

Water in lunar anorthosites and evidence for a wet early Moon

Hejiu Hui¹*, Anne H. Peslier^{2,3}, Youxue Zhang⁴ and Clive R. Neal¹

The Moon was thought to be anhydrous since the Apollo era¹, but this view has been challenged by detections of water on the lunar surface²⁻⁴ and in volcanic rocks⁵⁻⁹ and regolith¹⁰. Part of this water is thought to have been brought through solar-wind implantation^{2-4,7,10} and meteorite impacts^{2,3,7,11}, long after the primary lunar crust formed from the cooling magma ocean^{12,13}. Here we show that this primary crust of the Moon contains significant amounts of water. We analysed plagioclase grains in lunar anorthosites thought to sample the primary crust, obtained in the Apollo missions, using Fourier-transform infrared spectroscopy, and detected approximately 6 ppm water. We also detected up to 2.7 ppm water in plagioclase grains in troctolites also from the lunar highland upper crust. From these measurements, we estimate that the initial water content of the lunar magma ocean was approximately 320 ppm; water accumulating in the final residuum of the lunar magma ocean could have reached 1.4 wt%, an amount sufficient to explain water contents measured in lunar volcanic rocks. The presence of water in the primary crust implies a more prolonged crystallization of the lunar magma ocean than a dry moon scenario and suggests that water may have played a key role in the genesis of lunar basalts.

Dissolved water in silicates can alter their structure, and hence significantly change their physical and chemical properties¹⁴⁻¹⁷, which can further influence geologic processes. One of the most important conclusions resulting from the Apollo and Luna missions was that no water was detected in returned samples or at the surface of the Moon¹. The Moon was thought to have lost its volatiles as it formed from ejecta of the impact of a Mars-size planetesimal with the proto Earth, the favoured Moon formation scenario¹⁸, and during degassing of an early planet-wide magma ocean^{12,13}. This notion has been included in most geophysical and geochemical models of formation and evolution of the Moon^{12,18}. The view of a dry lunar interior, however, has been challenged by recent discoveries of water in picritic glass beads⁵, apatites⁶⁻⁸ and olivine melt inclusions⁹, which were facilitated by the improvements of the analytical detection limit of hydrogen. Indigenous water is suggested to be heterogeneously distributed in the lunar interior and some parts of lunar mantle may contain as much water as Earth's upper mantle^{5,9}. Hydrogen isotopic compositions of apatites in mare basalts have been interpreted to indicate a hybrid source of the water, that is, a combination of lunar mantle, comets and solar-wind protons⁷. The chlorine isotope compositions in the lunar pyroclastic deposits, however, have been interpreted as suggesting an essentially anhydrous lunar interior¹⁹. It has been further suggested using magma ocean crystallization modelling that

the water content of the bulk lunar magma ocean (LMO) was less (possibly far less) than 100 ppm and water was later added during mantle cumulate overturn or through impacts¹¹.

Here we have measured water in primary products of the LMO, thereby bypassing the processes of later addition of water to the Moon through impact events or during mantle overturn as suggested by previous studies^{7,11}. These data are used to estimate the water content of the Moon's interior at the time of the magma ocean, as well as that of the mare magma source regions. So far, ferroan anorthosite (FAN) is the only available lithology that is believed to be a primary product of the LMO (refs 12,13). It is generally accepted that plagioclase, after crystallization, floated in the magma ocean and formed FAN as the original crust of the Moon¹². Therefore, any indigenous water preserved in pristine FAN was partitioned from the magma ocean. Fourier-transform infrared spectroscopy (FTIR) was used to measure water contents in plagioclases of FANs 15415,238 and 60015,787 (see Supplementary Information S1). Both these samples have >98 vol% of plagioclase with anorthite contents >96%. To assess the water inventory in the lunar highland upper crust, nominally anhydrous minerals in troctolite 76535,164 (see Supplementary Information S1) were also analysed using FTIR. Troctolite, an olivine-rich end member of the Mg suite that composes about half of the highland upper crust²⁰, is thought to be derived from the magma ocean crystallization products, but its detailed origin is under debate²⁰.

