556, USA.

**Introduction:** Since the long standing paradigm of an anhydrous Moon [1] was challenged there has been a renewed focus on investigating volatiles in a variety of lunar samples (e.g., [2-9]). However, the current models for the Moon's formation have yet to fully account for its thermal evolution in the presence of H<sub>2</sub>O and other volatiles [10-11]. When compared to chondritic meteorites and terrestrial rocks (e.g., [12-13]), lunar samples have exotic chlorine isotope compositions [7,14-17], which are difficult to explain in light of the abundance and isotopic composition of other volatile species, especially H, and the current estimates for chlorine and H<sub>2</sub>O in the bulk silicate Moon [2,18].

In order to better understand the processes involved in giving rise to the heavy chlorine isotope compositions of lunar samples, we have performed a comprehensive *in situ* high precision study of chlorine isotopes, using NanoSIMS, of lunar apatite from a suite of Apollo samples covering a range of geochemical characteristics and petrologic types.

**Results and discussion:** We show that the Cl isotopic composition of apatite from low- and high-Ti mare basalts are consistent with previous studies [7,14], with  $\delta^{37}\text{Cl}$  values from  $\sim+2$  to  $+18$  ‰. In contrast, apatite from KREEP-rich basalts such as KREEP basalt 72275 [14] and very high potassium (VHK) basalt 14304 have distinctly heavier Cl isotopic compositions than apatite found in mare basalts. Similarly apatite from highlands samples display very heavy Cl isotopic compositions ( $>+20$  ‰).

We investigated whether the heavy  $\delta^{37}\text{Cl}$  values of lunar rocks could be related to the proportion of KREEP component they contain, by comparing the Cl isotope compositions of apatite with bulk-rock incompatible trace element data. Our results strongly indicate mixing between a mantle source with low Cl isotopic composition ( $\sim 0$  ‰) and a KREEP-rich component characterized by a  $\delta^{37}\text{Cl}$  value  $\sim+30$  ‰.

The internal differentiation of the Moon via a LMO predicts a volatile-rich urKREEP layer dominated by Cl [19], containing at least 1350 ppm Cl [2]. Boyce et al. [7] proposed that degassing of Cl from the LMO would account for the fractionation of Cl isotopes and  $\delta^{37}\text{Cl}$  values  $\sim+30$  ‰ in the residual urKREEP layer. Whilst the LMO model provides an elegant mechanism for concentrating Cl in the Moon, the solubility of Cl in

basaltic silicate liquids is high (e.g., [20]) and the confining pressure beneath the 30-40 km of lunar crust [21] would be sufficient to prevent the loss of Cl by degassing.

Therefore, in order to explain the fractionated Cl isotopic composition of urKREEP, we envisage a scenario in which, during the latter stages of LMO crystallization ( $>95$  %), a large bolide(s) punctured the lunar crust [22] to a depth sufficient to bring KREEP-rich material to lower pressures, drastically decreasing the solubility of Cl in the residual LMO magmatic liquids and enabled degassing of metal chlorides [14, 23], leading to the fractionation of Cl isotopes. If such an event was restricted to the nearside of the Moon, i.e., the Procellarum KREEP Terrane, then one would expect rocks from outside of this region to have relatively unfractionated Cl isotope compositions.

**References:** [1] Taylor S. R. et al. (2006) *Rev. Min. Geochem.*, 60, 657-704. [2] McCubbin F. M. et al. (2015) *Am. Mineral.*, 100, 1668-1707. [3] Greenwood J. P. et al. (2011) *Nat. Geosci.*, 4, 79-82. [4] Tartèse R. et al. (2013) *GCA*, 122, 58-74. [5] Barnes J. J. et al. (2014) *EPSL*, 390, 244-252. [6] Tartèse R. et al. (2014) *Geology* 42, 363-366. [7] Boyce J. W. et al. (2015) *Sci. Adv.*, 1, e1500380. [8] Saal A. E. et al. (2013) *Science* 340, 1317-1320. [9] Füri E. et al. (2014) *Icarus* 229, 109-120. [10] Canup R. M. (2012) *Science* 338, 1052-1055. [11] Čuk M. and Stewart S. T. (2012) *Science* 338, 1047-1052. [12] Sharp Z. D. et al. (2007) *Nature* 446, 1062-1065. [13] Sharp Z. D. et al. (2013) *GCA*, 107, 189-204. [14] Sharp Z. D. et al. (2010) *Science* 329, 1050-1053. [15] Treiman A. H. et al. (2014) *Am. Mineral.*, 99, 1860-1870. [16] Tartèse R. et al. (2014) *Meteoritics & Planet. Sci.*, 49, 2266-2289. [17] Barnes J. J. et al. (In review, *EPSL*). [18] Hauri E. H. et al. (2015) *EPSL*, 409, 252-264. [19] Elkins Tanton L. T. et al. (2002) *EPSL*, 196, 239-249. [20] Webster J. D. et al. (1999) *GCA*, 63, 729-738. [21] Wieczorek M. A. et al. (2013) *Science* 339, 671-675. [22] Kamata S. et al. (2015) *Icarus* 250, 492-503. [23] Ustunisik G. et al. (2015) *Am. Mineral.*, 100, 1717-1727.

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