Oxygen isotopic evidence for accretion of Earth’s water before a high-energy Moon-forming giant impact

How to cite:

For guidance on citations see FAQs.

© 2018 The Authors

Version: Version of Record

Link(s) to article on publisher’s website:
http://dx.doi.org/doi:10.1126/sciadv.aao5928

Copyright and Moral Rights for the articles on this site are retained by the individual authors and/or other copyright owners. For more information on Open Research Online’s data policy on reuse of materials please consult the policies page.

oro.open.ac.uk
Oxygen isotopic evidence for accretion of Earth’s water before a high-energy Moon-forming giant impact

Richard C. Greenwood, Jean-Alix Barrat, Martin F. Miller, Mahesh Anand, Nicolas Dauphas, Ian A. Franchi, Patrick Sillard, Natalie A. Starkey

The Earth-Moon system likely formed as a result of a collision between two large planetary objects. Debate about their relative masses, the impact energy involved, and the extent of isotopic homogenization continues. We present the results of a high-precision oxygen isotope study of an extensive suite of lunar and terrestrial samples. We demonstrate that lunar rocks and terrestrial basalts show a 3 to 4 ppm (parts per million), statistically resolvable, difference in $\Delta^{17}O$. Taking aubrite meteorites as a candidate impactor material, we show that the giant impact scenario involved nearly complete mixing between the target and impactor. Alternatively, the degree of similarity between the $\Delta^{17}O$ values of the impactor and the proto-Earth must have been significantly closer than that between Earth and aubrites. If the Earth-Moon system evolved from an initially highly vaporized and isotopically homogenized state, as indicated by recent dynamical models, then the terrestrial basalt-lunar oxygen isotope difference detected by our study may be a reflection of post–giant impact additions to Earth. On the basis of this assumption, our data indicate that post–giant impact additions to Earth could have contributed between 5 and 30% of Earth’s water, depending on global water estimates. Consequently, our data indicate that the bulk of Earth’s water was accreted before the giant impact and not later, as often proposed.

INTRODUCTION

The now classic formulation of the Moon-forming giant impact hypothesis envisaged an oblique impact between the proto-Earth and a Mars-sized body (1). Numerical simulations based on this model indicated that the Moon accreted from a debris disc containing approximately 70% impactor-derived material (1). If the impactor had a different oxygen isotopic composition ($\Delta^{17}O$) to the proto-Earth, a prediction of this model is that Earth and the Moon should display resolvable isotopic differences (see Results for the definition of $\Delta^{17}O$) (2, 3). However, with a sole exception (4), high-precision studies have failed to detect a difference between Earth and the Moon (5–8). To explain this apparent discrepancy, it has been proposed that isotopic equilibration took place within a post-impact, melt-vapor disc (9). Studies of silicon (10) and titanium (11) isotopic variation have also revealed no differences between Earth and the Moon. In addition, tungsten isotopic studies indicate that Earth and the Moon initially had a similar $^{182}W$ composition (12). The fact that both tungsten and titanium show no isotopic differences between Earth and the Moon is potentially significant because both are very refractory elements and, thus, unlikely to have been significantly affected by the proposed post-impact equilibration (9).

The isotopic similarity between Earth and the Moon, combined with a reassessment of the angular momentum constraints, has led to the formulation of high-energy models, which invoke nearly complete mixing between the impactor and the target (2, 3). Recent modeling studies suggest that typical rocky planets may be vaporized multiple times by giant impacts (13, 14). This process results in the formation of an extended structure termed a “synestia,” initially composed principally of silicate vapor and comprising a co-rotating inner region connected to a disc-like outer region. When applied to the formation of the Earth-Moon system, the synestia model suggests that the Moon formed from condensing liquid beyond the Roche limit, with the bulk of the structure contracting to form Earth (13). Such a structure would involve complete isotopic equilibration for the bulk of the Earth-Moon system (13), with the possibility that restricted regions of Earth’s deep mantle might still retain some evidence of pre–giant impact isotopic signatures (15). Potassium isotope analyses, which show a small resolvable Earth-Moon difference, have been interpreted as being consistent with results of high-energy impact simulations (16).

However, complete isotopic re-equilibration in the wake of the giant impact has been questioned by a study that detected a 12 ± 3 ppm (parts per million) (SEM) Earth-Moon $\Delta^{17}O$ difference (4). Subsequently, this finding was challenged by a study that was unable to detect this isotopic difference at a level of ±5 ppm (SEM) (5). Lack of significant isotopic differences between Earth and the Moon has also been explained by a terrestrial accretion model, based on the contrasting affinities of a range of elements (O, Ca, Ti, Cr, Ni, Mo, and Ru), which predicts that both the impactor and the proto-Earth formed from the same enstatite chondrite–like precursor materials, making large Earth-Moon isotopic differences unlikely (17).

