

HYDROGEN ISOTOPES, VOLATILE, AND REFRACTORY TRACE ELEMENT COMPOSITION OF MELT INCLUSIONS AND APATITE IN A CONSANGUINEOUS SUITE OF APOLLO 12 OLIVINE BASALTS. J. P. Greenwood¹, S. Itoh^{2,3}, N. Kawasaki², N. Sakamoto², and H. Yurimoto². ¹Dept. of Earth and Environmental Sciences, Wesleyan University, Middletown, CT 06459 (jgreenwood@wesleyan.edu), ²Natural History Sciences, Hokkaido University, Sapporo, Japan, ³Graduate School of Science, Kyoto University, Kyoto, Japan.

Introduction: The last decade has led to a revolution in our knowledge of the volatile content of the Moon [1], but our understanding of the origins, abundances, reservoirs, and processes that have affected these volatiles is still in its infancy. To address these problems, we have undertaken a comprehensive study of volatile and trace elements of one of the only known examples of an extraterrestrial suite of basalts, the Apollo 12 olivine basalts [2,3]. These basalts differ only in cooling rate and amounts of added olivine (possibly via crystal settling), and range from glassy to crystalline olivine basalts, and have been argued to be samples of a thick lava flow or small sill [2,3]. Thus, these unique samples can be used to assess the effects of crystallization, cooling rate, degassing and secondary alteration on volatile contents and isotopic composition. Here we present results of H, D, F, Cl, Nb, Nd, and Ce on olivine-hosted melt inclusions in five of these basalts (12004, 12009, 12018, 12035, and 12040) and H and D of apatite in two samples (12018 and 12040).

Methods: Sample chips were requested from NASA-JSC and CAPTEM, then sectioned, mounted in low-temperature melting point metals, and polished without the use of water. Prior to SIMS analyses, sections were carefully imaged with SEM to locate analytical targets. The modified and renovated Cameca ims 1270 was used for H and D measurements, and the Cameca ims 1280 was used for F, Cl, Nb, Nd, and Ce measurements, both machines at Hokkaido University. H and D were measured first, followed by sample re-polishing to expose new melt inclusions before volatile and trace element analyses. This was due to the longer times necessary for D analyses. New melt inclusions were analyzed for F and Cl in negative ion mode, followed by FEG-SEM imaging before analyses of Nb, Nd, and Ce in positive ion mode, on the same melt inclusions as F and Cl.

Results and Discussion:

D/H. The results of D/H analyses vs. H₂O content are shown in Figs. 1 and 2. Basalt 12018 is an intermediately cooled sample in this suite, and has both olivine-hosted melt inclusions and apatite and has been reported on previously by us [4]. The melt inclusions of 12018 are high in water content (62-740 ppm H₂O; [4]) and low in δD (δD : $-183 \pm 212\%$ to $+6 \pm 162\%$ (2σ))

[4]), which are in extreme hydrogen isotope disequilibrium with apatite, which has a very high δD of $+1439 \pm 103\%$ (2σ) in this sample (Fig. 1). Loss of H₂ from lunar magmas with originally low chondritic δD has been used to explain high δD of apatite [5] and olivine-hosted melt inclusions [6], with δD values below $\sim +1000\%$. Current fractionation factors for isotope fractionation of H from D cannot replicate the δD of apatite in 12018 from chondritic or Earth-like sources of water, suggesting that the δD of the magma that apatite crystallized from was originally $> +300\%$, as has been hypothesized for the lunar mantle [7,8].

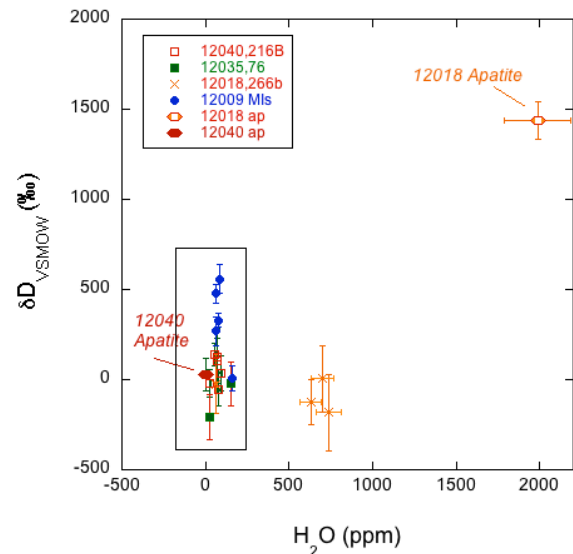


Figure 1. δD vs. H₂O of olivine-hosted melt inclusions and apatite in basalts 12009, 12004, 12018, and 12040. The box represents Fig. 2.

The δD of olivine-hosted melt inclusions in 12009 are higher in general than those from the more slowly-cooled samples. This suggests that low δD of melt inclusions is not a primary feature, but due to D/H exchange during cooling, on or near the lunar surface, an idea first suggested by Treiman [9]. Singer et al. [4] argued that olivine-hosted melt inclusions in 12018, 12035, and 12040 suffered D/H exchange, while apatite in 12018 is able to preserve its original δD , likely due to slower diffusive exchange [10]. They also suggested that D/H exchange was occurring while the magmas were still molten, to explain the low δD of

apatite in 12040 [4], rather than by subsolidus metamorphism [9].