The mineral grains allocated for this study are from the interior portion of each individual rock. Therefore, potential hydrogen implanted by solar wind¹⁰ was avoided because direct solar implantation is limited to 0.2 μm depth from the sample surfaces²¹, and even though micrometeorite gardening and melting can transfer OH to some depth on the basis of a recent study of lunar agglutinitic glasses¹⁰, such OH is in glasses from impact remelting, not pristine minerals. Layers of tens to a few hundred micrometres in thickness on both sides of each grain were also removed in the preparation of doubly polished parallel surfaces for FTIR analyses (see Methods), which further ensured the removal of any layer affected by solar implantation. Infrared spectra of plagioclase from FAN 15415,238 and 60015,787 are characterized by a small wide absorption band in the O–H region (Fig. 1 and Supplementary Fig. S2) that resembles those observed in terrestrial plagioclases^{22,23}. This broad band ($\sim 3,700$ to $\sim 3,100$ cm^{-1}) is interpreted as absorption by structural O–H bond vibrations in plagioclase for two reasons. First, one of our doubly polished grains of 15415 was heated to 1,000 °C for 24 h in a high-purity N_2 atmosphere at the University of Michigan and then cleaned with the same procedure (see Methods). The band is strongly diminished in the heated sample, demonstrating that

¹Department of Civil and Environmental Engineering and Earth Sciences, University of Notre Dame, Notre Dame, Indiana 46556, USA, ²Jacobs Technology, ESCG, Mail Code JE23, Houston, Texas 77058, USA, ³ARES, NASA-Johnson Space Center, Mail Code KR, Houston, Texas 77058, USA, ⁴Department of Earth and Environmental Sciences, University of Michigan, Ann Arbor, Michigan 48109, USA. *e-mail: hhui@nd.edu.

