H isotope characteristics of apatite in lunar basalts (#2222)

Romain Tartèse[1], Mahesh Anand[1,2], Jessica Barnes[1,2], Natalie Starkey[1] and Ian Franchi[1]
[1]The Open University, Milton Keynes, UK; [2]The Natural History Museum, London, UK
Romain.Tartese@open.ac.uk

1. Summary

→ Apatites in high-Ti basalts display a restricted OH range (~ 1500-3000 ppm) with large δD variations (~ 600-1000 ‰) whereas apatites in low-Ti basalts display a larger OH range (~ 500-15000 ppm), each group displaying restricted δD variations.

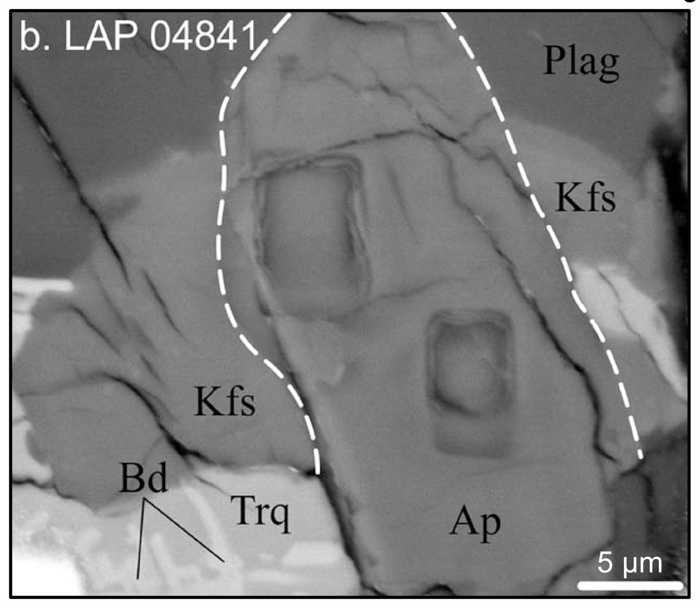
→ Apatites in basaltic meteorites MIL 05035 and LAP 04841 expand the lower bound for basalt δD values down to ~ 100 ‰.

→ ?D variations between ~ 200 to 1000 ‰ resulted from different amounts of **degassing of H-bearing species**. Average δD values of low-Ti basalts are consistent with ~ 85 to 99 % degassing of H as H_2, starting from a **chondritic, CI-type, δD value of 100 ‰**, which was favoured by the reduced nature of lunar magmas.

→ **In low-Ti basalts, apatite crystallised after H_2 degassing**, the OH variations reflecting different degrees of fractional crystallisation. **In high-Ti basalts**, large δD variations with relatively restricted range in OH contents imply that **apatite crystallisation and degassing were mostly coeval**.

→ Geochemical modelling suggests that **the mantle source regions of the different low-Ti mare basalts could have contained ~ 5 to 50 ppm H** (~ 45 to 450 ppm H_2O), similar to the estimated water content of the Earth's upper mantle.

