LETTERS

Volatile content of lunar volcanic glasses and the presence of water in the Moon's interior

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The Moon is generally thought to have formed and evolved through a single or a series of catastrophic heating events[1], during which most of the highly volatile elements were lost. Hydrogen, being the lightest element, is believed to have been completely lost during this period[2]. Here we make use of considerable advances in secondary ion mass spectrometry[3] to obtain improved limits on the indigenous volatile (CO_2, H_2O, F, S and Cl) contents of the most primitive basalts in the Moon—the lunar volcanic glasses. Although the pre-eruptive water content of the lunar volcanic glasses cannot be precisely constrained, numerical modelling of diffusive degassing of the very-low-Ti glasses provides a best estimate of 745 p.p.m. water, with a minimum of 260 p.p.m. at the 95 per cent confidence level. Our results indicate that, contrary to prevailing ideas, the bulk Moon might not be entirely depleted in highly volatile elements, including water. Thus, the presence of water must be considered in models constraining the Moon's formation and its thermal and chemical evolution.

Volatile elements provide insight into models of planet formation, and play a fundamental role in planetary evolution through their influence on melting[4], viscosity[5], magma crystallization[6] and volcanic eruption. An important conclusion resulting from the Apollo and Luna programmes is that the Moon is deficient in highly volatile elements relative to the Earth. This is especially the case for hydrogen, which is thought to have been completely lost during the giant collision event that generated the Moon[2].

The volatile budget of the lunar mantle can, at present, only be reconstructed from the record preserved in the mare basalts and the lunar volcanic glasses, the most primitive basalts from the Moon. Reconstructing the volatile content of the lunar mantle from basaltic melts is compromised by volatile degassing at the time the lava erupted and subsequent contamination from external sources such as low-pressure condensation following impact, solar wind implantation, and assimilation or sublimation of cometary or meteoritic material[7]. Over the past 40 years there have been considerable efforts to measure the volatile contents in these lunar samples[8–15] (see Supplementary Information). From these studies, we have reliable evidence that there is an indigenous component containing sulphur, and, to a lesser extent, chlorine, fluorine and carbon in these materials. Yet the evidence for indigenous H_2O in the lunar samples has remained elusive, consistent with the general consensus that the Moon is anhydrous.

Two main factors have limited the study of volatile abundances in lunar samples: first, most of the existing data represent bulk sample analyses, which makes it difficult to determine whether the volatile elements measured were indigenous to the glass beads or foreign (implanted, condensed or added during alteration of the sample); and second, the *in situ* analytical techniques used (Fourier transform infrared (FTIR), electron microprobe and secondary ion mass

spectrometry (SIMS)) have had relatively high detection limits, particularly for H_2O and CO_2. Recent substantial advances in SIMS provide improved detection limits for H_2O, CO_2, F, S and Cl, up to two orders of magnitude lower than electron microprobe, FTIR and earlier SIMS instrumentations (see Supplementary Information). Here we report, by virtue of the new SIMS technique[3], improved limits on the indigenous volatile (CO_2, H_2O, F, S, Cl) contents of the lunar volcanic glasses and evaluate the processes controlling their variation within and between glass beads. Our results represent the first evidence for the presence of indigenous water in the lunar interior.

We investigated three main compositional groups of glasses: very-low-Ti and low-Ti glasses (sample 15427,41), and high-Ti glasses (sample 74220,864). The glassy spherules range in size from 100 to 300 μm for 74220,864 and from 200 to 400 μm with one outlier at 700 μm for 15427,41. Not all of the glass beads are completely glassy; some of them, usually the larger beads, show crystallization of either olivine (15427,41) or olivine and ilmenite (74220,864). Also, we were able to recognize four of the five compositional subgroups (A, B, C and D; group E was not sampled) of Delano's very-low-Ti glasses[16]. The major and trace element contents of the lunar volcanic glasses are consistent with previously reported data and indicate that the glasses analysed in this study represent volcanic rather than impact glasses[14,17,18] (see Supplementary Tables 1 and 2, Fig. 1 and the Methods section for detailed discussion on the analytical methods).