RESULTS

Here, we present the results of a detailed, high-precision oxygen isotope investigation, based on a more extensive suite of both lunar and terrestrial samples than in any previous study. Oxygen isotopic data are reported using the δ notation: $\delta^{17}O = [(^{17}O/^{16}O)_{\text{sample}}/(^{17}O/^{16}O)_{\text{VSMOW}}] - 1$, where $i = 17$ or 18 and VSMOW is the Vienna Standard Mean Ocean Water reference material. Results are, by convention, reported as per mil (%). $\Delta^{17}O$, which represents the deviation from an assigned reference fractionation line, has been calculated according to $(18)\Delta^{17}O = \ln(1 + \delta^{17}O) - \lambda \ln(1 + \delta^{18}O) + \gamma$ and reported as parts per million. We chose to assign $\lambda = 0.5262$ and $\gamma = -64$ ppm (see Materials and Methods for further details).

---

1Planetary and Space Sciences, School of Physical Sciences, The Open University, Walton Hall, Milton Keynes MK7 6AA, UK. 2Université de Bretagne Occidentale, Institut Universitaire de France, 36 allée des Études, BP 20513, 29280 Brest, France. 3Max-Planck-Institut für Chemie, Ackermannweg 10, 55128 Mainz, Germany. 4INRSE, Centre National d’Études Spatiales, 12 rue des Études, 92190 Bagneux, France. 5Centre de recherche en énergie et statistique, 5 avenue Henry Le Chatelier, 91120 Palaiseau, France. 6Centre de recherche en énergie et statistique, 5 avenue Henry Le Chatelier, 91120 Palaiseau, France.
Lunar whole rock samples (n = 17) covering all the main lithological units, from all six Apollo landings, have been analyzed, as well as lunar mineral separates (n = 14) (see Materials and Methods) (table S1). Lunar rocks and mineral separates are compared to terrestrial mafic rocks, comprising basalts (n = 20) and a mantle xenolith (tables S1 and S3). In the terrestrial sample set, we also include our previously published olivine data (19). Data from previous studies (19, 20) have been recalibrated against VSMOW (see Materials and Methods).

The oxygen isotopic compositions of the lunar and terrestrial samples analyzed in this study, and other extraterrestrial materials that plot close to the terrestrial fractionation line (TFL), are shown in Fig. 1. Lunar whole rocks have relatively homogeneous oxygen isotope compositions, with δ18O values that range from 5.64 ± 0.02‰ (2 SD) to 6.19 ± 0.02‰ (2 SD) and Δ17O values from 2 to 20 ppm (Fig. 2 and table S1). In comparison, terrestrial whole rocks show a wider spread in δ18O, ranging from 5.03 ± 0.12‰ (2 SD) to 6.27 ± 0.15‰ (2 SD) and have Δ17O values from −4 to 15 ppm (Fig. 2 and table S1). However, the mean δ18O values of the lunar and terrestrial whole rocks are close, 5.92 ± 0.28‰ (2 SD) and 5.79 ± 0.69‰ (2 SD), respectively. Terrestrial and lunar samples show similar slopes and y-axis intercepts on plots of 103ln(1 + δ18O) versus 103ln(1 + δ18O) (figs. S1 to S3).

It is clear from Fig. 2 that lunar and terrestrial samples show a significant level of overlap with respect to Δ17O, whereas the aubrites (20) are fully resolved on this plot. There is a 3 ppm difference between the average Δ17O value of lunar samples compared to that of terrestrial samples, with the full suite of lunar whole rocks and mineral separates (n = 31) having a mean Δ17O composition of 10 ± 2 ppm (2 SEM), compared to 7 ± 2 ppm (2 SEM) for all terrestrial samples and mineral separates (n = 37) (Fig. 2 and table S1). When terrestrial basalts [Δ17O = 6 ± 2 ppm (2 SEM) (n = 20)] are compared to lunar whole rocks, this difference increases to 4 ppm (Fig. 3).

To test the significance of the 3 ppm difference between the two data sets, we performed an unpaired t-test (test 1) (table S2). This gave a P value of 0.032, which is below the 0.05 threshold and indicates that this 3 ppm difference is statistically significant. Excluding samples with SEM values >6 ppm (test 2) (table S2) does not significantly alter this result. The results of a t test for terrestrial basalts and lunar whole rocks (test 3) returned a P value of 0.014, well below the 0.05 threshold (table S2). Although this P value increased when samples with SEM values >6 ppm were excluded, the results of both tests (tests 3 and 4) indicate that this 4 ppm difference between terrestrial basalts and lunar whole rocks is statistically significant (table S2). In comparison, all t tests on terrestrial olivine samples (tests 4 to 8) (table S2) indicate that the 1 to 2 ppm Δ17O differences they show with lunar samples are not statistically significant, returning P values that are considerably above the 0.05 threshold.

To further scrutinize the statistical significance of our data, we used the bootstrap technique with 10^5 replications on both the averaged data (table S1) and raw data (see separate Excel file in other Supplementary Materials). The results of these analyses are given in the “Further statistical analysis” section (see the Supplementary Materials) and, in conformity with the t tests, indicate that the 3 to 4 ppm difference between the lunar and terrestrial data sets is statistically significant. Our results contrast with those of Young et al. (5), undertaken on a somewhat smaller data set than the present one, which concluded that lunar and terrestrial rocks are indistinguishable with respect to Δ17O at a level of ±5 ppm.