2. NanoSIMS 50 analysis of apatite



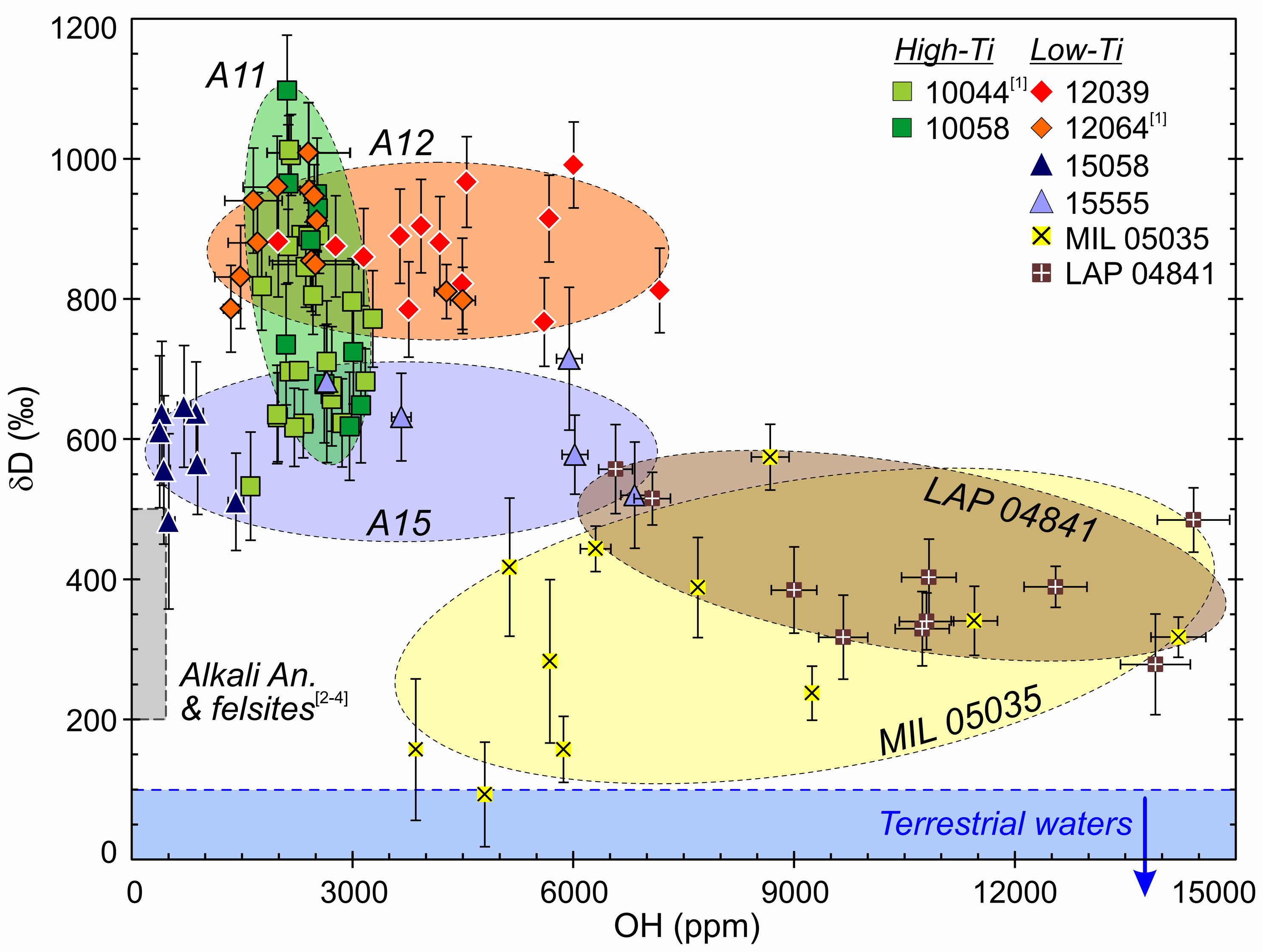
→ 250 pA Cs^+ primary beam.

→ ^1H, ^2H, ^{12}C and ^{18}O collected simultaneously from a 5 × 5 µm area for ~ 20 minutes.

→ OH calibration from $^1H/^{18}O$ ratios of reference apatites.

→ Reproducibility of D/H measured on reference apatites = 29 ‰ (2σ SD).

3. Results



→ Apatites in Apollo basalts display elevated δD values > ~ 400 ‰; heaviest δD values are ~ 1000 ‰; wide range of OH contents from ~ 300 ppm up to ~ 7300 ppm. These observations are consistent with previous reports [1-3].