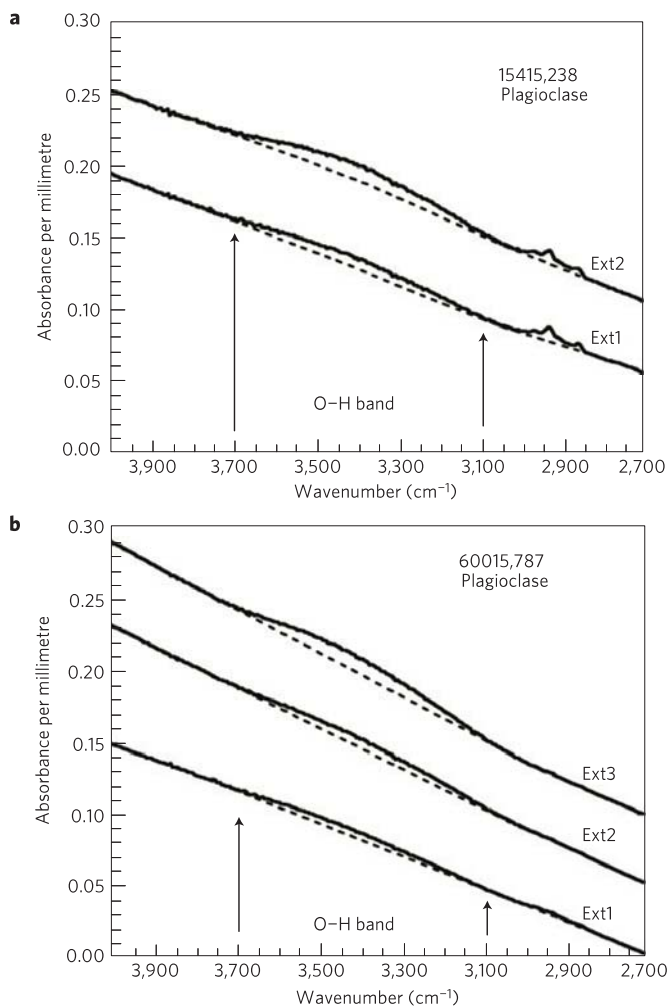


Figure 1 | Representative polarized FTIR spectra of plagioclase from FANs. a,b, Spectra for 15415,238 (a) and 60015,787 (b) at mutually perpendicular orientations (Ext1, Ext2 and Ext3: optical extinction directions 1, 2 and 3) are normalized to 1 mm and shifted vertically for comparison. The dashed line indicates the baseline position used for water content estimations. The narrow peaks (3,000–2,800 cm^{-1}) most probably come from organic contamination on the mineral surface during sample preparation^{22,23}. The spectra with the same label (for example, Ext1) for different crystals were not taken at the same crystal orientation relative to the mineral crystallographic axis.

dehydration occurred (Fig. 2). Second, the anisotropy of the O–H absorption band height or absorbance area during rotation of the infrared polarizer relative to the plagioclase crystals, and the 90° interval between maximum and minimum (Supplementary Fig. S4) demonstrate that this band (Fig. 1 and Supplementary Fig. S2) cannot be caused by water in minute melt or fluid inclusions²³ or by contamination during sample preparation. Furthermore, O–H absorbance area does not seem related to the degree of plagioclase fracturing that was probably produced during impact. Total integrated absorption areas of the OH bands (A_{tot} in cm^{-2}) along three mutually perpendicular directions (see Supplementary Information S2) were converted to water contents ($C_{\text{H}_2\text{O}}$ in parts per million by weight of H_2O) using the Beer–Lambert law in the form $C_{\text{H}_2\text{O}} = A_{\text{tot}}/I'$, where I' is the calibrated specific integral absorption coefficient ($15.3 \pm 0.7 \text{ ppm}^{-1} \text{ cm}^{-2}$ for feldspars²²). Although infrared absorbances are typically reproducible between different laboratories²⁴, we nonetheless verified the accuracy of our measurement by analysing an external standard, the plagioclase used

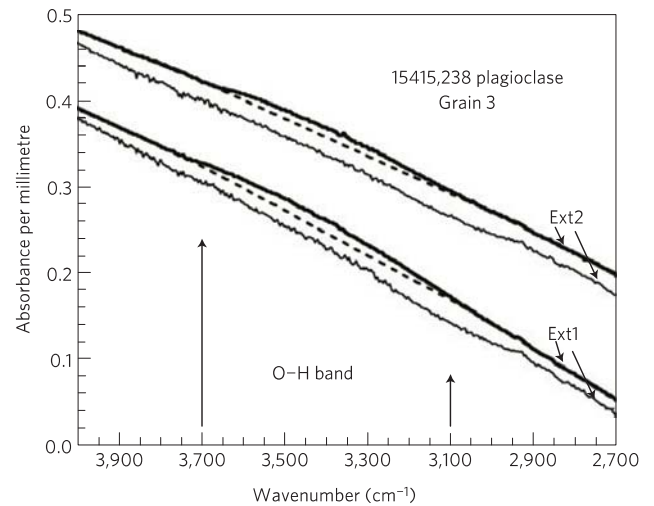


Figure 2 | FTIR spectra of plagioclase from 15415,238 before and after heating at 1,000 °C for 24 h. FTIR analyses were performed on the sample before (upper thick curve with the dashed baseline used for water content estimation) and after the heating experiment (lower thin curve) at the same orientations of the sample relative to the polarizer (Ext1 and Ext2, respectively). The diminished band ($\sim 3,700$ to $\sim 3,100 \text{ cm}^{-1}$) in the spectrum of the heated sample demonstrates that dehydration occurred. The band in the untreated sample is due to absorption of O–H bond vibration, and not an artefact in the baseline.