Our results indicate a dichotomy in terrestrial Δ17O values, with no significant difference between lunar rocks and terrestrial olivine (both high- and low-3He/4He varieties), but a statistically significant difference of 3 to 4 ppm when basaltic samples are included in the terrestrial data set. Contamination of the terrestrial basalts (mainly submarine quenched glasses) by seawater is an unlikely explanation for this effect. When compared to VSMOW, natural seawater samples have a Δ17O composition of −5 ppm (21), which, relative to our reference line, would give seawater a Δ17O value of +59 ppm (see Materials and Methods), and so any interaction between seawater and the terrestrial basalts would have the effect of increasing their Δ17O values and thereby reducing the difference between them and the lunar rocks. It could be argued that some form of seawater

---

**Fig. 1.** Oxygen isotope composition of terrestrial and lunar samples shown in relation to various meteorite groups that plot close to the TFL. Enstatite chondrites (EH and EL groups) (26) are shown as circular filled and unfilled fields. Aubrites, HEDs (howardites, eucrites, diogenites), angrites, and Martian meteorites are shown as bars to represent the δ18O range and mean average Δ17O value for each group (Δ17O calculated as per samples in this study). Data sources: terrestrial and lunar samples, this study and Starkey et al. (19); aubrites, Barrat et al. (20); other groups, Greenwood et al. (42).

**Fig. 2.** Oxygen isotopic composition of terrestrial and lunar samples and aubrites. Aubrites are the meteorites with the closest oxygen isotope composition to terrestrial and lunar rocks and, until the study of Barrat et al. (20), were thought to be indistinguishable from them. TWR, terrestrial whole rock analyses; LWR, lunar whole rock analyses.
interaction might explain why we find a significantly smaller $\Delta^{17}O$ difference between lunar and terrestrial samples than the $12 \pm 3$ ppm reported by Herwartz et al. (4). However, this is clearly not the case because our olivine samples (table S1), obtained predominantly from subaerially erupted lavas (19), have an average $\Delta^{17}O$ composition that is $3 \text{ ppm}$ higher than the terrestrial basalts, which is opposite to what would be predicted if basalts had incorporated significant amounts of seawater-derived oxygen. With a $\Delta^{17}O$ of $-346 \text{ ppm}$ relative to the reference line used in this study, a ~1% addition of atmospheric oxygen would be sufficient to account for the measured offset between lunar whole rocks and terrestrial basalts. However, lunar samples would also be sensitive to post-collection air contamination, and identical procedures were used for both sets of specimens. Our pre-reaction procedures should have been efficient to account for the measured offset between lunar whole rocks and terrestrial basalts. Nonetheless, our pre-reaction procedures should have been efficient to account for the measured offset between lunar whole rocks and terrestrial basalts.

We therefore conclude that the $3$ to $4 \text{ ppm} \Delta^{17}O$ difference between terrestrial and lunar samples observed in our data, while significantly lower than the $12 \pm 3 \text{ ppm}$ (SEM) value obtained in a previous study (4), is nonetheless real. We now consider the implications of this slight $\Delta^{17}O$ difference between lunar and terrestrial samples for the origin and evolution of the Earth-Moon system.

**DISCUSSION**

**Testing an aubritic composition for Theia**

There are strong geochemical and isotopic arguments that, throughout its accretion history, Earth formed from material with a high enstatite-chondrite-like component (E-type) and that the final 40% of accretion, including the Moon-forming impactor, was composed almost exclusively of E-type material (17). This is further supported by evidence from the FeO composition, and Nb/Ta and Hf/W ratios, of Earth and the Moon, which favor a reduced (FeO $\sim 0.3\%$) Mercury-like impactor (24). However, the actual enstatite chondrites are poor candidate materials for the Moon-forming impactor, having low Mg/Si ratios and being relatively enriched in volatile elements. They may have formed from the same isotopic reservoir as Earth, but subsequently diverged in their chemical composition from Earth’s building blocks (25). In the canonical model (1), the impactor was taken to be Mars-sized and so would have been a fully differentiated body and hence homogeneous with respect to oxygen isotopes. Consequently, when looking for a proxy for this impactor, commonly referred to as Theia, it makes geochemical sense to use an achondrite, which, as a result of high degrees of melting on its parent body, has a homogeneous oxygen isotopic composition (20).