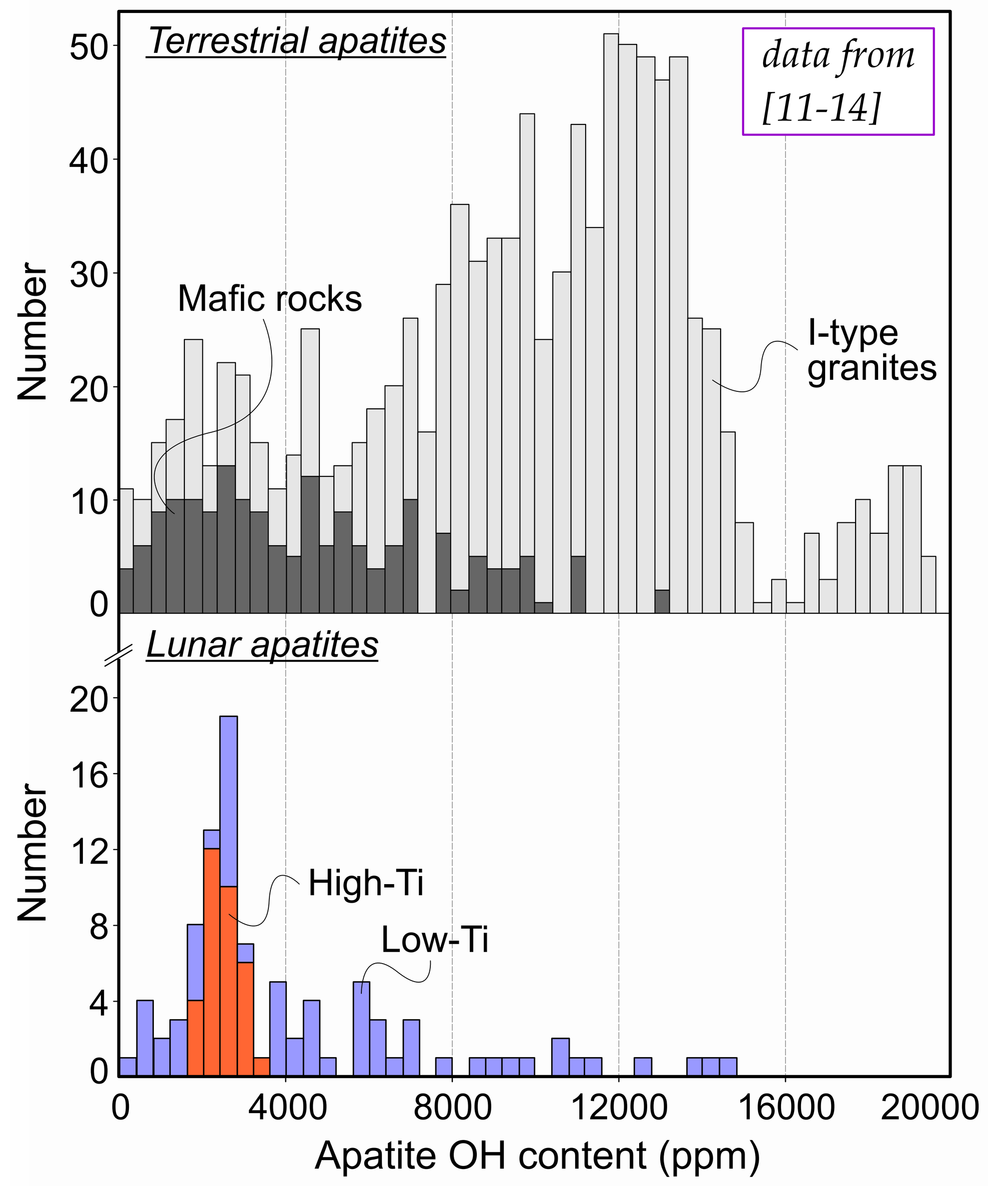
→ Apatites in A-12 and A-15 **low-Ti basalts** characterised by a **large range of OH contents at relatively restricted δD values**, whereas apatites in A-11 **high-Ti basalts** display a **restricted range of OH contents with highly variable δD values**.

