LUNAR FORMATION

Oxygen isotopic evidence for vigorous mixing during the Moon-forming giant impact

Edward D. Young,1* Issaku Kohl,1* Paul H. Warren,1 David C. Rubie,2 Seth A. Jacobson,2,3 Alessandro Morbidelli3

Earth and the Moon are shown here to have indistinguishable oxygen isotope ratios, with a difference in $\Delta^{17}$O of $\pm 5$ parts per million (2 standard errors). On the basis of these data and our new planet formation simulations that include a realistic model for primordial oxygen isotopic reservoirs, our results favor vigorous mixing during the giant impact and therefore a high-energy, high-angular-momentum impact. The results indicate that the late veneer impactors had an average $\Delta^{17}$O within approximately 1 per mil of the terrestrial value, limiting possible sources for this late addition of mass to the Earth-Moon system.

The Moon is thought to be the consequence of a giant collision between the proto-Earth and a planetary embryo (named Theia, “mother of the Moon”) $\sim 10^8$ years after the birth of the solar system (1, 2). However, the distinct oxygen isotopic signatures of solar system bodies (3, 4) have presented a problem for the impact hypothesis for the formation of the Moon (5, 6). In order to create an iron-poor Moon and simultaneously reproduce the angular momentum of the Earth-Moon system, early models required a glancing blow by a Mars-sized impactor that resulted in the Moon being composed mainly of impactor material (7). Therefore, in the general case the Moon and Earth should not be identical in their oxygen isotopic compositions. Nonetheless, until recently the Moon and Earth have not been identified to be indistinguishable in their oxygen isotope ratios (8–10). Proposed higher-energy giant impacts offer potential solutions to this conundrum (11), although at the expense of the need to shed substantial angular momentum from the system via orbital resonances (12).

Oxygen reservoirs comprising rocky bodies of the solar system are characterized by distinct relative concentrations of oxygen isotopes. These relative concentrations are customarily represented by $\Delta^{17}$O, the departure in $^{17}$O/16O relative to a given $^{18}$O/16O under the assumption that these two isotope ratios covary as a consequence

---

Fig. 1. Oxygen isotope mass balance diagram. (A) Contours of $\Delta^{17}$O$_{\text{Moon}}$ − $\Delta^{17}$O$_{\text{Earth}}$, in parts per million versus fractional differences in Theia content of the bulk silicate Moon and Earth and $\Delta^{17}$O$_{\text{Theia}}$ − $\Delta^{17}$O$_{\text{proto-Earth}}$. The contour interval is 2 ppm. The pink region indicates that the contour intervals are consistent with the $\Delta^{17}$O$_{\text{Moon}}$ − $\Delta^{17}$O$_{\text{Earth}}$ reported by Herwartz et al. (21). The yellow region encompasses the contours consistent with our data ±2 SE. Corresponding values for $\delta$$_{\text{Theia}}$ are shown at right. One set of $\delta$$_{\text{Theia}}$ values applies if the fraction of the present-day bulk silicate Earth composed of Theia is 0.1, whereas the values in parentheses apply where the fraction of Theia in present-day Earth is 0.5. For comparison, the ranges in Theia contents of the Moon and Earth for four simulated Moon-forming impact scenarios are shown as dashed horizontal lines. The models include the “canonical” model requiring no subsequent angular momentum loss by Canup (2008; Canup08), the hit-and-run model of Reufer et al. (2012; RMBW012), and the high angular momentum scenarios, including Cuk & Stewart (2012; C&S012) and Canup (2012; Canup012). (B) The cumulative probability for $\Delta^{17}$O$_{\text{Theia}}$ − $\Delta^{17}$O$_{\text{proto-Earth}}$ in per mil based on simulations in this study. Three cases are shown: those with late accreted mass to Earth <5%, those with late accreted mass <1%, and all simulations.
of mass-dependent isotope fractionation. The small fractional differences in isotope ratios can be replaced with 
\[ \delta^{17}O = 10^3 \ln \left( \frac{R}{R_0} \right) \] values, where \( R \) is \( ^{17}O/^{16}O \), \( R_0 \) is \( ^{18}O/^{16}O \), and \( \delta^{18}O \) refers to the initial isotope ratios (as those characterizing bulk Earth) (14). These \( \delta \) values are nearly equivalent to the fractional differences in per mil (‰) but are linearly related by the mass fractionation exponent \( \beta \). The exact values for \( \beta \) depend on the processes involved in fractionation but are usually near 0.5, as prescribed by oxygen isotope mass (13). With these definitions, \( \Delta^{17}O \) is written as

\[ \Delta^{17}O = \delta^{17}O - \beta \delta^{18}O \]  