The aubrites provide the closest match to the hypothesized reduced impactor (24), being virtually FeO-free and having an isotopic composition that is closely similar to both Earth and enstatite chondrites (Fig. 1) (20, 26). High-precision oxygen isotope data for aubrites ($n = 8$) (Figs. 1 and 2) show that their oxygen isotopic composition [$\Delta^{17}O = 28 \pm 3 \text{ ppm}$ (2 SEM)] (table S1) is close to, but fully resolvable from that of Earth and the Moon (Fig. 2). Using the canonical giant impact model (1) (10.6% impactor and 89.4% proto-Earth in the final Earth) and taking the isotopic composition of the impactor to be that of the aubrites, we have calculated the relative proportions of impactor and target material that are required in Earth and the Moon to account for the oxygen isotopic differences observed in our data (model S1). The $\sim 4 \text{ ppm}$ Earth-Moon difference observed between terrestrial basalts and lunar rocks can be reproduced by a lunar impactor component of $25$ to $28\%$ of the Moon’s mass, compared to the terrestrial impactor component of $10.4\%$ (Fig. 4). The required impactor contribution is significantly lower than the $70\%$ predicted by the canonical model (1) and also less than other low-velocity scenarios (Fig. 4) (27). The SE of our observed $4 \text{ ppm}$ Earth-Moon difference is $\pm 3 \text{ ppm}$ (2 SE), which would indicate that the range of permissible impactor contributions to the Moon is between $13$ and $39\%$ (Fig. 4). It has been shown that the proto-Earth and the impactor were isotopically similar before collision (28). Our analysis indicates that aubrites are distinct enough to exclude them as an impactor candidate if no Earth-Moon homogenization took place. EH (high-Fe) and EL (low-Fe) enstatite chondrites are also possible candidates, but these meteorites have heterogeneous oxygen isotopic compositions, resulting in group average $\Delta^{17}O$ values that are highly uncertain (Fig. 1). The EH and EL impactor scenarios therefore cannot be tested with currently available oxygen isotope data. Assuming that aubrites represent faithful proxies for the oxygen isotopic composition of all enstatite-type impactors, we conclude that the present $\Delta^{17}O$ similarity between Earth and the Moon is unlikely to be due to the impactor and the proto-Earth having nearly identical isotopic compositions. If correct, this implies that the isotopic compositions of Earth and the Moon were homogenized as part of the equilibration processes associated with the giant impact event itself.

Although high-energy collisional models (2, 3) predict a lower compositional difference between Earth and the Moon than the canonical model (1), they do not envisage complete isotopic homogenization. Thus, the average of all the $\Delta^{17}O$ values in table 3 of the work by Ćuk and Stewart (2) ($\Delta^{17}O$ = difference in projectile mass fraction between the silicate portions of the planet and disc) is $8.8\%$, which, with the use of...
a terrestrial $\Delta^{17}O$ value of 6 ppm and an impactor value of 28 ppm (aubritic), equates to a Moon-Earth difference of 2 ppm, that is, about half that represented by our lunar and terrestrial whole rock analyses. A similar value is obtained for those runs that are deemed by Çuk and Stewart (2) to be successful Moon-forming scenarios. In the simulations of Canup (3), the disc can contain more or less impactor material than the final planet. For those runs in which the disc contains more impactor material, the overall average difference between the disc and the final planet was approximately 8%, similar to that predicted by the simulations of Çuk and Stewart (2) and indicating a Moon-Earth difference of about 1.8 ppm. It is worth noting that some of the runs of Canup (3), such as run 17, essentially envisage complete mixing between the target and the impactor. The synestia scenario for the formation of the Earth-Moon system, involving substantial and possibly multiple vaporization events (13, 14), is likely to result in essentially complete isotopic homogenization of the entire system, with the possible exception of some very deep primordial mantle reservoirs (15).

As discussed above, the 3 to 4 ppm $\Delta^{17}O$ difference between the terrestrial and lunar rocks analyzed in this study is not consistent with an aubritic impactor, unless some form of post-impact equilibration also took place. In the absence of such an equilibration event, the impactor would have had to be much closer to the proto-Earth in its oxygen isotopic composition than the aubrites. This is not impossible, but we would argue that it is unlikely. Our results are consistent with high-energy impact simulations (2, 3) and potentially consistent with a limited differential impactor component in the Moon compared to Earth. However, if total oxygen isotopic equilibration took place in the aftermath of the giant impact, as appears to be implied by the synestia model (13, 14), then the 3 to 4 ppm Earth-Moon $\Delta^{17}O$ difference requires a post-impact explanation. We now explore this possibility further here.

### Differential post-impact additions to Earth and the Moon

Highly siderophile element data indicate that following the giant impact, both Earth and the Moon received an input of chondritic material, generally referred to as the late veneer (29). However, the amounts accreted by Earth and the Moon were very different: ~0.5 weight % (wt %) of the terrestrial mass and ~0.02 wt % of the lunar mass (29). This may reflect the involvement of a limited number of larger asteroids, which differentially impacted Earth (30). From an oxygen isotope perspective, the relatively small late veneer contribution to the Moon can be neglected. We assume that the average lunar $\Delta^{17}O$ value is representative of the post–giant impact, pre-late veneer, terrestrial composition ($\Delta^{17}O = 10 \pm 2$ ppm) and show the effects of adding various chondritic components to it in Fig. 5 and fig. S4. The shaded vertical band in Fig. 5 is the error (±2 SEM) on the average terrestrial basalt $\Delta^{17}O$ value. Addition