→ In lunar meteorite MIL 05035, OH contents and δD range from ~ 3800 to 14200 ppm and ~ 100 to 570 ‰, respectively.
→ In lunar meteorite LAP 04841, OH contents and δD range from ~ 6600 to 14400 ppm and ~ 280 to 560 ‰, respectively.

→ Interestingly, apatites in **MIL 05035 and LAP 04841** display **large OH variations at relatively restricted δD values**, similar to A-12 and A-15 low-Ti basalts.

→ Apatite δD values in these 2 meteorites 1) are outside the terrestrial range and 2) considerably expand the lower bound for δD in apatites in lunar basalts (*see talk by Anand et al., Fri. AM, abstract #1957*).

4. OH in lunar apatites

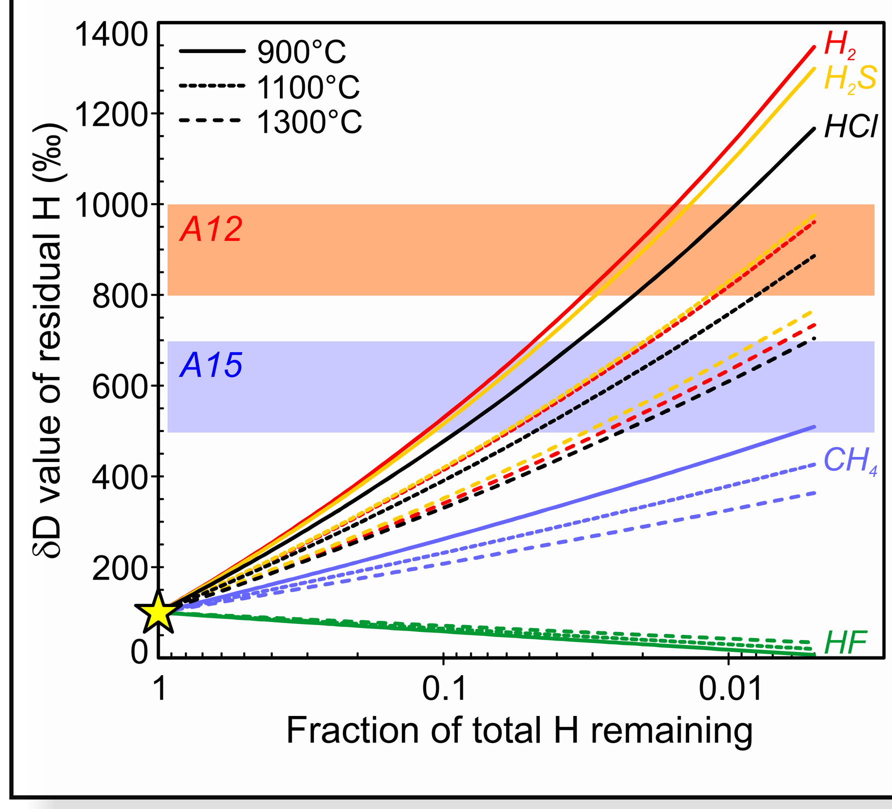


→ OH content of lunar apatites range between **~ 0 and 1.5 wt.%**. Similar to the OH content range of terrestrial apatites from mafic magmas.

→ Lunar and mafic terrestrial distributions of apatite OH contents are also similar, with a majority of analyses yielding between **~ 0 and 0.5 wt.% OH**.

→ Apatites [1-8], volcanic glasses [9] and their melt inclusions [10] are all consistent with terrestrial water content.