for the absorption coefficient calibration²², GRR1968. The total absorbance area of spectra at three mutually perpendicular directions and with sample thickness normalized to 1 cm is $1,712 \text{ cm}^{-2}$, differing from that of $1,688 \text{ cm}^{-2}$ in ref. 22 by 1.4% relative, thereby verifying inter-laboratory reproducibility. The water contents in plagioclases are $\geq 5.0 \text{ ppm H}_2\text{O}$ by weight (grain Pl3) for 15415,238 and 6.4 ppm for 60015,787 (Supplementary Table S1). Note that there could be a systematic error in the calibration for plagioclase, which would act to underestimate water contents calculated using this calibration (see Supplementary Information S2).

The water partition coefficient between plagioclase and silicate melt is not well constrained (see Supplementary Information S3), which is a main source of uncertainty in the following discussion. Using a partition coefficient of 0.004 between plagioclase and silicate melt²⁵, the water content of a melt in equilibrium with 60015 plagioclase is calculated to be $\sim 1,600 \text{ ppm H}_2\text{O}$. Co-crystallized pyroxene cumulates should contain $\sim 11 \text{ ppm H}_2\text{O}$ using a partition coefficient of 0.007 between pyroxene and silicate melt²⁶. About 1,600 ppm represents the amount of water in the residual melt of the magma ocean, when floating plagioclase was forming the original lunar crust. At that point, approximately 80 vol% of the LMO is thought to have been solidified¹². Using this degree of crystallization, the amount of water in the parental magma of FAN 60015, that is, in the initial magma ocean, is inferred to be $\sim 320 \text{ ppm H}_2\text{O}$ (Fig. 3). The first crystallized olivine cumulate in the LMO could have $\sim 0.6 \text{ ppm}$ of water using a partition coefficient of 0.002 between olivine and silicate melt²⁷, which is much higher than $\sim 90 \text{ ppb}$ of water in the lunar mantle inferred from Cl isotope studies¹⁹. As crystallization of the LMO continued, volatiles and other incompatible trace elements became enriched in the magma ocean residuum. On the basis of the LMO model¹², the final 2 vol% of the magma ocean residuum (urKREEP) that may be the source of the potassium, rare-earth and phosphorus (KREEP)-rich lithologies unique to the Moon potentially could have had as much as $\sim 1.4 \text{ wt\%}$ of water. This is an order of magnitude higher than the thousands of parts per million maximum suggested previously¹¹, and also 1.5 orders of magnitude higher than 850–1,100 ppm in

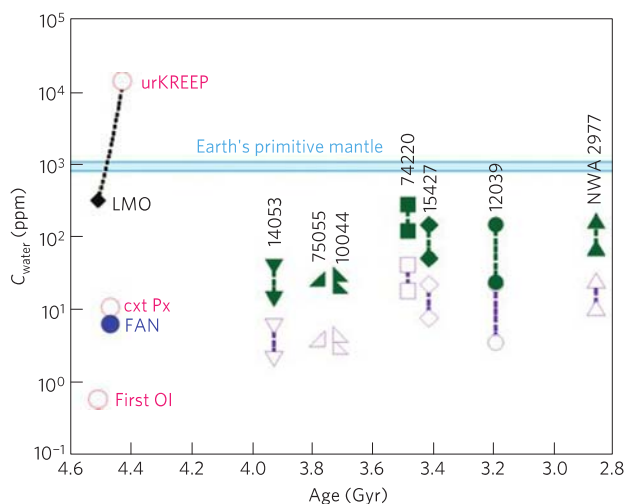


Figure 3 | Water contents in LMO products and mantle sources of basalts through time. Model ages are used for primary magma ocean products^{12,13} and isochron ages for the basalts (Supplementary Table S2). Water contents of the initial magma ocean (LMO), the first crystallized olivine cumulate (first OI), co-crystallized pyroxene cumulate (cxt Px) and urKREEP were estimated from the water content measured in FAN plagioclases. The black dashed line from LMO to urKREEP shows the water content evolution in magma ocean residua. The water contents of mantle sources with isochron ages <4.0 Gyr were calculated assuming 20% (green) or 3% partial melting (purple; Supplementary Table S2).