---

**Fig. 5.** Diagram showing how the addition of various chondritic components as part of the late veneer would alter the average $\Delta^{17}O$ value of pristine terrestrial mantle. The $\Delta^{17}O$ composition of pristine terrestrial material just after the giant impact is taken to be equivalent to that of present-day lunar basalts. A late-stage addition of any single chondritic component in an amount equivalent to the late veneer mass would result in a $\Delta^{17}O$ isotopic shift greater than that defined by the 2 SEM error envelope of the terrestrial basalts (purple vertical band). An appropriate mix of chondritic components such as CI and CM would not violate the constraints imposed by our data. However, such a high percentage of chondritic material would violate Ru isotope constraints (31). A late veneer addition of 0.5% terrestrial mass of enstatite chondrite material (EL) (short black line) would add little water and result in only a very slight deviation to the $\Delta^{17}O$ value of the lunar basalts. A CM late veneer fraction of approximately 20% (horizontal blue dashed line) can account for the 3 to 4 ppm $\Delta^{17}O$ shift measured in the terrestrial basalts, while maximizing the amount of water delivered to Earth and minimizing the CC component within the late veneer, as required by Ru isotope systematics (31). An input of about 20% CV3 (Vigarano-type carbonaceous chondrite) would also satisfy the $\Delta^{17}O$ constraints, but reduce the amount of water delivered by the late veneer. On the basis of the lowest estimates of Earth’s water content (33), the late veneer, at best, could only have supplied about one-third of our planet’s water. Higher global water estimates (32) would decrease this to about 5% (see the Supplementary Materials). Dots on the lines refer to 0.1% of terrestrial mass. OC, ordinary chondrite; LV, late veneer.
CV3 chondrites, which are essentially dry, would equally fulfill the role of hydrated CC end members (CI, CM, and Tagish Lake) could provide the 4 ppm $\Delta^{17}$O shift required by our terrestrial basalt data, while excluding Cls (Fig. 5 and fig. S4). Therefore, the late veneer likely contained a chondritic component with a significantly negative $\Delta^{17}$O composition, with the most obvious candidates being carbonaceous chondrites (CCs), excluding Cls (Fig. 5 and fig. S4).

In terms of hydrated CCs, both CMs (Mighei-type carbonaceous chondrites) and the ungrouped CC Tagish Lake have the potential to explain the $\Delta^{17}$O offset between terrestrial basalts and lunar whole rocks and could also have provided a significant proportion of Earth’s water (Fig. 5). At present, there is little consensus concerning the amount of water present in Earth, with estimates varying between about 2 and 12 global ocean units (32–34) (global ocean unit = total mass of hydrosphere = 1.38 x $10^{21}$ kg) (35). On the basis of the lowest of these estimates (33), a late veneer composed exclusively of any of the hydrated CC end members (CI, CM, and Tagish Lake) could have furnished all, or most, of Earth’s water. However, such a high CC content would violate the oxygen isotope constraints imposed by our data, as well as those from Ru isotopes (31). CM chondrites could provide the 4 ppm $\Delta^{17}$O shift required by our terrestrial basalt data, while forming a relatively low fraction of the late veneer, as required by the Ru isotopes (31). A late veneer composition consisting of approximately 20% CM and 80% enstatite chondrite best fits the $\Delta^{17}$O and Ru isotope constraints (Fig. 5). However, this would provide only about 0.7 of a global ocean unit and, based on the most conservative estimates (33), represents only about 30% of Earth’s water budget. If higher global water estimates are realistic (32), then the late veneer, at best, delivered only about 5% of our planet’s water (see Materials and Methods) (fig. S4). CV3 chondrites, which are essentially dry, would equally fulfill the $\Delta^{17}$O constraints set by our study, but provide even less water (Fig. 5 and fig. S4).

A late veneer explanation for the 3 to 4 ppm $\Delta^{17}$O Earth-Moon difference implies that a large fraction of Earth’s water was delivered earlier than the giant impact event. Terrestrial hydration would have been synchronous with the main phase of Earth’s accretion and not the result of a late-stage delivery of water from the outer solar system (36). Fortuitously for the evolution of life on our planet, despite the high energy of the Moon-forming event, Earth retained enough of its primordial water to remain a habitable environment. These findings are consistent with modeling studies, which indicate that Earth would have had an ocean before the era of giant impacts and that this ocean was retained despite the high energy of this terminal accretion phase (37). Retention of early accreted water on Earth may have more general implications for the habitability of exoplanetary systems, which commonly experience similar early-stage, high-energy collisional processing (38).

### Laser fluorination analysis

Oxygen isotopic analysis was undertaken at the Open University using an infrared laser fluorination system (41). ~2 mg aliquots of samples and standards were loaded into a Ni sample block containing 22 drilled wells. The sample block was then placed in a two-part chamber, made vacuum-tight using a compression seal with a copper gasket and a quick-release KFX clamp (41). A 3 mm-thick BaF$_2$ window at the top of the chamber allowed simultaneous viewing and laser heating of samples. After sample loading, the cell was heated under vacuum for a minimum of 24 hours and to a temperature of at least 70°C to remove any adsorbed atmospheric moisture. Before fluorination, the system blank was systematically reduced by flushing the chamber with aliquots of BrF$_5$, such that the final blank was less than 60 nmol O$_2$. As a consequence of these procedures, potential problems associated with retained adsorbed moisture were minimized (5). Sample heating in the presence of BrF$_5$ was carried out using an integrated 50 W infrared CO$_2$ laser (10.6 μm) and video system mounted on an X-Y-Z gantry supplied by Photon Machines Inc. (42). After fluorination, the released O$_2$ was purified by passing it through two cryogenic (liquid nitrogen) traps and over a bed of heated KBr. The isotopic composition of the purified oxygen was analyzed using a Thermo Fisher MAT 253 dual-inlet MS.
mass spectrometer (mass resolving power, 200). Interference at m/z (mass/charge ratio) = 33 by NF³⁻ was monitored by performing scans for NF³⁻ on the sample gas before analyzing each sample; this was below interference levels during all sample analyses reported here. Our current system precision based on repeat analyses (n = 39) of our obsidian internal standard is ±0.052‰ for δ¹⁷O, ±0.094‰ for δ¹⁸O, and ±0.017‰ for Δ¹⁷O (2σ) (19).