5. High δD of lunar apatites

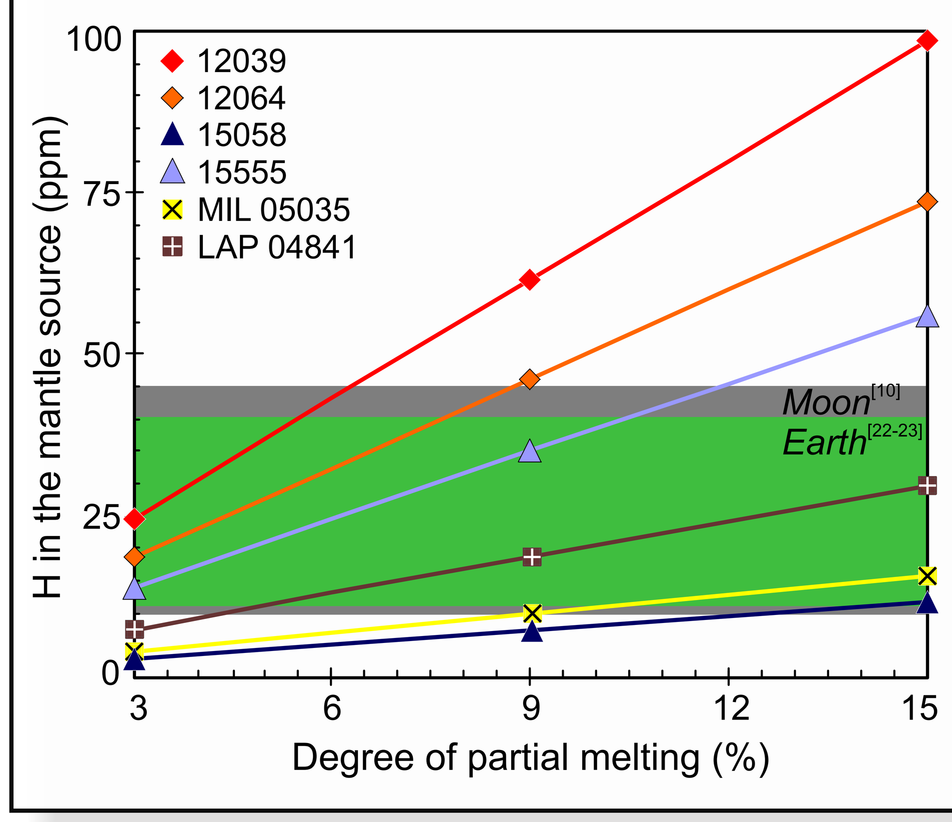


→ At low P and fO_2 < IW-1, **$H_2/(H_2+H_2O_t)$** in the degassed phase > 0.8 [15].
→ A bit of CH_4 if lots of C.
→ S, F and Cl likely soluble in the melt [16-17].

→ **Degassing mostly as H_2**, which strongly **fractionates H and D isotopes** [18]. Residual melt enriched in D.

→ Degassing of **~ 98 to more than 99 % of total H** as H_2 to reach δD of A12 and A15, starting from δD = 100 ‰.