Earth's primitive mantle²⁸ (Fig. 3). This implies that the LMO crystallization products could have spanned a wide range of water contents, from <1 ppm to ~1.4 wt% (Fig. 3). After the LMO solidification, these materials are thought to have undergone gravitational overturn driven by density difference²⁹. Overturned lunar cumulate mantle provided the source regions for mare basalts^{12,29}. Even assuming 20% of partial melting of the source regions of mare basalts in which water was detected^{5–9}, calculated water contents of their source regions are still well within the range of those we calculated for the primary magma ocean products inferred from water content in plagioclase from FANs (Fig. 3).

Even a small amount of water can change the liquid line of descent of melt and suppress crystallization of plagioclase relative to olivine and clinopyroxene, such as in mid-ocean ridge basalts¹⁵. Therefore, the amount of water we calculated could affect the LMO crystallization dynamics, especially for the last few tens of volume per cent of magma ocean residuum. The depression of the liquidus due to increased water contents would also prolong the crystallization of the LMO and potentially explain an extraordinarily young age ($4,360 \pm 3$ Myr) for FAN 60025 (ref. 30) in the framework of a magma ocean model. Note that an alternative explanation of the young age has been suggested by challenging the existence of a global magma ocean³⁰. Even if the latter argument is correct, the measured water concentration in plagioclase can still be used to infer water contents of parental magmas of cumulates that formed the earliest lunar crust. Moreover, the relatively high abundance of water (~1.4 wt%) in urKREEP can significantly change its physical properties, such as lowering density¹⁶ and viscosity¹⁷, which could affect the dynamics of magma ocean cumulate overturn²⁹. In summary, the variable amounts of water in urKREEP and earlier cumulates (Fig. 3) could play a critical role on the genesis of lunar basalts, in which indigenous water has been recently discovered^{5–9}, in a similar way to the role of water in terrestrial oceanic mantle melting regimes¹⁴.

Intrinsic water was also detected in plagioclase of troctolite 76535,164 (Fig. 4 and Supplementary Fig. S3). The minimum