Calibration of samples using the VSMOW scale
Oxygen isotope measurements of rocks and minerals are generally reported relative to VSMOW. However, direct calibration of the “laboratory standard” O₂ gas by comparison with O₂ prepared by direct fluorination of VSMOW is technically challenging. Therefore, most laboratories that measure oxygen triple-isotope ratios in rocks and minerals calibrate their own laboratory standard O₂ against oxygen generated from fluorination of one or more widely used silicate standards, such as NBS-28, UWG-2 garnet, or San Carlos olivine. However, this procedure is problematic and, for high precision analysis, the laboratory standard O₂ should be calibrated against VSMOW directly (43). The Open University laboratory standard gas (referred to as O₂-7) used in earlier studies (44) subsequently became exhausted and was replaced by O₂-8, which was used in this study. Pending a full VSMOW calibration, O₂-8 was initially calibrated against a limited range of secondary standards, as is normal practice in many laboratories. A more direct calibration of O₂-8 relative to VSMOW was subsequently undertaken at the Hebrew University of Jerusalem. All δ¹⁷O and δ¹⁸O data obtained during this study were then recalculated to the VSMOW scale based on the independent measurements of our O₂-8 laboratory standard gas. Data for terrestrial olivine samples (19) and aubrites (20) analyzed at the Open University, using the same (O₂-8) laboratory standard gas, were recalibrated in the same way.

Choice of assigned reference fractionation line (slope λ and ordinate axis offset γ)
With regard to an appropriate value of λ, some authors have assigned a value based on the actual fractionation line given by a collection of terrestrial samples (7, 18, 45), whereas others have assigned the high temperature limit value for oxygen isotope exchange under equilibrium conditions, 0.5305 (43, 46). There is, as yet, no consensus on a reference line for defining Δ¹⁷O values of silicate rocks and minerals. This can lead to misleading comparisons, if care is not taken to ensure that all Δ¹⁷O values are defined consistently. An additional complication is that it has recently been shown that terrestrial rocks and minerals form fractionation arrays that are slightly offset (by approximately −30 to −70 ppm) from the VSMOW reference (18, 47). Accordingly, and based on the fractionation line obtained from measurements at the Open University laboratory for a set of eclogitic garnets supplied by D. Rumble of the Carnegie Institution of Washington, DC, Δ¹⁷O values reported in this study, including those of terrestrial olivines (19) and aubrites (20) (table S1), are reported using a λ value of 0.5262 and a VSMOW offset (γ) of −64 ppm. Our reason for using this particular reference line is that it is both well constrained and reproducible. We reanalyzed those garnets at the start of this project and obtained an identical slope value to our previously published results (48). These new analyses of the eclogitic garnets are given in table S4 and plotted in fig. S5.

Slope and intercept values for lunar and terrestrial samples
The 10¹⁰ln(1 + Δ¹⁷O) versus 10¹⁰ln(1 + δ¹⁸O) values of all the terrestrial and lunar samples discussed in this paper (table S1) are plotted in fig. S1. The best-fit line had a slope of 0.5285 ± 0.0016 and a y-axis intercept of −0.068 ± 0.009. Because of the limited range of δ¹⁸O and δ¹⁷O values, the error on this line was significantly greater than that for the eclogitic garnets (table S4 and fig. S5). Note that, at the level of precision in this study, the concept of a single TFL is not valid (44). All lunar oxygen isotope data measured in this study, filtered such that samples with Δ¹⁷O reproducibility of greater than 6 ppm SEM were excluded, are plotted in fig. S2. The best-fit line through the data had a slope of 0.5301 ± 0.0024 and a y-axis intercept of −0.077 ± 0.014. While the slope through the data was close to the theoretical upper limit of 0.5305 (18, 43), it should be noted that the error associated with this slope was large due to the limited range in δ¹⁸O and δ¹⁷O values. All of the oxygen isotope data from terrestrial basalt samples measured in this study, filtered to exclude samples with Δ¹⁷O reproducibility of greater than 6 ppm SEM, are plotted in fig. S3. The best-fit line through the data had a slope of 0.5270 ± 0.0037 and a y-axis intercept of −0.062 ± 0.021. The slope through the terrestrial basalt data was somewhat lower than that for the lunar samples (fig. S2), but in both cases, the limited range in δ¹⁸O and δ¹⁷O values meant that there was a significant level of uncertainty on the slope and y-axis intercept values for both.

