

**Distinct petrogenesis of low- and high-Ti mare basalts revealed by OH content and H isotope composition of apatite.** R. Tartèse<sup>1</sup>, M. Anand<sup>1,2</sup>, J. J. Barnes<sup>1</sup>, N. A. Starkey<sup>1</sup>, I. A. Franchi<sup>1</sup>, <sup>1</sup>Planetary and Space Sciences, The Open University, Walton Hall, Milton Keynes, MK7 6AA, UK. <sup>2</sup>Department of Earth Sciences, The Natural History Museum, Cromwell Road, London, SW7 5BD, UK. (Romain.Tartese@open.ac.uk)

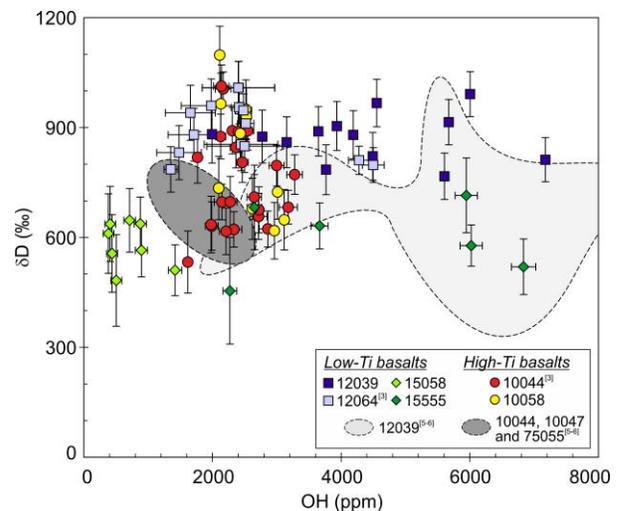
**Introduction:** In the last few years, re-examination of lunar material, using instruments with better sensitivity and detection limits, permitted the successful detection of water in samples from the lunar interior. To date, significant but variable quantities of water have been measured in lunar 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  $\delta D$  values ( $> 500$  ‰) of apatite in most mare basalts have led to a proposal for the existence of a high- $\delta D$  lunar water reservoir of cometary origin [5]. In contrast, geochemical modeling shows that a CI-chondrite type source, with an initial  $\delta D$  of  $\sim 100$  ‰, is also a viable source for lunar H, the high- $\delta D$  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  $\sim 250$  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  $\sim 20$  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  $\delta$  notation, are reported in Fig. 1 with their  $2\sigma$  uncertainties, which include uncertainties on counting statistics and reproducibility of measurements carried out on standards.

**Results:** All the apatites analyzed display elevated  $\delta D$  values above  $\sim 400$  ‰, consistent with previous reports [3, 5-6]. The heaviest  $\delta D$  values measured in the analyzed samples are  $\sim 1000$ - $1100$  ‰, which is also in line with the values reported in these previous studies. However, Fig. 1 shows that our  $\delta D$  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  $\sim 300$  ppm up to  $\sim 7300$  ppm. Yet, we did not measure very high OH contents of 8000-12000 ppm such as those reported in [5-6].



**Fig. 1:  $\delta D$  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  $\delta D$  values, whereas apatites in Apollo 11 high-Ti basalts display a restricted range in OH contents with highly variable  $\delta D$  values (Fig. 1). In samples 10044 and 10058, average OH contents and  $\delta D$  values are very similar (OH =  $2401 \pm 422$  &  $2552$

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

**Discussion:** Several observations can be made from the new OH- $\delta D$  dataset obtained on apatites in Apollo mare basalts:

- Apatites in samples 10044 and 10058 have identical average OH contents and  $\delta D$  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  $\delta D$  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  $\delta D$  values ( $\sim 500 - 700$  ‰ and  $\sim 800 - 1000$  ‰, respectively).

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

- Apollo 15 low-Ti basalts have average  $\delta D$  values  $\sim 300$  ‰ 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  $\delta D$  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  $\delta D$  values measured in apatites in mare basalts thus likely result from complex interplay between these two processes.

The large  $\delta D$  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  $\delta D$  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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