Essentially all volcanic glasses have carbon content (reported as CO_2) within 2σ (standard deviation) of the detection limit, with concentrations of ~6 ± 7 p.p.m. CO_2 after background correction. Carbon will not be considered further, beyond mentioning that our values give an upper limit on the concentration of carbon dissolved in the volcanic glasses. However, it is important to point out that two high-Ti glasses have 13 ± 7 and 18 ± 7 p.p.m. CO_2; if confirmed, these would be the first direct evidence for measurable dissolved carbon in any of the lunar volcanic glasses. The other volatiles, after background correction, have measurable abundances of H_2O (4–46 p.p.m.), F (4–40 p.p.m.), S (115–576 p.p.m.) and Cl (0.06–2 p.p.m.) (see Supplementary Table 1).

There are no clear correlations between the volatile contents and major and trace element contents when we consider all the compositional groups (very-low-, low- and high-Ti glasses). Yet each group has a specific range in F and S contents, suggesting differences in their initial volatile content that have not been completely erased by the degassing process acting during melt transport and eruption.

An important feature of the data is the clear correlation between H_2O, other volatile species and major elements among the very-low-Ti glasses (Fig. 1; Supplementary Figs 2, 3 and 4). These correlations indicate that H_2O in the glasses is indigenous, not a product of solar wind implantation or laboratory contamination, and support the

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hypothesis that there were significant differences in the initial volatile content and/or the extent of degassing among the lunar glasses. The correlations also suggest that the major element composition of the melt may have influenced the degassing dynamics through volatile
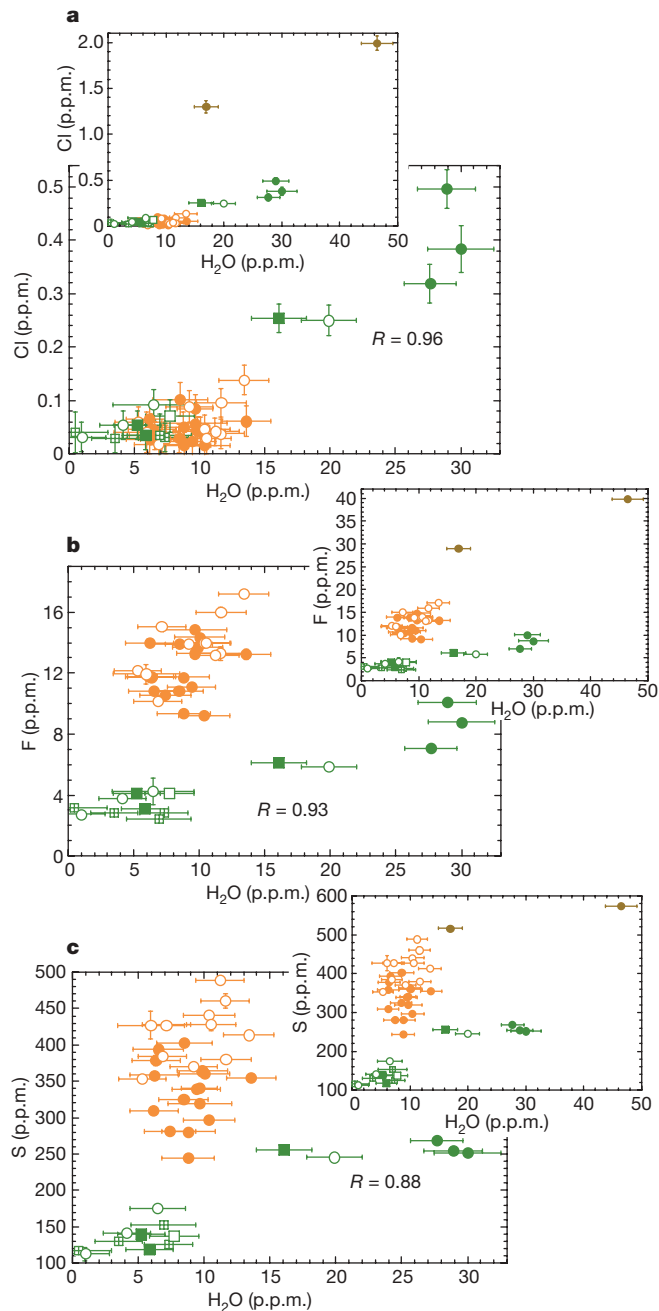