Statistical analysis
The mean Δ¹⁷O values of the lunar whole rocks and terrestrial basalts measured in this study were very similar, 10 ± 10 ppm (2 SD) and 6 ± 10 ppm (2 SD), respectively (SD) (table S1). Previous claims that lunar and terrestrial samples had essentially identical oxygen isotope compositions were also based on the close similarity of their respective mean Δ¹⁷O values and overlapping distributions about those means, as measured using SD (6–8). However, if no systematic bias is present, a more appropriate test to compare the two populations is to use the SEM = SD/√(n) (4). On this basis, the full suite of lunar whole rocks and mineral separates analyzed in this study (n = 31) had a mean Δ¹⁷O composition of 10 ± 2 ppm (2 SEM) and the terrestrial samples (n = 20) had a mean Δ¹⁷O composition of 6 ± 2 ppm (2 SEM) (table S1). One study (4) detected a 12 ± 3 ppm oxygen isotope difference between Earth and the Moon. However, this was based on only 3 lunar basalts and 8 terrestrial samples (11 if mineral separates are counted as individual samples). These findings were challenged by a subsequent study, which concluded that the Moon and Earth were isotopically indistinguishable at the ±5 ppm (2 SEM) level (5). However, this study was also based on a relatively small suite, comprising 8 lunar samples and 4 terrestrial samples (6 if mineral separates are counted as individual samples). The present study was based on 16 distinct lunar samples (32 if mineral separates were counted as individual samples) and 21 distinct terrestrial samples. The terrestrial data were augmented by 13 distinct olivine fractions (19) analyzed at the Open University under identical conditions to the data in the present study.

In view of the small difference between the mean Δ¹⁷O composition of the terrestrial and lunar suites, one potential problem in using analyses collected over extended time periods is the possibility of some form of analytical drift, perhaps resulting from a change in the isotopic composition of the reference gas. To examine this possibility, we have compiled all the obsidian standards data obtained throughout the course of this study. The analyses from our olivine study (19) were made during 2012 to 2014, whereas the terrestrial and lunar samples data were obtained during 2014 to 2016. Longer-term systematic drift between the lunar whole rocks and mineral separates and terrestrial samples was unlikely because these were analyzed sequentially. There was a slight
overlap in time between the two studies, of about 3 months. For the
compilation of obsidian standards data (data are available in a
spreadsheet file), we have eliminated the first obsidian run in each tray
because this is sometimes affected by a comparatively high blank con-
tribution, as reflected in a systematically higher δ17O value than obsid-
ian samples run later in the same tray. Figure S6 shows a histogram of
obsidian standards data collected during 2012 to 2014 compared with
obsidian data collected during 2014 to 2016. Both sets of data show
almost identical distributions, with the exception of a few higher values
obtained during 2012 to 2014. The mean values for δ17O in the two
periods were essentially identical: 15.7 ± 2.6 ppm (2 SEM) (n = 91)
for the period 2012 to 2014 and 15.5 ± 2.4 ppm (2 SEM) (n = 64) for
the period 2014 to 2016. On the basis of these data, it is clear that the
Open University system was analytically very stable throughout the pe-
riod of this study and that it was entirely reasonable to combine the data
for terrestrial olivines (19) with the lunar and terrestrial analyses
collected as part of the present study.

The large sample suite provided by our study allows for a full statis-
tical analysis of possible differences between the oxygen isotopic com-
positions of Earth and the Moon. It is likely that the more limited
number of samples used in previous studies (4, 5) was the main reason
for their seemingly contradictory results. The larger sample set used in
this study allowed us to demonstrate that a lunar-terrestrial δ17O differ-
cence does exist, in contradiction to the findings of Young et al.
(5), but is much less pronounced than claimed by Herwartz et al. (4).
Results of Student t tests for unpaired data with equal variance are given
in table S2. Details of additional statistical analysis undertaken to test the
significance of the difference in mean values between our terrestrial and
lunar samples are given in the Supplementary Materials.

SUPPLEMENTARY MATERIALS
Supplementary material for this article is available at http://advances.sciencemag.org/cgi/ content/full/4/3/eaa5928/DC1
Supplementary Text
fig. S1. Linearized oxygen isotope plot for all terrestrial and lunar samples analyzed in this
study (n = 68), including the terrestrial olivines (19).
fig. S2. Linearized oxygen isotope plot for all filtered lunar samples (n = 24) analyzed in this
study.
fig. S3. Linearized oxygen isotope plot for all filtered terrestrial basalt samples (n = 18)
analyzed in this study.
fig. S4. Diagram showing how addition of various chondritic components would alter
the isotopic and water abundance compositions of the post–giant impact Earth.
fig. S6. Obsidian standards data collected during this study compared to data collected during
the earlier terrestrial olivine study (19).
fig. S7. Kernel estimate densities from samples’ average values.
fig. S8. Kernel estimate densities from raw data (all replicates run for all samples).
table S1. Full listing of oxygen isotope data.
table S2. Results of Student t tests for unpaired data with equal variance.
table S3. Whole rock terrestrial samples.
table S4. Analyses of eclogitic garnet samples.
table S5. Analyses of additional statistical analysis undertaken to test the
difference in mean values between our terrestrial and
lunar samples are given in the Supplementary Materials.

