

**WATER AND VOLATILES IN APOLLO ROCKS: THE VIEW FROM SAPPORO AND CONNECTICUT.**

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**Introduction:** Since the discovery of water in lunar soil samples [1], there has been an explosion in research on the new field of lunar water. We have been analyzing water, D/H, and other volatile elements in Apollo rock samples since 2009, and have now conducted thousands of analyses, using SIMS spot analyses, SCAPS ion image analyses, FEG-EPMA, FEG WDS K $\alpha$  mapping, FEG-EDS, and micro-Raman spectroscopy in high titanium mare basalts, low titanium mare basalts, AI-basalts, KREEP basalts and highland rocks. This extensive analysis of Apollo rock samples allows us to understand the history and distribution of volatiles in lunar samples that cannot be attained by studying lunar soil samples alone.

**High Titanium Basalts:** We have now found abundant evidence for volatile-rich and water-rich glasses and melt inclusions in high-titanium basalts [2-4]. We have also found evidence for a change to more oxidizing conditions in the high-titanium basalts upon emplacement near the lunar surface, wherein we find Fe metal becoming oxidized to form hercynite (FeAl<sub>2</sub>O<sub>4</sub>). We have also found a new lunar volatile mineral, with the preliminary name of Ce-Chlor-Britholite, that crystallizes *after* apatite in slowly-cooled high titanium basalts. That this mineral crystallizes after apatite, and is F-,Cl-rich, shows that apatite crystallization did not deplete the melt in fluorine, as predicted by the Lunar Apatite Paradox model [5]. We predict that all high-titanium basalts were similarly enriched in volatile elements. We will present results that demonstrate that some high-titanium basalts have only an order of magnitude depletion in H<sub>2</sub>O relative to terrestrial magmas. If high-titanium magmas underwent significant degassing [6], then this would predict at least earth-like levels of water, and possibly higher.

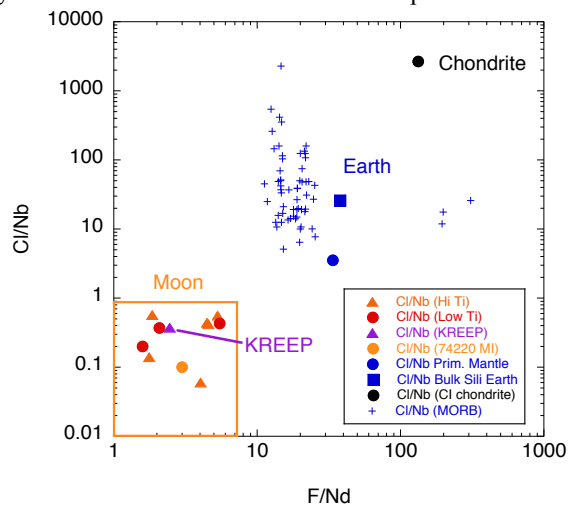
**Low Titanium Basalts:** The low-titanium basalts have proven especially fruitful for disentangling the D/H history of lunar magmas. We will present the results of a comprehensive and cohesive model to explain D/H systematics of the Moon. This model indicates a high D/H for the lunar mantle, as originally found by [7].

According to the Lunar Apatite Paradox model, OH-rich apatites are due to low overall volatile element contents of lunar magmas. OH-rich apatites are only found in low-titanium basalts, suggesting overall

lower volatile contents for low-titanium basalts relative to high-titanium basalts. Conversely, chromite-hosted melt inclusions have high F and Cl abundances [8], suggesting that water behavior may be decoupled from F and Cl in these magmas, and especially during their subsolidus history [9].

**KREEP basalts:** We have found the most Cl-rich extraterrestrial glasses in KREEP basalts 15382 and 15386, with up to 1000 ppm Cl [10]. Comparison of volatile/refractory elements such as F/Nd and Cl/Nb of KREEP basalts, shows an order of magnitude depletion in F and double that in chlorine relative to the Earth (Fig. 1). All lunar samples analyzed for F and Cl thus far, including 74220 water-rich olivine hosted melt inclusions, show a similar relationship (Fig. 1).

**Summary:** Comprehensive analyses of volatile element distributions in Apollo rock samples since 2009 have finally unveiled the history of lunar volatiles and the origins of the Moon's water. High D/H of the lunar mantle is still best explained as delivery of cometary water to the Moon after the Giant Impact.



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

**References:** [1] Saal A. E. et al. (2008) *Nature*, 454, 192-196. [2] Greenwood J. P. et al. (2016) *In submission*. [3] Lowe M. E. et al. (2016) *LPS XLVII*. [4] Mahmood S. (2016) *LPS XLVII*. [5] Boyce J. W. et al. (2014) *Science* 344, 400-402. [6] Hauri E. H., et al. (2015) *Earth Planet. Sci. Lett.* 409, 252-264. [7] Greenwood J. P. et al. (2011) *Nature Geosci.*, 4, 79-82. [8] Singer J. A. et al. (2016) *Geochem J.* in submission. [9] Treiman A. H. et al. (2016) *Am. Mineral.* In press. [10] Greenwood J. P. et al. (2016) *Nature Geosci.* In review.