A positive \( \Delta^{17}O \) signifies that a reservoir is enriched in \( ^{17}O \) relative to Earth, whereas a negative value signifies that a reservoir is relatively depleted in \( ^{17}O \) compared with expectations from mass fractionation. At the scale of individual mineral grains, solar system materials exhibit variations in \( \Delta^{17}O \) spanning ~200‰ (15). The dispersion in \( \Delta^{17}O \) decreases drastically with mass. Differences in \( \Delta^{17}O \) among meteorite whole-rock samples are ~5 to 8‰ (~4, 16), representing parent asteroids with masses of ~10^10 to 10^17 kg. Differences between differentiated bodies with metal cores and silicate mantles are smaller still: Mars (6.4 x 10^23 kg) has a \( \Delta^{17}O \) value of about +0.3‰, whereas Vesta (2.6 x 10^20 kg) has a value of ~0.25‰ (17, 18). The reduced dispersion in \( \Delta^{17}O \) with mass evidently reflects averaging as smaller rocky bodies coalesced to form larger bodies in the solar system (19, 20). Historically, the identical \( \Delta^{17}O \) values for Earth and the Moon have stood out against this backdrop of variability in the solar system.

However, some high-precision measurements on lunar samples indicated that the Moon has a greater \( \Delta^{17}O \) than that of Earth by 12 ± 3 parts per million (ppm) (21). The importance of this finding can be gauged by considering contours for \( \Delta^{17}O_{\text{Moon}} - \Delta^{17}O_{\text{Earth}} \). Plotted as functions of the difference in \( \Delta^{17}O \) between Theia and the proto-Earth and the difference in the fractions of the Moon and Earth inherited from Theia (Fig. 1A). The mass-balance equation plotted is

\[ x_{\text{Moon}} - x_{\text{Earth}} = \frac{\Delta^{17}O_{\text{Moon}} - \Delta^{17}O_{\text{Earth}}}{\Delta^{17}O_{\text{Theia}} - \Delta^{17}O_{\text{Proto-Earth}}} \]  

where \( x_{\text{Moon}} \) and \( x_{\text{Earth}} \) refer to the oxygen fraction of body \( i \) derived from Theia (essentially, mass fraction of the bulk silicate portions of the bodies). For convenience, we also use the fractional difference \( \delta_{\text{Theia}} \) rather than the absolute difference in Eq. 2:

\[ \delta_{\text{Theia}} = (x_{\text{Moon}} - x_{\text{Earth}})/x_{\text{Earth}} \]  

The implications of a difference in oxygen isotopic composition between the Moon and Earth depend on the fraction of Theia contained within Earth (Eqs. 2 and 3). Four recent proposed giant impact scenarios (5, 11, 12, 22) predict disparate differences in the Theia fractions in the Moon and Earth (Fig. 1A). If the difference in \( \Delta^{17}O \) between Theia and the proto-Earth was zero, there is no oxygen isotope constraint on \( \delta_{\text{Theia}} \) (Fig. 1A). Similarly, if Earth and the Moon are composed of precisely the same concentrations of Theia, there is no constraint on differences in \( \Delta^{17}O \) between Theia and the proto-Earth.

A positive \( \Delta^{17}O \) of 12 ± 3 ppm for the Moon (21) requires a difference in the proportions of Moon and Earth composed of remnants of Theia because the contours representing this range of values (Fig. 1A, pink regions) do not include the center of the diagram (Fig. 1A). For a Mars-sized differentiated body with \( \Delta^{17}O \sim 0.3% \) (such as Mars or Vesta), the difference in Theia contents between the Moon and Earth is ± 50% or more (Fig. 1A). For the case of a proto-Earth-sized Theia, the result is a difference of ± 8% or more (Fig. 1A). Alternatively, assuming enstatite-chondrite-like material better represents the terrestrial planet-forming region (23, 24), differences in oxygen isotope ratios between Theia and proto-Earth would have been smaller (~0.1%) (21, 25), and the lunar \( \Delta^{17}O \) of 12 ± 3 ppm (21) requires \( \delta_{\text{Theia}} \) values of 150 and 30% for the Mars and proto-Earth-sized impactors, respectively (Fig. 1A). Such large \( \delta_{\text{Theia}} \) values would effectively remove the constraint imposed by oxygen isotopes that the Earth-Moon system was well mixed.

