

VOLATILE CONTENT OF THE LUNAR MAGMA OCEAN: CONSTRAINTS FROM KREEP BASALTS 15382 AND 15386. J. P. Greenwood¹, N. Sakamoto², S. Itoh^{2,3}, J. A. Singer¹, P. H. Warren⁴ and H. Yurimoto², ¹Dept. Earth & Environmental Sciences, Wesleyan University, 265 Church St., Middletown, CT 06459, ²Natural History Sciences, Hokkaido University, Sapporo, Japan 060-0810, ³Graduate School of Science, Kyoto University, Kyoto, Japan, ⁴Institute of Geophysics & Planetary Physics, UCLA, Los Angeles, CA 90095.

Introduction: The volatile content of the Moon and lunar samples has been undergoing a revolution of data and ideas in the last decade, but with little consensus [1-14]. The formerly dominant paradigm of an anhydrous Moon still has support in the heavy isotopes of Cl and Zn [10, 14], but the number of studies that have found direct evidence of water/OH in glasses and minerals argues for a Moon that could possibly have had (or has) as much water and volatiles as the Earth.

High water contents in the Moon have important implications for the evolution of the lunar magma ocean (LMO). For example, if the LMO had 1000 ppm H₂O (as found in 74220 olivine-hosted melt inclusions), then this would predict 5% wt.% H₂O for the last vestiges of the lunar magma ocean [6], also known as urKREEP (for discussion purposes, urKREEP is assumed to represent the last 1% of the molten magma ocean). This much water would lead to saturation at the base of the lunar crust, a likely place for the urKREEP to be at the end of LMO crystallization [6]. The lack of hydrous minerals or evidence for aqueous alteration in lunar samples would seem to argue against such high levels of water [13].

Recent estimates of the chlorine content of the lunar mantle urKREEP vary widely. McCubbin et al. [13] argue for a Cl-enriched urKREEP due to partitioning effects during magma ocean crystallization. McCubbin et al. infer 1100-1350 ppm Cl, 660 ppm F, and 300-1250 ppm H₂O. Treiman et al. [15] from elemental ratios in KREEP samples infer that urKREEP had 660 ppm F and 150 ppm Cl (they do not make an estimate for the water content of urKREEP).

The KREEP basalts 15382 and 15386 are considered some of the most pristine samples of the lunar KREEP component, while not being directly representative of urKREEP. Here we use analyses of these two basalts to estimate the lunar volatile inventory (for H, F, and Cl).

Samples and Methods: Carbon-coated thin-sections of KREEP basalts 15382,17 and 15386,60 were studied using the Yale FEG electron microprobe and a Cameca ims 1280 HR ion microprobe at Hokkaido University. Appropriate terrestrial glasses were used for reduction of SIMS data.

Results and Discussion: We find the highest amounts of chlorine yet reported for an extraterrestrial glass (to our knowledge) with 243±24 to 1016±102

ppm Cl for late-stage glasses in KREEP basalts 15382 and 15386 by ion microprobe and electron microprobe. These glasses are likely the last materials to solidify in these rocks, and are associated with typical late-stage lunar minerals, such as apatite, merrillite, ferrohedenbergite, K-, Ba-rich feldspar and tranquillityite.

Late-stage glasses in KREEP basalts 15382 and 15386 are the main carriers of chlorine in these samples, while apatite is the main carrier of fluorine. By estimating the volume of apatite and glass in 15382, we calculate 313 ppm F and 27 ppm Cl in 15382. If we scale this to the urKREEP component, using established methodology [15, 16], we obtain 1159 ppm F and 101 ppm Cl for the urKREEP component. Our results are similar to Treiman et al. [15] estimate of urKREEP, but very different than the estimate of McCubbin et al. [13].

If urKREEP represents the last 1% of the LMO to crystallize then our results would predict 12 ppm F and 1 ppm Cl for the LMO, which are indistinguishable from estimates for the LMO derived from the most volatile-rich sample from the Moon, the olivine-hosted melt inclusions of 74220 [9].

