

Distinct petrogenesis of low- and high-Ti mare basalts revealed by OH content and H isotope composition of apatite. R. Tartèse¹, M. Anand^{1,2}, J. J. Barnes¹, N. A. Starkey¹, I. A. Franchi¹, ¹Planetary and Space Sciences, The Open University, Walton Hall, Milton Keynes, MK7 6AA, UK. ²Department of Earth Sciences, The Natural History Museum, Cromwell Road, London, SW7 5BD, UK. (Romain.Tartese@open.ac.uk)

Introduction: In the last few years, re-examination of lunar material, using instruments with better sensitivity and detection limits, permitted the successful detection of water in samples from the lunar interior. To date, significant but variable quantities of water have been measured in lunar volcanic glasses [1], in olivine-hosted melt inclusions in volcanic glasses [2] and in the mineral apatite present in both lunar basalts as well as magmatic rocks representing the lunar highlands [3-9]. These analyses complement direct measurements of hydroxyl in agglutinates in the lunar regolith [10] and observations made since the late 1990s by orbiting spacecraft (see [11] for a review). Altogether, these observations challenged the long-standing paradigm of a bone-dry Moon.

Clues to determine the origin of lunar H are likely given by its isotopic composition. H isotope composition of OH in agglutinates in the regolith suggests that H is in part derived from solar wind sources [10]. In mare basalts, the H isotope composition of OH, structurally bound in the mineral apatite, has only been reported for 7 samples from Apollo missions 11, 12, 14 and 17 [3, 5-6]. The high δD values (> 500 ‰) of apatite in most mare basalts have led to a proposal for the existence of a high- δD lunar water reservoir of cometary origin [5]. In contrast, geochemical modeling shows that a CI-chondrite type source, with an initial δD of ~ 100 ‰, is also a viable source for lunar H, the high- δD values measured in apatite in mare basalts reflecting intense H_2 degassing during magma ascent and emplacement [12-13]. To gain further insights into the source(s) of lunar H and the processes that might have fractionated H isotopes, we carried out new analyses of OH content and H isotope composition in apatites from Apollo mare basalts.

Analytical techniques: OH content and H isotope composition were measured in apatites using the Cameca NanoSIMS 50L at the Open University, following the method detailed in [3]. A large Cs^+ primary beam of ~ 250 pA current was rastered on the sample over a $12 \mu m \times 12 \mu m$ area during a 3 minute pre-sputter to eliminate any surface contamination. Secondary ion images of 1H and ^{12}C were monitored during pre-sputtering to ensure that the analyzed areas were free of cracks and hotspots. For the analysis, secondary ions of 1H , 2H , ^{12}C and ^{18}O were collected simultaneously from the central $5 \mu m \times 5 \mu m$ area of a 10

$\mu m \times 10 \mu m$ raster for ~ 20 minutes. OH contents were calibrated using the measured $^1H/^{18}O$ ratio and calibrations calculated for reference apatites with known OH contents [3, 14], which were also used to correct D/H ratios for instrumental mass fractionation. The OH contents and D/H ratios, given in the δ notation, are reported in Fig. 1 with their 2σ uncertainties, which include uncertainties on counting statistics and reproducibility of measurements carried out on standards.

Results: All the apatites analyzed display elevated δD values above ~ 400 ‰, consistent with previous reports [3, 5-6]. The heaviest δD values measured in the analyzed samples are ~ 1000 - 1100 ‰, which is also in line with the values reported in these previous studies. However, Fig. 1 shows that our δD values and those of [3] for Apollo 11 and 12 basalts are generally heavier than those reported in [5-6]. The OH content of apatites covers a wide range, from ~ 300 ppm up to ~ 7300 ppm. Yet, we did not measure very high OH contents of 8000-12000 ppm such as those reported in [5-6].

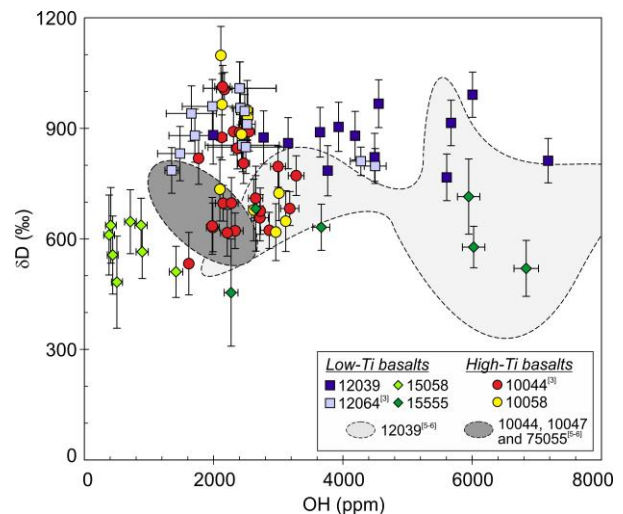


Fig. 1: δD values vs. OH contents of apatite from low- and high-Ti mare basalts.