6. H content of the lunar mantle

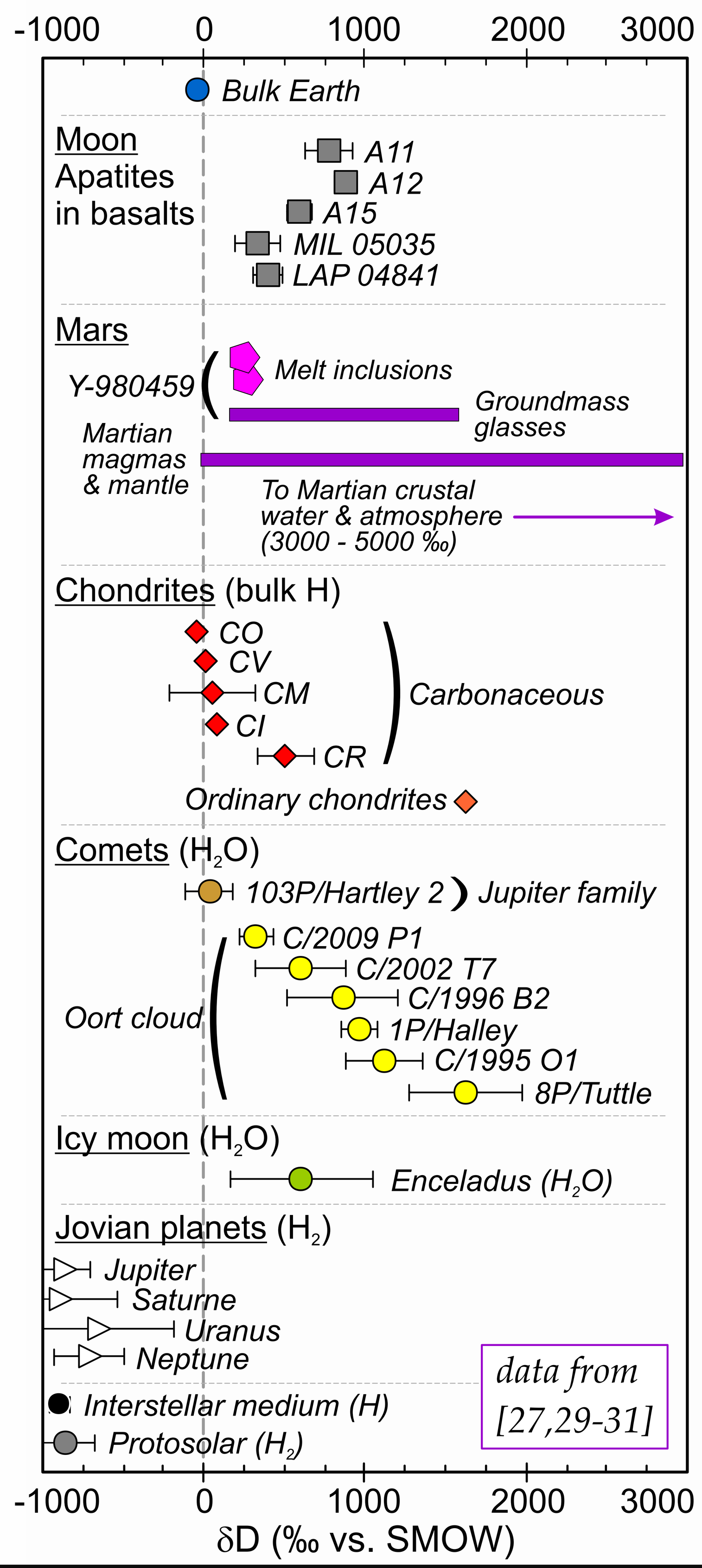


→ $D_{OH}^{ap/melt}$ = 0.3 [8,19-20].
→ Highest OH in apatite formed after 99.5 % FC [21].
→ 85-99 % total H lost via degassing.

→ Primitive low-Ti melts contained **~ 75 to 600 ppm H** (700 to 5400 ppm eq. H_2O).
→ Mantle source regions contained **~ 5 to 60 ppm H** (45 to 540 ppm eq. H_2O).

→ Consistent with estimates for **Earth's upper mantle** [22-23].

7. Source(s) of lunar H



→ Modelling LMO crystallisation suggests ~ 1 ppm H max. in lunar mantle [24]. **Apatites in KREEP-rich samples are mostly dry** [4,8]. Moon accreted "dry" as volatiles were lost after the giant impact [25]?. **But**, olivine and plagioclase in FAN contain water, implying a wet LMO [26].

→ Mantle source regions of low-Ti basalt contain ~ 5 to 60 ppm H, which may indicate **H delivery to the upper mantle after LMO crystallisation** [2,21].

→ Elevated δD of apatites have been linked to H delivery by comets [2]. Yet, accretion of cometary material may have also included D-enriched organic material. Hence, bulk D/H ratios of comets are likely higher than those of apatites in lunar basalts [27].

