

HYDROGEN ISOTOPES OF WATER IN THE MOON: EVIDENCE FOR THE GIANT IMPACT MODEL FROM MELT INCLUSIONS AND APATITE IN APOLLO ROCK SAMPLES. J. P. Greenwood¹, S. Itoh^{2,3}, N. Sakamoto², K. Yanai², J. A. Singer¹, and H. Yurimoto², ¹Dept. of Earth & Environmental Sciences, Wesleyan University, Middletown, CT 06459 USA, ²Natural History Sciences, Hokkaido University, Sapporo 060-0810, Japan, ³Kyoto University, Kyoto, Japan.

Introduction: Since the discovery of water in lunar glasses [1] and apatite [2,3,4], and its subsequent ubiquity in other phases such as olivine-hosted melt inclusions [5,6], lunar agglutinates [7], plagioclase [8] and more apatite [9-11], the answers to the fundamental questions of how much water is in the Moon and where did it come from have not yet become clear. Recent studies of hydrogen isotopes of water in lunar samples from olivine-hosted melt inclusions [6] and apatite [9-11] have suggested a carbonaceous chondrite origin for lunar water, as opposed to comets [4]. These newer studies have confirmed elevated D/H of lunar water relative to Earth [6, 9-11], and while both proposed a chondritic origin for lunar water, differ on whether the water is from the Earth [6] or from late delivery of chondrites to the Moon [9-11], followed by volcanic degassing under reducing conditions to raise D/H of lunar water either via equilibrium hydrogen isotope fractionation of H₂ [9] or differential diffusive degassing of H and D from a melt containing H₂, H₂O, and OH [6].

In order to understand the volatile history of the Apollo crystalline basalts, we have begun a study of early, trapped melts with late-stage apatite in the Apollo 12 olivine basalt suite. The Apollo 12 olivine basalt suite rocks are believed to be consanguineous and can be related to each other via olivine addition [12], and different cooling histories [13], from olivine vitrophyres (12009) to cumulates (12040). Here we present results of water and D/H of olivine-hosted melt inclusions in rapidly-cooled vitrophyre 12009 and 12004 with apatite grains from more slowly cooled members of the Apollo 12 olivine basalts (12006, 12018, 12040). We also compare these results with those of apatite from all other lunar samples that we have studied to date (Apollo 11, 12, 14, 15, 17, highlands, KREEP), to develop a model to explain the elevated D/H of the lunar interior.

Methods: Ion microscope analysis was conducted using the modified Cameca ims 1270 w/ SCAPS detector for 2D ion imaging at Hokkaido University. Apollo basalt chips were mounted in liquid metal and then cut and polished without water to prevent terrestrial contamination during sample preparation. Ion microscopy of apatite followed our previously published methodology [4].

Results: Water and D/H of Apollo 12 olivine basalts from early olivine-hosted melt inclusions to late-stage apatites. Melt inclusions and mesostases from basalts 12004 and 12009 are shown in Fig. 1 and compared to apatite in more slowly cooled basalts 12006 and 12018 in Fig. 2. D/H values of melt inclusions overlap with those of apatite from olivine basalts, but at much lower water contents, suggesting that D/H values of Apollo 12 basalts were obtained prior to melt entrapment in early olivines, and also that magmatic processes capable of fractionating D/H (such as degassing or assimilation) were likely not operative during crystallization of the Apollo 12 olivine basalts.

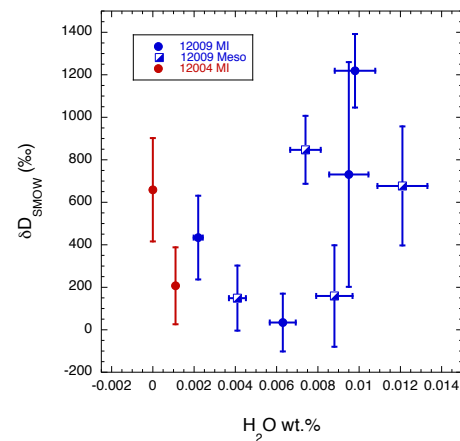


Figure 1. δD vs. H₂O for melt inclusions and mesostates in olivine basalts 12004 and 12009.

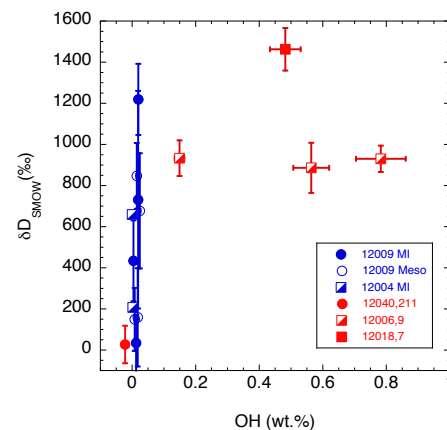


Figure 2. δD vs. OH (wt. %) for melt inclusions, mesostates and apatites in Apollo 12 olivine basalts.