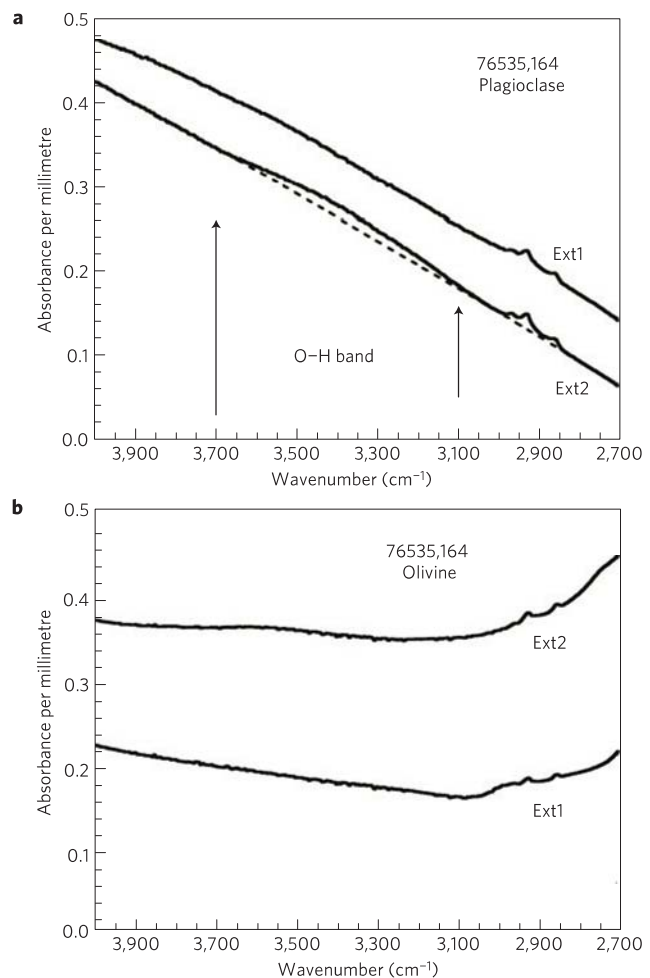


Figure 4 | Representative polarized FTIR spectra of troctolite 76535,164. **a, b**, Spectra of plagioclase (**a**) and olivine (**b**) at two mutually perpendicular orientations (Ext1 and Ext2) are normalized to 1 mm and shifted vertically for comparison. The dashed line indicates the baseline position used to calculate water concentrations (see Supplementary Information S2). No obvious OH bands are observed in the spectra taken with orientation Ext1 of plagioclase or in any of the olivine spectra. The narrow peaks between 3,000 and 2,800 cm^{-1} most probably come from organic contamination on the mineral surface during sample preparation^{22,23}.

water contents vary from 0.8 to 2.7 ppm (Pl1 of 76535,164) (Supplementary Table S1). No O–H absorption band has been observed in a 1.055-mm-thick olivine from this troctolite (Fig. 4), implying a H_2O content of <1 ppm. The fact that plagioclase is more hydrous than olivine is consistent with the H_2O partition coefficient between olivine and melt being smaller than that between plagioclase and melt^{25,27}. The minimum whole-rock water content of troctolite 76535 is ~2 ppm on the basis of its mineral modal abundance, which is lower than that calculated for the initial magma ocean from our FAN data.

The presence of indigenous water in FAN and troctolite suggests that the highland upper crust is not anhydrous. Considering the distributions of two major lithologies (FAN and Mg suite) in the highland upper crust²⁰ and assuming that the results for 60015 (~6 ppm) and 76535 (~2 ppm) are representative of FANs and the Mg suite, respectively, the upper crust may contain ~4 ppm of indigenous water. Incidentally, trace amounts of water/hydroxyl have been detected in the lunar highlands surface by various spacecrafts, although lack of hydroxyl reflectance calibration meant that it could not be quantified³. Hence, another implication of

the results presented here is that the water measured in lunar highland lithologies may contribute a significant portion of the water detected by spacecraft.

Methods

Plagioclase grains from FANs 15415,238 and 60015,787, and plagioclase and olivine grains from one troctolite 76535,164 were analysed by FTIR to determine water contents. Each mineral grain was embedded in crystal bond and a doubly polished section was prepared manually using sandpaper and alumina powder (down to 1 µm). The grain was not polished at any orientation relative to the crystallographic axis (that is, with polished surface perpendicular to the optic normal, acute bisectrix or obtuse bisectrix directions). Instead a mineral section of random orientation was made as thick as possible to get maximum infrared signal for O–H bond vibrations with a relatively good spectrum signal–noise ratio. One plagioclase grain of 60015 was large enough to be polished into a mineral cube with two sets of polished mutually perpendicular surfaces. The polished grains were cleaned successively with acetone, ethanol, deionized water and CH₂Cl₂ in an ultrasonic bath. A plagioclase (GRR1968) previously analysed by another laboratory²² was also polished into a cube using the same procedure to check for inter-laboratory reproducibility. The thickness of each grain was measured using a Mitutoyo digital micrometer. Before FTIR analysis of each grain, the sample chamber was flushed with N₂ for at least an hour.