Figure 1 | Correlations between water and other volatile content in the lunar volcanic glasses. a, Chlorine; **b,** fluorine; and **c,** sulphur against H_2O content. Green symbols represent the very-low-Ti glasses: group B and C (filled circles), A (filled squares) and D (crossed open squares); partially crystallized glasses in each group are represented by open circles (group B and C) and open squares (group A). Orange filled circles represent high-Ti glasses; open orange circles indicate partially crystallized glasses. Inset shows all the glasses including the two low-Ti glasses (filled brown circles). Error bars represent standard deviation (2σ) uncertainties. Volatile contents are reported in parts per million. There are significant correlations between the volatile contents measured for the very-low-Ti glasses (see Supplementary Tables 1 and 3 and Fig. 2). Note that although the high-Ti glasses have similar Cl and H_2O contents to the very-low-Ti glasses, they have significantly higher F and S contents, suggesting different initial volatile concentrations between the different major compositional groups of glasses.
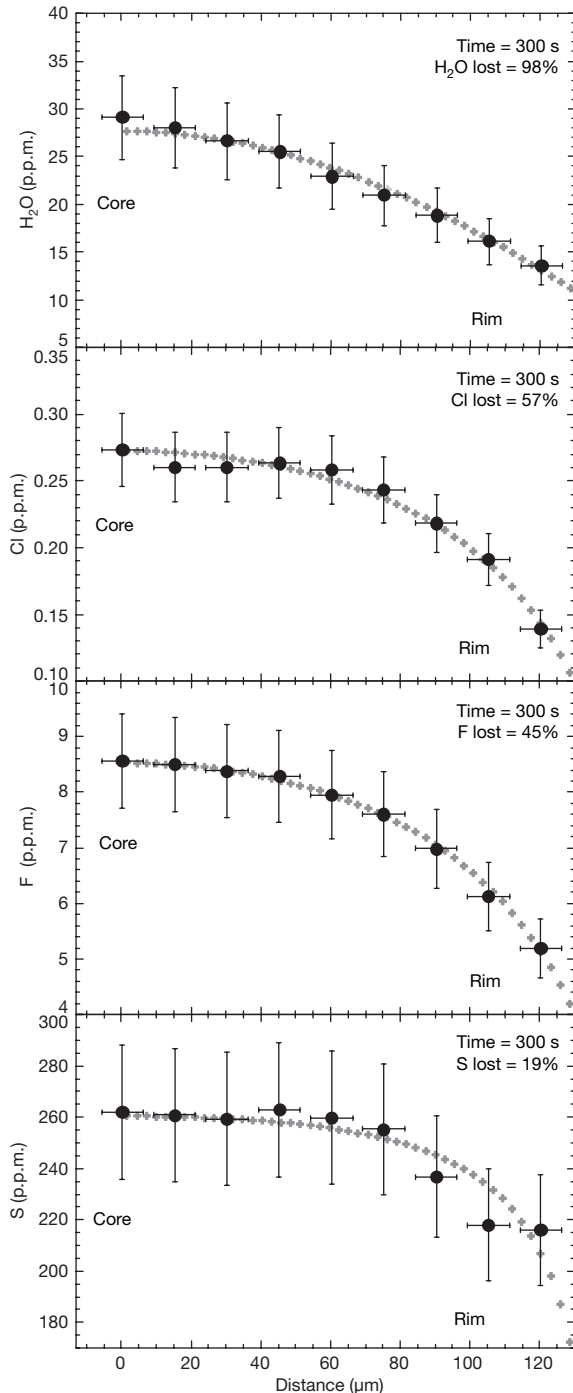
diffusion and bubble formation kinetics (see Supplementary Figs 5 and 6, and detailed discussion in the Supplementary Information on the implications of our results).