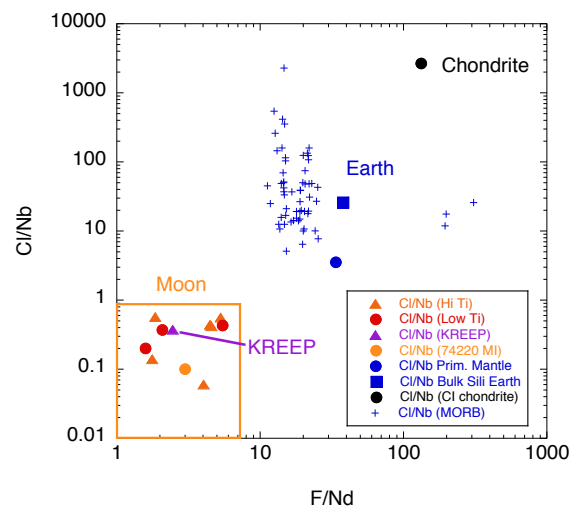


Figure 1. Cl/Nb vs. F/Nd of the Moon, Earth, and Cl chondrite.

Cl/Nb vs. F/Nd: A case for depletion in lunar volatiles. Volatile elements can be fractionated from each other during melting, crystallization, and degassing. If we consider volatile/refractory element ratios with similar partition coefficients, we see that the Cl/Nb and

F/Nd of lunar materials are depleted relative to Earth and CI chondrite (Fig. 1). A very surprising result is the similarity between the volatile-rich 74220 olivine-hosted melt inclusions and KREEP; in fact the agreement between all lunar samples is unexpected. The similarity in Cl/Nb and F/Nd of all lunar samples argues against fractionation due to degassing, unless all samples are similarly degassed. It would appear that this is a global signature for lunar samples, and is consistent with an order of magnitude depletion in fluorine and chlorine for the Moon relative to the Earth. Whether this depletion is due to the giant impact or signifies a fundamental difference in volatile delivery between the Earth and Moon is not clear.

Estimate of the LMO water content. If we assume the order of magnitude depletion in fluorine and chlorine can be extended to water, then we calculate 3500-6000 ppm H₂O for urKREEP using an H₂O/Ce=30 for the LMO. This would yield 35-60 ppm H₂O in the bulk lunar magma ocean. For comparison, the 74220 olivine-hosted melt inclusion has an H₂O/Ce=77 [17].

KREEP and the highlands Mg-suite. The intimate relationship between KREEP and the ultramafic Mg-suite rocks of the highlands has long been recognized, and has previously been ascribed to mixing of partial melt of the Mg-suite ultramafic cumulate source rocks and a KREEP liquid [18]. We propose a simpler solution—that the volatile-rich KREEP lowered the solidus of the Mg-suite cumulate source rocks during early cumulate overturn.

Implications for the lunar chlorine isotope anomaly. The KREEP samples typically have the largest chlorine isotope anomalies in the solar system [10, 12]. The late-stage glasses in the KREEP basalts are highly enriched in chlorine, which would argue against a fractionation in chlorine isotopes occurring during extrusion of these basalts. It would argue that the chlorine isotope anomaly was set during an earlier event, such as the giant impact event.

References: [1] Saal A. E. et al. (2008) *Nature*, 454, 192-196. [2] Greenwood J. P. et al. (2011) *Nature Geosci.*, 4, 79-82. [3] McCubbin F. M. et al. (2010) *PNAS* 107, 11223. [4] Boyce J. W. et al. (2010) *Nature* 466, 466. [5] Albarede et al. (2014) *MAPS*. [6] Elkins-Tanton L. E. and Grove T. L. (2011) *EPSL* 307, 173. [7] Robinson K. and Taylor G. J. (2014) *Nat. Geosci.* [8] Tartese R. et al. (2014) *Geology* [9] Hauri E. et al. (2011) *Science*, doi: 10.1126/science.1204626. [10] Sharp Z. et al. (2010) *Science* doi:10.1126/science.1192606. [11] Boyce J. W. et al. (2014) *Science* 344, 400-402. [12] Boyce J. W. et al. (2015) *Science Advances* Sept. 25. [13] McCubbin F. M. et al., (2015) *Am. Mineral.* 100, 1668-1707. [14] R. C. Paniello, J. M. D. Day, F. Moynier (2012) *Nature*

490, 376-380. [15] Treiman A. H. et al., (2014) *Am. Mineral.* 99, 1860-1870. [16] B. L. Jolliff, in *Planetary Petrology and Geochemistry*, G. A. Snyder, C. R. Neal, W. G. Ernst, Eds. (Bellweather Publishing for Geological Society of America, 1998), pp. 135-154. [17] E. H. Hauri, et al. (2015) *Earth Planet. Sci. Lett.* 409, 252-264.