REFERENCES AND NOTES
1. R. M. Canup, E. Asphaug, Origin of the Moon in a giant impact near the end of the Earth’s
2. M. Cuk, S. T. Stewart, Making the Moon from a fast-spinning Earth: A giant impact
4. D. Herwartz, A. Pack, B. Friedrichs, A. Bischoff, Identification of the giant impactor Theia in
isotopic evidence for vigorous mixing during the Moon-forming giant impact. Science
on the origin and differentiation of the Moon. Earth Planet. Sci. Let. 253, 254–265
(2007).
oxygen isotope composition, petrology and geochemistry of mare basalts: Evidence for
(2010).
9. K. Pahelean, D. J. Stevenson, Equilibration in the aftermath of the lunar-forming giant
rocks: Implications for the Moon’s formation and the early history of the Earth. Geochim.
11. J. Zhang, N. Dauphas, A. M. Davis, I. Leya, A. Fedkin, The proto-Earth as a significant
(2014).
A new model for lunar origin: Equilibration with Earth beyond the hot spin stability
limit, paper presented at the 47th Lunar and Planetary Science Conference, 21 to
15. S. J. Lock, S. T. Stewart, S. Mukhopadhyay, Preservation of primordial chemical signatures
in Earth’s mantle by pressure induced freezing after a giant impact, paper presented
at the Lunar and Planetary Science Conference, 20 to 24 March 2017; www.hou.usra.edu/
16. K. Wang, S. B. Jacobsen, Potassium isotopic evidence for a high energy giant impact
17. N. Dauphas, The isotopic nature of the Earth’s accreting material through time. Nature
18. M. F. Miller, Isotopic fractionation and the quantification of δ17O anomalies in the
19. N. A. Starkey, C. R. M. Jackson, R. C. Greenwood, S. Parman, I. A. Franchi, M. Jackson,
J. G. Fitton, F. M. Stuart, M. Kurz, L. M. Larsen, Triple oxygen isotopic composition
The origin of aubrites: Evidence from lithophile trace element abundances and
22. I. E. Kohl, P. H. Warren, E. A. Schauble, E. D. Young, Limitations on >17 as a tracer
of provenance revealed by mineral specific values from lunar and terrestrial anorthosites.
fractionation in lunar and terrestrial samples, paper presented at the AGU Fall Meeting,
New Orleans, 11 to 15 December 2017.
25. N. Dauphas, F. Poitrasson, C. Burkhardt, H. Kobayashi, K. Kurosawa, Planetary and
meteoritic Mg/Si and δ53Si variations inherited from solar nebula chemistry. Earth Planet.
221, 296–299 (2012).

Downloaded from http://advances.sciencemag.org on April 9, 2018
R.C.G. and I.A.F. were responsible for the oxygen isotope analysis.


A. C. Davison, D. V. Hinkley, Bootstrap Methods and Their Applications (Cambridge Univ. Press, 1997).


Acknowledgments: The late Colin Pillinger was passionate about all aspects of lunar science and was significantly involved in this project during its early stages. We dedicate this paper to his memory. We would also like to dedicate this paper to the memory of Robert Clayton who died recently. Robert Clayton provided assistance at an early stage in this study and his pioneering work in the field of oxygen isotope cosmochemistry has been an inspiration to all the authors of this contribution. J. Gibson is thanked for her help with all aspects of sample preparation and oxygen isotope analysis. We acknowledge B. Luz and E. Barkan (Hebrew University of Jerusalem) for their assistance with reference gas calibration. We thank NASA CAPTEM for the allocation of Apollo lunar samples. Funding: Oxygen isotope studies at the Open University were funded by consolidated grants (#ST/001964/1 and #ST/000776/1) from the UK Science and Technology Facilities Council. Author contributions: R.C.G. and I.A.F. were responsible for the oxygen isotope analysis program. R.C.G. and M.F.M. undertook oxygen isotope calibration and data handling. J.-A.B., M.A., N.A.S., and N.D. selected and provided sample materials. R.C.G. prepared the manuscript, figures, and tables and undertook the oxygen isotope canonical model calculations. P.S. undertook statistical analysis of the data. All the coauthors contributed to the intellectual development of the final manuscript. Competing interests: The authors declare that they have no competing interests. Data and materials availability: All data needed to evaluate the conclusions in the paper are present in the paper and/or the Supplementary Materials. Additional data related to this paper may be requested from the authors.

Submitted 6 August 2017
Accepted 14 February 2018
Published 28 March 2018
10.1126/sciadv.aao5928

Oxygen isotopic evidence for accretion of Earth's water before a high-energy Moon-forming giant impact
Richard C. Greenwood, Jean-Alix Barrat, Martin F. Miller, Mahesh Anand, Nicolas Dauphas, Ian A. Franchi, Patrick Sillard and Natalie A. Starkey

DOI: 10.1126/sciadv.aao5928