Discussion: *Origin of highly elevated D/H of lunar water in melt inclusions and apatite.* The large range of D/H of melt inclusions from Apollo 12 basalts is similar to the large range of D/H from apatite grains we have measured in lunar samples (Fig. 3). A number of apatite grains from a range of Apollo samples (Apollo 11, 12, 15, 17, and KREEP) have δD well above +1000‰ (δD of mare apatite: $+391 \pm 62$ ‰ to $+2069 \pm 78$ ‰), which are very difficult to achieve during degassing of H_2 [6,9]. Only cometary materials continue to be similarly elevated in D/H as lunar apatite [4].

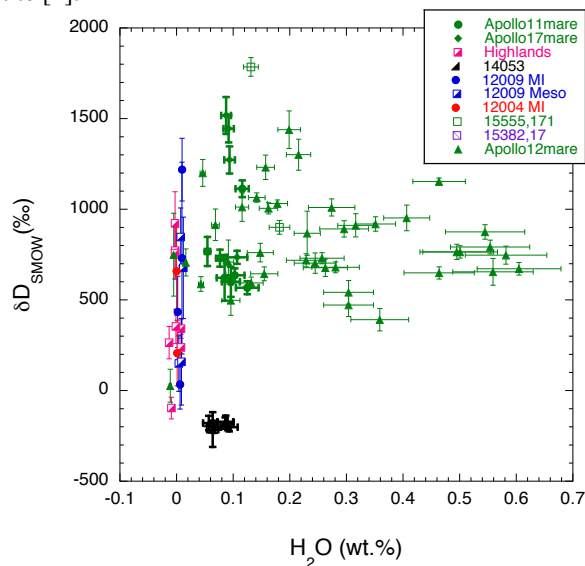


Figure 3. δD vs. OH (wt.%) for melt inclusions, mesostases and apatite in lunar samples.

Elevated D/H of lunar mantle relative to Earth

To explain the lower range of D/H of lunar apatites, we originally proposed that the lunar mantle may have an elevated D/H similar to that found in the highlands alkali anorthosite clast 14305,303, and that highly elevated D/H values were a remnant of a cometary origin [4]. The average of five olivine-hosted melt inclusions in Apollo 17 glasses reported by [6] are nearly identical to the average of two analyses of apatite in the highlands alkali anorthosite clast in 14305,303. We propose that the Apollo 17 melt inclusions and the highlands clast are the best representatives of the primordial lunar mantle D/H. The lower range of D/H of Apollo 12 melt inclusions (Fig. 1) and mare basalt apatite (Fig. 3) are also consistent with an elevated lunar mantle D/H of $\sim +200$ - $+300$ ‰. Samples with lower D/H are affected by hydrogen addition during impact into the hydrogen-rich lunar regolith (e.g. apatite in basalt 14053 [4]). All other samples

with D/H $> +400$ ‰ are either affected by degassing of H_2 or are a relict of a cometary source.

Elevated lunar mantle D/H due to hydrodynamic escape of hydrogen in the aftermath of the Giant Impact

The Moon is unique in the solar system with having highly fractionated Cl and Zn isotopes [14,15]. One possibility is that the lunar mantle has an elevated D/H due to hydrodynamic escape of hydrogen in the aftermath of the giant impact. A model for mass fractionation during hydrodynamic escape of gases from an inner planet predicts a logarithmic decrease in abundance of gases with atomic mass from their initial inventory [16]. We suggest that the magnitude of the isotope fractionations of H, Cl, and Zn isotopes are consistent with such an episode of hydrodynamic escape in the aftermath of the giant impact.

References: [1] Saal A. E. et al. (2008) *Nature*, 454, 192-196. [2] McCubbin F. M. et al. (2010) *PNAS* 107, 11223. [3] Boyce J. W. et al. (2010) *Nature* 466, 466. [4] Greenwood J. P. et al. (2011) *Nature Geosci.*, 4, 79-82. [5] Hauri E. et al. (2011) *Science*, doi:10.1126/science.1204626. [6] Saal A. E. et al. (2013) *Science* doi:10.1126/science.1235142. [7] Liu Y. et al. (2012) *Nature Geosci.* doi:10.1038/NGEO1601. [8] Hui H. et al. (2013) *Nature Geosci.*, doi:10.1038/NGEO1735. [9] Tartese R. and Anand M. (2013) *EPSL*, 361, 480-486. [10] Barnes J. J. et al. *Chem. Geol.* 337-338, 48-55. [11] Tartese R. et al. (2013) *GCA* 122, 58-74. [12] Kushiro I. and Haramura H. (1971) *Science*, 171, 1235-1237. [13] Walker D. et al. (1976) *Proc. Lunar Sci. Conf. 7th*, 1365-1389. [14] Sharp Z. et al. (2010) *Science* doi:10.1126/science.1192606. [15] Paniello R. C. et al. (2013) *Nature*, doi:10.1038/nature11507. [16] Hunten D. M. et al. (1987) *Icarus*, 69, 532-549.