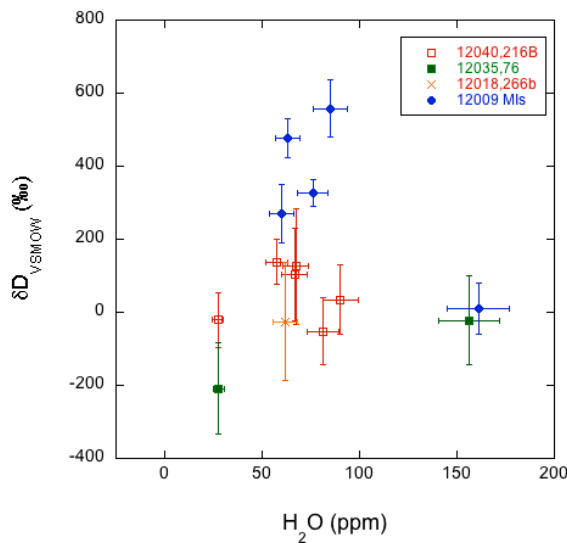


Figure 2. Inset of Fig. 1 showing δD vs. H_2O of olivine-hosted melt inclusions in 12009, 12018, 12035, and 12040.

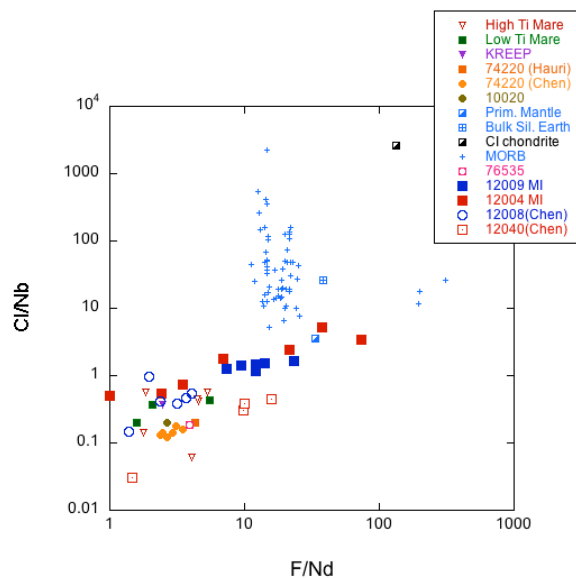


Figure 3. Cl/Nb vs. F/Nd of 12004 and 12009 olivine-hosted melt inclusions with comparison to other lunar samples and Earth (see [11]).

Cl/Nb vs. F/Nd. The Cl/Nb vs. F/Nd of olivine-hosted melt inclusions from 12004 and 12009 are shown compared to the Earth and Moon [11]. The melt inclusions of 12004 and 12009 are characterized by higher Cl/Nb and F/Nd than most previously analyzed lunar samples (Fig. 3). They are almost an order of magnitude higher in Cl/Nb than the olivine-hosted melt inclusions of 74220 [12,13], with almost

Earth-like abundances of F/Nd (Fig. 3). They have similar F/Nd to melt inclusions from 12040 [12], suggesting that F is preserved in Apollo 12 olivine-hosted melt inclusions during slow cooling. The highest values of Cl/Nb and F/Nd for 12004 and 12009 are for trapped melt pockets, rather than bona fide melt inclusions, suggesting effects of differentiation for the highest values. Regardless, these results point to higher volatile contents for the Apollo 12 olivine basalts than for 74220 picritic glasses. Our results are also consistent with high Cl/Nb measured in 12008 olivine-hosted melt inclusions [12].

Summary: D/H results for Apollo 12 olivine basalt phases suggest that originally high δD values of magma were altered to lower δD values during emplacement on or near the lunar surface. Lunar regolith, that is either assimilated or undergoes vapor exchange with the Apollo 12 olivine basalts during cooling has been suggested as the source of the low-D contaminant [9]. Lunar agglutinate glasses contain ~100-300 ppm H_2O [14] and comprise ~20-30% of lunar soils [15], suggesting a reservoir of low-D hydrogen for near surface basalts. The low δD of olivine-hosted melt inclusions in the more slowly-cooled basalts show enhanced exchange, supporting this model [4,9].

Loss of H_2 into a vacuum during Rayleigh distillation cannot increase δD to ~+1400‰ if starting δD is <0‰ which is needed for apatite in 12018. This argues for a source magma δD >+300‰.

Cl/Nb and F/Nd are higher in the Apollo 12 olivine-hosted melt inclusions than in 74220 olivine-hosted melt inclusions, suggesting that the Apollo 12 olivine basalts either had higher starting Cl/Nb and F/Nd than 74220 or that more F and Cl were lost from 74220 than 12004 or 12009. Future work will assess the F, Cl, and S content of olivine-hosted melt inclusions in the more slowly-cooled members of this suite, to better understand how slow cooling affects these volatile elements in lunar basalts.

References: [1] Greenwood J. P. et al. (2018) *Space Sci. Rev.* 214, 92. [2] Walker D. et al. (1976) *GSA Bull.*, 87, 646. [3] Walker D. et al. (1976) *Proc. LPSC VII*, 1365. [4] Singer J. A. (2017) *Geochem. J.* 51, 95. [5] Tartèse R. and Anand. M. (2013) *EPSL* 361, 480. [6] Saal A. E. et al. (2013) *Science* 340, 1317. [7] Greenwood J. P. et al., (2011) *Nat. Geosci.* 4, 79. [8] Hui. H. et al. (2017) *EPSL* 473, 14. [9] Treiman A. H. et al., (2016) *Am. Min.* 101, 1596. [10] Higashi Y. et al., (2017) *Geochem. J.* 51, 115. [11] Greenwood J. P. et al. (2017) *Geochem. J.* 51, 105. [12] Chen Y. et al. (2015) *EPSL* 427, 37. [13] Hauri E. H. et al. (2013) *Science* 333, 213. [14] Liu Y. et al. (2012) *Nat. Geosci.* 5, 779. [15] McKay D. S. et al. (1991) in *Lunar Sourcebook* (eds. Heiken G. H. et al.) Cambridge Univ. Press, Cambridge UK.