We analyzed seven Apollo 12, 15, and 17 lunar samples and one lunar meteorite and compared their \( ^{17}O/^{16}O \) and \( ^{18}O/^{16}O \) isotope ratios with those for a suite of terrestrial igneous samples. The 1- to 4-mg lunar samples include high-Ti mare basalts, low-Ti Mg-rich olivine cumulate basalts, a quartz normative basalt, and a highland

<table>
<thead>
<tr>
<th>Sample</th>
<th>( \delta^{17}O )</th>
<th>( \delta^{18}O )</th>
<th>( \Delta^{17}O )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lunar basalt</td>
<td>Average (n = 8)</td>
<td>3.004</td>
<td>5.691</td>
</tr>
<tr>
<td></td>
<td>Standard deviation</td>
<td>0.090</td>
<td>0.172</td>
</tr>
<tr>
<td></td>
<td>Standard error</td>
<td>0.032</td>
<td>0.061</td>
</tr>
<tr>
<td>Lunar basalt-fused beads</td>
<td>Average (n = 4)</td>
<td>2.940</td>
<td>5.572</td>
</tr>
<tr>
<td></td>
<td>Standard deviation</td>
<td>0.133</td>
<td>0.245</td>
</tr>
<tr>
<td></td>
<td>Standard error</td>
<td>0.067</td>
<td>0.123</td>
</tr>
<tr>
<td>Lunar troctolite</td>
<td>Average (n = 2)</td>
<td>3.178</td>
<td>6.050</td>
</tr>
<tr>
<td></td>
<td>Standard deviation</td>
<td>0.009</td>
<td>0.026</td>
</tr>
<tr>
<td></td>
<td>Standard error</td>
<td>0.007</td>
<td>0.019</td>
</tr>
<tr>
<td>San Carlos olivine</td>
<td>Average (n = 17)</td>
<td>2.711</td>
<td>5.134</td>
</tr>
<tr>
<td></td>
<td>Standard deviation</td>
<td>0.072</td>
<td>0.134</td>
</tr>
<tr>
<td></td>
<td>Standard error</td>
<td>0.017</td>
<td>0.033</td>
</tr>
<tr>
<td>Mauna Loa olivine</td>
<td>Average (n = 4)</td>
<td>2.736</td>
<td>5.189</td>
</tr>
<tr>
<td></td>
<td>Standard deviation</td>
<td>0.090</td>
<td>0.170</td>
</tr>
<tr>
<td></td>
<td>Standard error</td>
<td>0.045</td>
<td>0.085</td>
</tr>
<tr>
<td>Mauna Loa whole-rock samples</td>
<td>Average (n = 5)</td>
<td>2.796</td>
<td>5.298</td>
</tr>
<tr>
<td></td>
<td>Standard deviation</td>
<td>0.031</td>
<td>0.063</td>
</tr>
<tr>
<td></td>
<td>Standard error</td>
<td>0.014</td>
<td>0.028</td>
</tr>
<tr>
<td>San Carlos spinel</td>
<td>Average (n = 2)</td>
<td>2.171</td>
<td>4.104</td>
</tr>
<tr>
<td></td>
<td>Standard deviation</td>
<td>0.135</td>
<td>0.285</td>
</tr>
<tr>
<td></td>
<td>Standard error</td>
<td>0.096</td>
<td>0.202</td>
</tr>
<tr>
<td>Bushveld anorthosite</td>
<td>Average (n = 2)</td>
<td>3.522</td>
<td>6.694</td>
</tr>
<tr>
<td></td>
<td>Standard deviation</td>
<td>0.002</td>
<td>0.002</td>
</tr>
<tr>
<td></td>
<td>Standard error</td>
<td>0.001</td>
<td>0.002</td>
</tr>
<tr>
<td>Gore Mountain garnet</td>
<td>Average (n = 2)</td>
<td>3.174</td>
<td>6.020</td>
</tr>
<tr>
<td></td>
<td>Standard deviation</td>
<td>0.017</td>
<td>0.026</td>
</tr>
<tr>
<td></td>
<td>Standard error</td>
<td>0.012</td>
<td>0.019</td>
</tr>
</tbody>
</table>
anorthositic troctolite (table S1). The terrestrial samples include San Carlos mantle xenolith olivines, San Carlos mantle xenolith spinels, Mauna Loa basalt samples, Mauna Loa olivine separates, an anorthosite from the Bushveld complex, and a sample of Gore Mountain metamorphic garnet. We obtained our analyses (Table 1) using infrared laser heating (26) modified to include F₂ as the fluorinating agent and purification of the analyte O₂ gas for analysis of both ¹⁷O/¹⁶O and ¹⁸O/¹⁶O (27). We have improved our precision compared with many previous efforts by more thoroughly desiccating samples before analysis and by regular rebalancing of standard and sample ion beam intensities throughout the mass spectrometer analyses (28). We analyzed a range of lunar and terrestrial sample lithologies to account for the fact that β values vary with process (13, 26, 30). We use the traditional standard mean ocean water (SMOW) as the reference for δ¹⁸O, but we use San Carlos (SC) olivine as the reference for Δ¹⁷O when characterizing oxygen isotope reservoirs of rocks (28). We adopt a typical igneous β of 0.528 passing through the mean value for San Carlos olivine as our reference fractionation line for calculating Δ¹⁷O (28).