Polarized FTIR spectra with wavenumbers from 7,800 to 600 cm⁻¹ were collected using a Hyperion 3000 microscope attached to a Bruker Vertex 70 FTIR spectrometer at the Astromaterial and Research Exploration Science (ARES) directorate of the NASA-Johnson Space Center. The standard mercury cadmium telluride detector and KBr beam splitter were used during FTIR analysis, as well as a Zn–Se wire-grid polarizer. Aperture size from 255 × 255 µm to 425 × 425 µm (mainly 340 × 340 µm) during each analysis was chosen on the basis of the grain size. During each analysis, 256 scans were performed for each infrared measurement under a nitrogen environment, to minimize interference from atmospheric water vapour. A new background was collected before each infrared measurement on a new grain or the same grain using a different polarizing angle. Polarized infrared spectra (wave numbers from 9,000 to 1,500 cm⁻¹) were also acquired using an AutoImage microscope on a Perkin-Elmer Spectrum GX FTIR spectrometer at the University of Michigan. A near-infrared source, CaF₂ beam splitter, KRS-5 infrared wire-grid polarizer, mercury cadmium telluride detector and N₂ gas purge and an aperture size of 340 × 340 µm were used during these FTIR analyses. The spectra from two different FTIR are consistent with each other.

Received 21 June 2012; accepted 17 January 2013; published online 17 February 2013

References

- Lucey, P. *et al.* Understanding the lunar surface and space–Moon interactions. *Rev. Mineral. Geochem.* **60**, 83–219 (2006).
- Clark, R. N. Detection of adsorbed water and hydroxyl on the Moon. *Science* **326**, 562–564 (2009).
- Pieters, C. M. *et al.* Character and spatial distribution of OH/H₂O on the surface of the Moon seen by M³ on Chandrayaan-1. *Science* **326**, 568–572 (2009).
- Sunshine, J. M. *et al.* Temporal and spatial variability of lunar hydration as observed by the deep impact spacecraft. *Science* **326**, 565–568 (2009).
- Saal, A. E. *et al.* Volatile content of lunar volcanic glasses and the presence of water in the Moon's interior. *Nature* **454**, 192–195 (2008).
- Boyce, J. W. *et al.* Lunar apatite with terrestrial volatile abundances. *Nature* **466**, 466–469 (2010).
- Greenwood, J. P. *et al.* Hydrogen isotope ratios in lunar rocks indicate delivery of cometary water to the Moon. *Nature Geosci.* **4**, 79–82 (2011).
- McCubbin, F. M. *et al.* Nominally hydrous magmatism on the Moon. *Proc. Natl Acad. Sci. USA* **107**, 11223–11228 (2010).
- Hauri, E. H., Weinreich, T., Saal, A. E., Rutherford, M. C. & Van Orman, J. A. High pre-eruptive water contents preserved in lunar melt inclusions. *Science* **333**, 213–215 (2011).
- Liu, Y. *et al.* Direct measurement of hydroxyl in the lunar regolith and the origin of lunar surface water. *Nature Geosci.* **5**, 779–782 (2012).
- Elkins-Tanton, L. T. & Grove, T. L. Water (hydrogen) in the lunar mantle: Results from petrology and magma ocean modelling. *Earth Planet. Sci. Lett.* **307**, 173–179 (2011).
- Shearer, C. K. *et al.* Thermal and magmatic evolution of the Moon. *Rev. Mineral. Geochem.* **60**, 365–518 (2006).