To evaluate further the hypothesis that volatiles in the lunar volcanic glasses are indigenous but affected by partial degassing during eruption, we measured radial concentration profiles for the volatiles within a single very-low-Ti glass bead (see Fig. 2; Supplementary Table 4 and the Methods section for detailed discussion on the analytical methods). Volatile contents in this bead decrease systematically from core to rim. This decrease is especially significant for H_2O, which has a concentration of ~30 p.p.m. in the centre, decreasing steadily to ~14 p.p.m. near the rim. Similar depletion towards the rim of the glass bead is observed in the data for F, Cl and S. This observation supports the hypothesis that H_2O and the other volatiles were indigenous to the glass bead but were affected by degassing during eruption. The depletion within the single glass bead reproduces essentially the same correlations between volatile elements as those defined by the volatile contents of all the very-low-Ti glasses (see Supplementary Fig. 4). This reinforces the hypothesis that degassing has been the main process affecting the primitive volatile contents of the lunar volcanic glasses.

To evaluate diffusive volatile loss from the lunar volcanic glasses during eruption, we applied a model of diffusion from a sphere with concomitant surface evaporation to the measured volatile concentration profiles within the selected glass bead[10] (Fig. 2). We emphasize that our calculations consider only volatile loss by diffusive degassing from the time of eruption until deposition, and do not consider volatile loss during the period of bubble formation and growth preceding magma fragmentation and eruption. Furthermore, we assume that there was no significant change in the distribution of volatiles within the glass beads during the period of 3.4–3.8 Gyr following their deposition[10]. This assumption is reasonable because at the average temperature on the sunlit side of the Moon (−20 to 0 °C) diffusion in the silicate glasses is negligible, and the beads have been exposed directly to the lunar surface for no more than 30 Myr (refs 19, 20). The crucial input parameters of the diffusion model are the sphere radius, the temperature of the melt during eruption, the cooling rate, the initial volatile concentrations in the glass beads, the diffusion coefficients of the volatiles within the melt, and the rates of evaporation at the surface of the melt sphere. We examined a wide range of cooling rates and times, and considered the concentration profiles for all volatiles simultaneously to determine the parameters that provided the best fit (see Supplementary Information for details on the model).

The degassing model provides excellent fits to the measured radial concentration profiles for all species simultaneously, at reasonable cooling rates and cooling times (Fig. 2). We found that cooling rates greater than 4 K s⁻¹ did not provide acceptable fits for all volatile species (see Supplementary Fig. 7). Cooling rates of 2 to 3 K s⁻¹ over a period of ~2 to 5 min between eruption and quenching provided the best fit to all volatile profiles together; at these conditions the glass bead loses approximately 19% S, 45% F, 57% Cl and 98% H_2O. The initial H_2O content is not precisely constrained by the modelling, but the best fit, again considering cooling rates and times that allow acceptable fits for all volatile profiles simultaneously, is obtained for an initial H_2O content of 745 p.p.m., and the H_2O content must be at least 260 p.p.m. to obtain an acceptable fit (at the 95% confidence level).

Several different origins of the lunar volatiles might be proposed. An undifferentiated lunar mantle reservoir comparatively rich in volatiles might exist at a depth greater than that of the postulated lunar magma ocean, or a less-processed cumulate that kept the primitive lunar mantle signature may have retained significant volatile elements[18]. Another possibility would be the recycling of an ilmenite-rich dense layer enriched in incompatible and volatile elements formed during the late-stage cooling and crystallization of the lunar magma ocean[21]. This process may have been responsible for the

Figure 2 | Volatile concentration profiles from core to rim in a single bead of the very-low-Ti glasses. The glass used is 'Green #5' (see Supplementary Tables 1 and 4). The black filled circles represent the measured profiles, the grey filled crosses define the output data of the model describing the diffusive volatile loss from a homogeneous sphere with concomitant surface evaporation; see text for details and Supplementary Tables 4 and 5 (Case 1) for model parameters. Error bars represent standard deviation (2σ) uncertainties, and the size of the rastered ion beam. Volatile contents are in parts per million. To avoid any possible influence of ions implanted by solar wind, we did not analyse the outermost rim of the glass bead; the measured concentration profiles stop 18 μm before reaching the rim of the bead. The sharp decrease in volatile content from core to rim for H$_2$O, Cl, F and S suggests that the volatile contents are indigenous to the Moon and were affected by degassing during magma eruption. As expected, H$_2$O has the largest observed variation from core to rim, followed by Cl, F and S, indicating progressively less degassing for those elements, respectively.

re-fertilization of volatile elements into the source of the volcanic glasses.