Apatites in Apollo 12 and 15 low-Ti basalts are characterized by a large range in OH contents at relatively restricted δD values, whereas apatites in Apollo 11 high-Ti basalts display a restricted range in OH contents with highly variable δD values (Fig. 1). In samples 10044 and 10058, average OH contents and δD values are very similar (OH = 2401 ± 422 & 2552

± 380 ppm and $\delta D = 756 \pm 131$ & 823 ± 162 ‰, respectively). In Apollo 12 samples 12064 and 12039, average OH contents are 2437 ± 924 ppm and 4381 ± 1432 ppm, with very similar average δD values of 896 ± 76 ‰ and 873 ± 65 ‰, respectively. In Apollo 15 samples 15058 and 15555, average OH contents are 705 ± 354 ppm and 4565 ± 1945 ppm, also with very similar average δD values of 581 ± 62 ‰ and 597 ± 99 ‰, respectively.

Discussion: Several observations can be made from the new OH- δD dataset obtained on apatites in Apollo mare basalts:

- Apatites in samples 10044 and 10058 have identical average OH contents and δD values, which is consistent with the fact that they belong to the same B1 group of Apollo 11 basalts and sample the same lava flow [15]. Apatites in these high-Ti basalts display large variations of δD values ($\sim 600 - 1100$ ‰) at relatively restricted OH contents ($\sim 2000 - 3400$ ppm).

- In contrast, apatites in low-Ti basalts 15555 and 12039 display large variations in OH contents, $\sim 2200 - 6800$ ppm in 15555 and $\sim 2000 - 7200$ ppm in 12039, with relatively homogeneous δD values ($\sim 500 - 700$ ‰ and $\sim 800 - 1000$ ‰, respectively).

- Samples 12064 and 15058 display similar δD values to those of 12039 and 15555, respectively, but have lower OH contents.

- Apollo 15 low-Ti basalts have average δD values ~ 300 ‰ lower than Apollo 12 high-Ti basalts.

During basalt petrogenesis, two processes will have opposite effects regarding the H content in the melt: crystallization of nominally anhydrous phases such as pyroxene and plagioclase will lead to H-enrichment whereas H_2 degassing will lead to H-depletion. Moreover, H_2 degassing will strongly fractionate H from D [16], and therefore increase the δD of the melt whereas crystallization of nominally anhydrous phases will have very little effect on the D/H ratio [17]. It is worth pointing out that hydrogen is most likely to be an important H-bearing species at the very low oxygen fugacity prevailing in the lunar interior [18-19]. The OH contents and δD values measured in apatites in mare basalts thus likely result from complex interplay between these two processes.

The large δD variations with limited range of OH contents recorded in high-Ti basalts suggest that crystallization of apatite grains and H_2 degassing occurred simultaneously. Late-stage melt pockets, in which apatite crystallized, were possibly isolated from each other and thus might have undergone different degassing histories. In contrast, the large OH variations at relatively constant δD values in low-Ti basalts imply apa-

tite crystallization after H_2 degassing. In this case, the variable OH contents of apatites, especially in samples 12039 and 15555, may reflect protracted crystallization during slow cooling. Indeed, these two samples appear to have cooled very slowly [20-21]. The 200 - 300 ‰ difference between Apollo 12 and 15 low-Ti basalts indicate that the latter underwent less H_2 degassing before apatite crystallization, provided that their sources had similar initial D/H ratio.

Conclusion: New OH contents and D/H ratio measurements carried out in apatites in both low- and high-Ti Apollo basalts show that OH and D/H in basaltic melts result from complex interplay between degassing and crystallization processes. Our results suggest that apatite in low-Ti Apollo 12 and 15 basalts crystallized after H_2 degassing from the melt whereas apatite crystallization was coeval with H_2 degassing in high-Ti Apollo 11 basalts. We plan to carry out detailed investigations on these apatite grains (cathodoluminescence imaging, Cl isotope analyses) to get further insights into the petrogenesis of these mare basalts. In addition, we will continue measuring OH contents and D/H ratios in apatites in new Apollo samples to obtain better constraints on the source, abundance and the evolution of H in the lunar interior.

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