**urCl-KREEP? Cl-rich glasses in KREEP basalts 15382 and 15386 and their implications for lunar geochemistry.** J. P. Greenwood<sup>1</sup>, N. Sakamoto<sup>2</sup>, S. Itoh<sup>2,3</sup>, J. A. Singer<sup>1</sup>, and H. Yurimoto<sup>2 1</sup>Dept. of Earth & Environmental Sciences, Wesleyan University, Middletown, CT 06459 USA, <sup>2</sup>Natural History Sciences, Hokkaido University, Sapporo, 060-0810 Japan, <sup>3</sup>Kyoto University, Kyoto, 606-8502 Japan.

**Introduction:** Since the discovery of water in lunar glasses [1] and apatite [2-4], the debate has focused on volatile abundances, rather than their existence [5]. The KREEP signature in lunar samples has been ascribed to the incompatible-rich last vestiges of the lunar magma ocean [6]. While magma ocean modeling predicts less than 100 ppm water in the magma ocean [7], the expected late-stage KREEP liquid should still be volatile-rich. Yet measurements of water in apatite from KREEP-rich samples have found only low contents of water [8,9]. Here we present measurements of fluorine and chlorine in late-stage glasses from KREEP basalts 15382 and 15386.

**Methods:** Fluorine and chlorine were measured in late-stage glasses of carbon-coated thin-sections of KREEP basalts 15382,17 and 15386,60 using the new Hokkaido University Cameca ims 1280-HR, with natural and synthetic glasses for calibration. Chlorine was also measured using the FEG electron microprobe at Yale University.

**Results:** *15382,17.* This thin-section was analyzed by both the electron microprobe and the 1280 SIMS for Cl and F. Area used for electron microprobe analysis is shown in Fig. 2. Three electron microprobe analyses gave 435, 599, and 694 ppm of Cl. Detection limit for Cl in the electron microprobe was 90 ppm. Fluorine was below electron microprobe detection limit (D.L.: 450 ppm F). Mapping and electron microscopy shows that Cl-apatite in the electron beam volume is not the cause of the high Cl during the analyses, as  $P_2O_5$  is lower than Cl. Cl WDS mapping shows a uniform Cl enrichment in the glass (Fig. 2). The SIMS measurements are similar in Cl content (Fig. 1) to the electron microprobe analyses.

*15386,60.* This thin-section was only measured via SIMS. Similar levels of F and Cl were found in 15386 to 15382 (Fig.1).

**Discussion:** *Contamination?* Two different measurement techniques, with different analytical volumes, gave similar results on the same sample. More important is the similarity between chlorine and petrology of 15382,17 and 15386,60. While 15382,17 is an old thin-section that has been in multiple labs, we were the first group to analyze 15386,60, and were careful not to contaminate the sample. Similar levels of chlorine were found for the two thin-sections of different samples with different handling histories.

*Comparison to lunar glasses.* Lunar glasses are low in fluorine and chlorine, except for the high Cl of the two KREEP basalts (Fig. 1). Lunar glasses and melt inclusions from the literature [2,10] are plotted along with unpublished data from our group on 12009, 12035, 12039, and 15555 (see [11] this meeting). The KREEP basalts are only enriched in Cl, not F. Fluorine levels of KREEP basalts are similar to other lunar glasses.

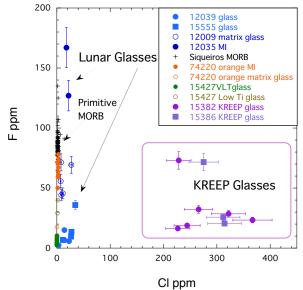


Figure 1. F (ppm) vs. Cl (ppm) of glasses and melt inclusions from picritic glasses 15427 [1], 74220 [10], and olivine basalts 12009 and 12035, compared to late stage glasses of mare basalts 12039, 15555, and KREEP basalts 15382 and 15386.

Comparison to primitive MORB and seawatercontaminated MORB. Fluorine levels of KREEP basalt glasses are similar to primitive MORB from the Siqueiros fracture zone (Fig. 1; [12]). Chlorine is highly elevated relative to primitive MORB, but is similar to seawater-contaminated MORB (not shown; [13]). The Moon has mare but no seawater, thus the high Cl in these samples must have another origin.

Is KREEP Cl rich? A lack of chlorine measurements of lunar samples seems to have left this important geochemical signature largely unnoticed, with the exception of [14,15]. They noticed a Cl correlation with the KREEP signal in lunar soils, but ascribed it to chlorapatite. They did not physically identify the carrier of the the chlorine component in the lunar soils. More recently, a correlation of elevated Cl isotopes and the KREEP signal has been seen [16,17]. This has important implications for the high Cl in KREEP glasses (see below).

We hypothesize that the high Cl we measure in the KREEP basalts 15382 and 15386 is indicative of its geochemical signature. We propose that ur-KREEP was Cl-rich.

*Implications of Cl-rich KREEP*. If KREEP is indeed Cl-rich, the implications are profound for lunar geochemistry. It would suggest that Cl-rich fluids and/or magmas permeated the lunar crust to deliver the KREEP signal. If KREEP is the last vestiges of the magma ocean, then it would suggest that this late-stage liquid was Cl-rich.

One of the mysteries of the KREEP geochemical signature has been its ability to permeate so many of the lunar samples without leaving evidence of its magmatic affinity. We suggest that Cl aided the transport of the KREEP signature to the upper lunar crust, possibly as Cl-rich fluids and/or magmas.

*Bearing on Chlorine isotopes.* KREEP samples have been found to be elevated in Cl isotopes [16,17]. We have not measured Cl isotopes of the KREEP glasses yet; if these samples have high Cl isotopes it would prove that elevated Cl isotopes in lunar samples were not a product of volcanic outgassing, as these two KREEP samples have elevated chlorine. Further work on the Cl isotopes of these samples are critical for our understanding of lunar chlorine isotope geochemistry.

**Conclusions:** Late-stage glasses in KREEP basalts 15382 and 15386 are enriched in Cl. We propose that KREEP is fundamentally Cl-rich and its chlorine-rich character aided its infiltration of the upper lunar crust.

**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] Warren P. H. and Wasson J. T. *Rev. Geophys. Space Phys. 17,* 73. [7] Elkins-Tanton L. E. and Grove T. L. (2011) *EPSL 307,* 173. [8] Robinson K. and Taylor G. J. (2014) *Nat. Geosci.* [9] Tartese R. et al. (2014) *Geology* [10] Hauri E. et al. (2011) *Science,* doi: 10.1126/science.1204626. [11] Singer J. A. et al. (this meeting) [12] Saal A. E. and Hauri E. H. (2002) *Nature,* doi:10.1038/nature01073. [13] Aiuppa et al. (2009) *Chem. Geol. 263,* 1. [14] Reed G. W. J. et al. *Proc. 3<sup>rd</sup> Lunar Conf. 2,* 1989. [15] Reed G. W. J. and Jovanovic S. *GCA 37,* 1457. [16] Sharp Z. et al. (2010) *Science* doi:10.1126/science.1192606. [17] Boyce J. W. et al. (2015) *PNAS* in press.

Figure 2. Ca WDS (top) and Cl WDS (bottom) maps of glass and apatite in 15382,17. BSE (middle) has 10 μm scale bar in red for all 3 images. Electron microprobe locations are shown.