Previous hypotheses suggest that the volatile elements either survived or were accreted after the giant impact event that probably led to the formation of the Moon. Pahlevan and Stevenson[22] suggested that the proto-Earth (having significant amounts of water) and proto-lunar disk would have diffusively equilibrated after the giant impact, and that the volatile depletion of the Moon may be explained by hydrodynamic escape from the proto-lunar disk driven by an outflow of hydrogen previously accreted to the Earth. Our results suggest either that hydrodynamic escape was not complete or that a significant amount of water was accreted to the Earth–Moon system immediately after the giant impact[23,24]. The existence of zircons on the Earth that are as old as 4,325 Myr and have oxygen isotopes of 6.5‰ provides evidence for the presence of liquid water near the Earth's surface within ~230 Myr of the Earth's accretion[25–27]. This observation strongly suggests that either the Earth–Moon system retained significant amounts of water after the giant impact, or that volatile-rich material accreted to both the Earth and Moon within a narrow time window after the giant impact but before 4.3 Gyr. At this point we do not have enough information to support or discard either of these hypotheses. Our results suggest that, contrary to the prevailing ideas, the bulk Moon might not be entirely depleted in highly volatile elements, and the presence of volatiles, especially water, must be included in models constraining the Moon's formation and its thermal and chemical evolution.

METHODS SUMMARY

Modelling. To evaluate diffusive volatile loss from the lunar volcanic glasses during eruption, we applied a model of diffusion from a sphere using a temperature-dependent diffusion coefficient with concomitant surface evaporation[10,28]. The equations and boundary conditions were solved numerically using a forward-time, centred-space finite-difference scheme[28] for each element independently. We selected the model outputs that minimized the sum of χ^2 for all of the volatiles together, using the optimum values of initial concentration and evaporation constant determined for each volatile at the cooling rate and cooling time of interest (see Supplementary Information)

Analytical method. The glass beads were individually selected and mounted in indium and analysed for major elements using the Cameca SX100 electron microprobe, and for trace and volatile elements using the Cameca IMS 6f and the NanoSIMS 50L (see online Methods and Supplementary Tables 1, 2 and 4)[3,29]. We measured the volatile contents by SIMS using methods recently developed for the simultaneous microanalysis of trace amounts of H$_2$O, CO$_2$, F, S and Cl in glasses and nominally anhydrous minerals[3].

Full Methods and any associated references are available in the online version of the paper at www.nature.com/nature.

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METHODS

The lunar glasses were mounted in indium and analysed for major elements using the Cameca SX100 electron microprobe at the Department of Geological Sciences, Brown University. We made the analyses using 15 kV accelerating voltage, 10 nA beam intensity, a 5–10 μm defocused beam and PAP correction procedures[30]. Most major elements reported have precision (2σ) of 1–1.5%, with the exception of Na_2O 20–60%, K_2O 20–80%, Cr_2O_3 ~15%, TiO_2 5–15%, P_2O_5 <100%, MnO <20%, which represents the average of the standard deviation of three to eight replicated analyses on a single glass bead. We reported Cr_2O_3, K_2O and P_2O_5 contents obtained using the Cameca 6f ion probe at DTM, Carnegie Institution of Washington. The precision for the trace elements measured by ion probe is better than 15% (2σ) and represents the average of the standard deviation of three to four replicated analyses on a single glass bead. SIMS calibrations are regressions of ion probe signals compared with known concentrations.