→ Apatite δD values may result from > 85 % **degassing of H_2**, starting from a δD of 100 ‰, typical of **CI chondrites** [27].

→ Easier for large chondrite-type objects to **breach the crust and reach the upper mantle**. Few impacts by planetesimals [28]?

References
[1] Barnes J.J. et al. (2013) *Chem. Geol.,* 337-338, 48-55. **[2]** Greenwood J.P. et al. (2011) *Nature Geosci.,* 4, 79-82. **[3]** Greenwood J.P. et al. (2012) *LPS XLIII,* Abstract #2089. **[4]** Robinson K.L. et al. (2012) *LPS XLIII,* Abstract #1727. **[5]** Boyce J.W. (2010) *Nature,* 466, 466-469. **[6]** McCubbin F.M. et al. (2010a) *PNAS,* 27, 11223-11228. **[7]** McCubbin F.M. et al. (2010b) *Am. Mineral.,* 95, 1141-1150. **[8]** McCubbin F.M. et al. (2010b) *GCA,* 75, 5073-5093. **[9]** Saal A.E. et al. (2008) *Nature,* 454, 192-196. **[10]** Hauri E.H. (2011) *Science,* 333, 213-215. **[11]** Boudreau A. & Somon A. (2007) *J. Petrol.,* 48, 1369-1386. **[12]** Chu M.F. et al. (2009) *J. Petrol.,* 50, 1829-1855. **[13]** Drinkwater J.L. et al. (1990) *Canadian Mineral.,* 28, 835-854. **[14]** Zhang C. et al. (2012) *Contrib. Mineral. Petrol.,* 154, 869-879. **[15]** Speciation of C-O-H species calculated using the GFluid package, Zhang C. & Duan Z. (2010) *Comput. Geosci.,* 36, 569-572. **[16]** Aiuppa A. et al. (2009) *Chem. Geol.,* 263, 1-18. **[17]** O'Neill H. S. C. & Mavrogenes J. (2002) *J. Petrol.,* 43, 1049-1087. **[18]** Richet P. (1977) *Ann. Rev. Earth Planet. Sci.,* 5, 65-110. **[19]** Mathez E.A. & Webster J.D. (2005) *GCA,* 69, 1275-1286. **[20]** Vander Kaaden K.E. et al. (2012) *LPS XLIII*, Abstract #1247. **[21]** Tartèse R. & Anand M. (2013) *EPSL,* 361, 480-486. **[22]** Albarède F. (2009) *Nature,* 461, 1227-1233. **[23]** Saal A.E. et al. (2002) *Nature,* 419, 451-455. **[24]** Elkins-Tanton L.T. & Grove T.L. (2011) *EPSL,* 307, 173-179. **[25]** Pahlevan K. & Stevenson D.J. (2007) *EPSL,* 262, 438-449. **[26]** Hui H et al. (2013) *Nature Geosci.,* doi: 10.1038/ngeo1735. **[27]** Alexander C.M.O'D. et al. (2012) *Science,* 337, 721-723. **[28]** Bottke W.F. et al. (2010) *Science,* 330, 1527-1530. **[29]** Bockelée-Morvan D. et al. (2012) *Astron. Astrophys.,* 544, L15. **[30]** Hartogh P. et al. (2011) *Nature,* 478, 218-220. **[31]** Usui T. et al. (2012) *EPSL,* 357-358, 119-129.

Acknowledgments
Diane Johnson, Andy Tindle and Susanne Schwenzer are thanked for their help with SEM and electron microprobe analyses. We are also grateful to Frank Gyngard (Washington University) for providing us the NanoSIMS DataEditor software. We thank NASA CAPTEM and the meteorite working group for allocation of lunar samples, STFC for a PhD studentship to JJB and a research grant to MA (Grant no. ST/I001298/1 to MA) and UKCAN (Grant no. ST/I001964/1 to IF) for NanoSIMS machine time allocation.