Water in lunar anorthosites and evidence for a wet early Moon

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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 rocks5–7 and regolith8,9. Part of this water is thought to have been brought through solar-wind implantation6,7,10 and meteorite impacts6,7,9, long after the primary lunar crust formed from the cooling magma ocean11,12. 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 properties13–17, 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 ocean12,19. This notion has been included in most geophysical and geochemical models of formation and evolution of the Moon20,21. The view of a dry lunar interior, however, has been challenged by recent discoveries of water in picritic glass beads19, apatites22–24 and olivine melt inclusions25, 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 mantle26. 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 protons27. The chlorine isotope compositions in the lunar pyroclastic deposits, however, have been interpreted as suggesting an essentially anhydrous lunar interior28. 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 studies27,11. 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, namely anhydrous minerals in troctolite 76533, 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 crust29, is thought to be derived from the magma ocean crystallization products, but its detailed origin is under debate30.

The mineral grains allocated for this study are from the interior portion of each individual rock. Therefore, potential hydrogen implanted by solar wind28 was avoided because direct solar irradiation is limited to 0.2 μm depth from the sample surfaces31, and even though micrometeorite gardening and melting can transfer OH to some depth on the basis of a recent study of lunar agglutinitic glasses32, 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 plagioclases33,34. This broad band (~3,700 to ~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 N₂ 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

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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. 1a and Supplementary Fig. S2) cannot be caused by water in minute melt or fluid inclusions22 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 absorbance areas of the OH bands ($A_{\text{abs}}$ in cm$^{-1}$) 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 $C_{\text{H}_2\text{O}} = A_{\text{abs}}/I'$, where $I'$ is the calibrated specific integral absorption coefficient ($19.3 \pm 0.7$ ppm$^{-1}$ cm$^{-2}$ for feldspars23). 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 for the absorption coefficient calibration23, GRR1968. The total absorbance area of spectra at three mutually perpendicular directions and with sample thickness normalized to 1 cm is $1.712 \pm 0.022$, differing from that of $1.688 \pm 0.017$ in ref. 22 by 1.4% relative, thereby verifying inter-laboratory reproducibility. The water contents in plagioclases are $\geq 5.0$ ppm $H_2O$ 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 melt26, the water content of a melt in equilibrium with 60015 plagioclase is calculated to be $\sim 1.600$ ppm $H_2O$. Co-crystallized pyroxene cumulates should contain $\sim 11$ ppm $H_2O$ using a partition coefficient of $0.007$ between pyroxene and silicate melt28. 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 $80 \text{ vol}\%$ of the LMO is thought to have been solidified. 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 $\sim 320$ ppm $H_2O$ (Fig. 3). The first crystallized olivine cumulate in the LMO could have $\sim 0.6$ ppm of water using a partition coefficient of $0.002$ between olivine and silicate melt27, which is much higher than $\sim 90$ ppb of water in the lunar mantle inferred from Cl isotope studies29. 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 $2 \text{ vol}\%$ 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 previously30, and also 1.5 orders of magnitude higher than $850–1,100$ ppm in...
Earth’s primitive mantle\(^{18}\) (Fig. 3). This implies that the LMO crystallization products could have spanned a wide range of water contents, from \(<1\) ppm to \(\sim 1.4\) wt% (Fig. 3). After the LMO solidification, these materials have thought to have undergone gravitational overturn driven by density difference\(^{29}\). Overturned lunar cumulate mantle provided the source regions for mare basalts\(^{16,29}\). Even assuming 20% of partial melting of the source regions of mare basalts in which water was detected\(^{29}\), 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 basalts\(^{15}\). 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 liquids due to increased water contents would also prolong the crystallization of the LMO and potentially explain an extraordinarily young age (4,360 ± 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 ocean\(^{20}\). 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 \((\sim 1.4\) wt%) in urKREEP can significantly change its physical properties, such as lowering density\(^{16}\) and viscosity\(^{17}\), which could affect the dynamics of magma ocean cumulate overturn\(^{26}\). 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 detected\(^{25,29}\), in a similar way to the role of water in terrestrial oceanic mantle melting regimes\(^{14}\).

Intrinsic water was also detected in plagioclase of troctolite 76535,164 (Fig. 4 and Supplementary Fig. S3). The minimum water contents vary from 0.8 to 2.7 ppm (P11 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\(_2\)O content of \(<1\) ppm. The fact that plagioclase is more hydrous than olivine is consistent with the H\(_2\)O 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 \(\sim 2\) 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 crust\(^{29}\) and assuming that the results for 60015 (\(\sim 6\) ppm) and 76535 (\(\sim 2\) ppm) are representative of FANS and the Mg suite, respectively, the upper crust may contain \(\sim 4\) 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 quantified\(^{1}\). 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 13415, 238 and 60015, 787, and plagioclase and olivine grains from one troctolite 76355, 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 a sapphirine and alumina powder (grain size of 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 detect maximum infrared signal for O=H bond vibration with a relatively good spectrum signal-to-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 saccharite, ethyl alcohol, deionized water and CH3Cl2 in an ultrasonic bath. A plagioclase (GRR1968) previously analysed by another laboratory23 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 Astronomical 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 1,300 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, GaFe 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.

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References

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Author contributions
H.H. conceived this study and performed the analyses and experiments. Y.Z. provided the terrestrial plagiolase 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
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Competing financial interests
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