In this study, we plotted standard trace element (and volatile) concentrations against measured trace element (volatile)/^{30}Si ratios[3,29]. We measured the volatile contents by SIMS using a Cameca IMS 6f and the NanoSIMS 50L at DTM, Carnegie Institution of Washington, using methods recently developed for the microanalysis of trace amounts of H_2O, CO_2, F, S and Cl in glasses and nominally anhydrous minerals[3,31–33]. For the Cameca IMS 6f a typical 10-min measurement for volatile abundances is made on a singly polished specimen using a Cs^+ primary beam (~14 nA accelerated to 10 kV) with collection of negatively charged secondary ions. We used a 10-μm primary beam rastered at 25 μm, which results in a 35-μm crater. We pre-sputter for 3–5 min before analysis. During this time, we monitored secondary ion images of ^{12}C, ^{17}OH, ^{19}F ^{32}S and ^{35}Cl projected on the channel plate. This procedure helped to avoid inclusions and cracks, which appear as bright features on the projected image (especially the ^{12}C image), and dendritic crystals (dark shapes on ^{32}S image). After each beam spot had been carefully examined a field aperture was inserted to permit transmission of ions only from the central 10 μm of the 35-μm crater (that is, always 12.5 μm away from the crater edge), thus avoiding transmission of ions from the edge of the sputter crater and the surface of the sample. Counting times were 10 s for ^{12}C and 5 s for all other elements. Pressure in the ion probe sample chamber was ~6×10^{-10} torr during the analyses. The sample mount was placed in the ion probe sample chamber for ~12 h before analysis; this approach allowed the best detection limits for H_2O. Synthetic forsterite (Allied, <0.4 p.p.m. H_2O by FTIR) was used for the determination of H_2O detection limits[3,31–33]. All the lunar glasses were contained on a single sample mount together with synthetic forsterite; the H_2O detection limit on this particular sample mount was 6.4 p.p.m., as determined by five separate measurements interspersed with analyses of the lunar glasses. These measurements of synthetic forsterite yielded an average ^{16}OH count rate of 150 counts per second with 3,750 total counts per analysis and a Poisson limit on the precision of 3.2% (2σ), which is much lower than the actual reproducibility of the detection limit (~25%, 2σ). As a result, none of the analyses is limited in any way by counting statistics; the limiting factor is reproducibility of

the detection limit. Similar statistics are obtained for the other volatile elements on forsterite; detection limits for F, S and Cl are ~0.09 p.p.m., ~0.27 p.p.m. and ~0.03 p.p.m. respectively.

Calibrations for H_2O and other volatiles were verified for glasses and nominally anhydrous mineral standards before each analytical session; abundances for the other volatile elements (CO_2, F, S, Cl) were calculated from the calibrations performed on glass standards. The reported volatile concentrations of lunar glasses are obtained by simply subtracting the detection limit from the measured concentrations, and the uncertainties are calculated by propagating the errors in the detection limit and the counting statistics. After the measurement by the IMS 6f, we re-polished the sample and measured the core to rim volatile variation with the Cameca NanoSIMS 50L at DTM. We followed the same analytical method used on the Cameca 6f, with the exception that crater edge contamination was eliminated by electronic gating rather than a field aperture. A typical 15-min measurement used a Cs^+ primary beam (~3 nA accelerated to 8 kV) with collection of negatively charged secondary ions on multiple detectors. We used an 800-nm primary beam rastered at 12×12 μm area divided into 64×64 pixels with 140-μs dwell time per pixel, and an electronic gating on the central 4.5×4.5 μm. We pre-sputter for 6 min before analysis and collected the data on six detectors in multi-collection mode: ^{12}C-^{16}OH-^{19}F-^{30}Si-^{32}S-^{35}Cl at mass resolving power of ~6,000 (sufficient to resolve ^{16}OH from ^{17}O). Counting times were 1 s for all masses, and we collected 100 ratios (100 s total counting time). Pressure in the ion probe sample chamber was ~3×10^{-10} torr or less during the analyses. We used synthetic forsterite (Allied, <0.4 p.p.m. H_2O by FTIR) to establish the H_2O detection limit of 13 p.p.m., as determined by five separate measurements interspersed with analyses of the lunar glasses. Count rates for ^{16}OH were 540 counts s^{-1}, with 54,000 total counts per analysis and a Poisson precision limit of 0.002% (2σ), well below the uncertainty in the detection limits ($\pm8\%$ 2σ). The limiting factor on the precision is the reproducibility of the detection limit. The reported volatile concentrations of lunar glasses are obtained by simply subtracting the detection limit from the measured concentrations. For the uncertainties, we assigned a conservative 15% (2σ) for H_2O and 10% (2σ) for F, S and Cl on all the measured concentration profiles, which represent the higher uncertainty calculated by propagating the errors in the detection limit and the counting statistics obtained with the NanoSIMS.

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