- Norman, M. D., Borg, L. E., Nyquist, L. E. & Bogard, D. D. Chronology, geochemistry, and petrology of a ferroan noritic anorthosite clast from Descartes breccia 67215: Clues to the age, origin, structure, and impact history of the lunar crust. *Meteorol. Planet. Sci.* **38**, 645–661 (2003).
- Asimow, P. D. & Langmuir, C. H. The importance of water to oceanic mantle melting regimes. *Nature* **421**, 815–820 (2003).
- Danyushevsky, L. V. The effect of small amounts of H₂O on crystallization of mid-ocean ridge and backarc basin magmas. *J. Volcanol. Geotherm. Res.* **110**, 265–280 (2001).
- Ochs, F. A. III & Lange, R. A. The density of hydrous magmatic liquids. *Science* **283**, 1314–1317 (1999).
- Hui, H. & Zhang, Y. Toward a general viscosity equation for natural anhydrous and hydrous silicate melts. *Geochim. Cosmochim. Acta* **71**, 403–416 (2007).
- Canup, R. M. & Asphaug, E. Origin of the Moon in a giant impact near the end of the Earth's formation. *Nature* **412**, 708–712 (2001).
- Sharp, Z. D., Shearer, C. K., McKeegan, K. D., Barnes, J. D. & Wang, Y. Q. The chlorine isotope composition of the Moon and implications for an anhydrous mantle. *Science* **329**, 1050–1053 (2010).
- Hess, P. C. Petrogenesis of lunar troctolites. *J. Geophys. Res.* **99**, 19083–19093 (1994).
- Keller, L. P. & McKay, D. S. The nature and origin of rims on lunar soil grains. *Geochim. Cosmochim. Acta* **61**, 2331–2341 (1997).
- Johnson, E. A. & Rossman, G. R. The concentration and speciation of hydrogen in feldspars using FTIR and ¹H MAS NMR spectroscopy. *Am. Mineral.* **88**, 901–911 (2003).
- Johnson, E. A. & Rossman, G. R. A survey of hydrous species and concentrations in igneous feldspars. *Am. Mineral.* **89**, 586–600 (2004).
- Behrens, H., Romano, C., Nowak, M., Holtz, F. & Dingwell, D. B. Near-infrared spectroscopic determination of water species in glasses of the system MAlSi₃O₈ (M = Li, Na, K): An interlaboratory study. *Chem. Geol.* **128**, 41–63 (1996).
- Johnson, E. A. Water in nominally anhydrous crustal minerals: Speciation, concentration, and geologic significance. *Rev. Mineral. Geochem.* **62**, 117–154 (2006).
- O'Leary, J. A., Gaetani, G. A. & Hauri, E. H. The effect of tetrahedral Al³⁺ on the partitioning of water between clinopyroxene and silicate melt. *Earth Planet. Sci. Lett.* **297**, 111–120 (2010).
- Hauri, E. H., Gaetani, G. A. & Green, T. H. Partitioning of water during melting of the Earth's upper mantle at H₂O-undersaturated conditions. *Earth Planet. Sci. Lett.* **248**, 715–734 (2006).
- Palme, H. & O'Neill, H. St. C. Cosmochemical estimates of mantle composition. *Treatise Geochem.* **2**, 1–38 (2004).
- Spera, F. J. Lunar magma transport phenomena. *Geochim. Cosmochim. Acta* **56**, 2253–2265 (1992).
- Borg, L. E., Connelly, J. N., Boyet, M. & Carlson, R. W. Chronological evidence that the Moon is either young or did not have a global magma ocean. *Nature* **477**, 70–72 (2011).

Acknowledgements

This work was supported by NASA (NNX11AH48G to H.H. and NNX10AH74G to Y.Z.). We thank the Apollo sample curators for allocating us the samples and G. Rossman for providing an aliquot of plagioclase GRR1968. H.H. thanks Y. Chen for technical assistance on heating experiments and electron microprobe analyses, and D. Draper and the LPI for help to access the JSC facility. This manuscript was greatly improved by the suggestions and comments of E. A. Johnson.

Author contributions

H.H. conceived this study and performed the analyses and experiments. Y.Z. provided the terrestrial plagioclase grains. A.H.P. and Y.Z. assisted in experiments and FTIR analyses. H.H., A.H.P., Y.Z. and C.R.N. discussed the data and wrote the paper.

Additional information

Supplementary information is available in the online version of the paper. Reprints and permissions information is available online at www.nature.com/reprints. Correspondence and requests for materials should be addressed to H.H.

Competing financial interests

The authors declare no competing financial interests.