Lunar basalts are relatively high in δ¹⁸O as compared with SC olivine and terrestrial basalts (Fig. 2). Nonetheless, the basalts show no clear deviation from the reference β of 0.528, allowing direct comparison of Δ¹⁷O values for these materials. No discernible difference exists in Δ¹⁷O between SC olivine and lunar basalt powders (−0.001 ± 0.002, 1 SE) or fused beads (0.000 ± 0.003, 1 SE). The mean for all mafic terrestrial samples, representing terrestrial mantle and its melt products, is 0.000 ± 0.001‰ (1 SE). Adding in quadrature, the analytical uncertainty in the SC olivine and the standard error for the lunar samples yields a difference between lunar basalt and SC olivine of −0.001 ± 0.0048‰ (−1 ± 4.8 ppm, 2 SE), which is indistinguishable from zero. Other mafic terrestrial whole rocks and olivines are within this uncertainty range (Table 1). We found no resolvable difference in Δ¹⁷O between lunar mantle melts represented by these basalts and terrestrial mantle and melts.

Our result does not agree with the conclusions of Herwartz et al. (21). Measurements on the one sample common to both studies (12018) agree within uncertainties when compared in the same reference frame (Fig. S2) (28). It is therefore conceivable that an unfortunate difference in sample selection could be a plausible explanation for the difference between the studies.

The lunar highland sample has a significantly lower Δ¹⁷O value of −0.016 ± 0.003‰ (1 SE) (or −16 ± 3 ppm), which is similar to a previous study (8). However, the terrestrial anorthosite sample has a similarly low value (Table 1). The low Δ¹⁷O values for both the terrestrial and lunar highland anorthositic anorthosites (anorthostic troctolite) imply a mass fractionation process related to formation of this rock type that results in low Δ¹⁷O values (Fig. 2). The low Δ¹⁷O value for the lunar highland rocks is not evidence for a distinction between the oxygen pools for the Moon and Earth because these samples are in the mass-fractionation envelope for Earth (Fig. 2), and low Δ¹⁷O values are found...
are consistent with Earth and the Moon having near-identical Thiea contents. Indistinguishable $^{17}$O values of the Moon and Earth at the $5$ ppm level of uncertainty suggests that the Moon-forming impact thorough mixed and homogenized the oxygen isotopes of Thiea and proto-Earth.

Our interpretation has implications for the composition of the LV of primitive bodies that impacted the silicate Earth. A disproportionately larger flux of LV planetaryesimals is implied by a higher average $^{18}$O/$^{16}$O for the Moon than for Earth and by previous estimates for the apparent differences in highly siderophile element (HSE) concentrations between the terrestrial and lunar mantles (37). The interpretation of these data is that the Moon and Earth began with the same W isotopic ratios, but that Earth inherited a greater fraction of low $^{18}$O/$^{16}$O material in the form of chondritic planetaryesimals after the Moon-forming giant impact (38, 39). If we adopt the conclusion from the W isotopes that the Earth-Moon system was well mixed as a result of the Moon-forming impact, then the nearly identical $^{17}$O values of Moon and Earth constrain the identity of the LV impactors by their oxygen isotope ratios. Estimates for the Earth/Moon ratio of the mass fluxes range from ~200 to 1200 (37, 40, 41). Using a late veneer flux to Earth of $2 \times 10^{25}$ kg (37) and a conservative maximum Earth/Moon flux ratio of 1200 (41), the difference in LV fractions comprising the silicate Earth and Moon is $0.000447$. Combining this value with our measured value for $^{17}$O/Moon = $^{17}$O/Earth, of zero (28) requires that the LV impactors had average $^{17}$O values within ~0.2‰ or less of Earth, similar to enstatite chondrites (25). Alternatively, with our maximum permitted $^{17}$O/Moon = $^{17}$O/Earth of ~5 ± ppm, the calculated $^{17}$O value for the LV is ±1.1‰. This value encompasses aqueously altered carbonaceous chondrites and some ordinary chondrites. For comparison, the same calculation using the 12 ppm difference between the Moon and Earth yields an LV $^{17}$O of ~2.7‰, suggesting that the impactors were composed mainly of relatively unaltered and dry carbonaceous chondrites (4). Our result suggests that if the LV was composed mainly of carbonaceous chondrites, the parent bodies must have included substantial fractions of high-$^{17}$O water either in the form of aqueous alteration minerals or as water ice.

REFERENCES AND NOTES

28. Materials and methods are available as supplementary materials on Science Online.

ACKNOWLEDGMENTS

We are grateful to NASA Johnson Space Center for approving use of the Apollo samples for this study. E.D.Y. acknowledges support from a grant from the NASA Emerging Worlds program (NNXISAH43G). D.C.R., S.A.J., and A.M. acknowledge support from the European Research Council Advanced Grant “ACCRETE” (contract 339868). Development of the Panorama instrument was supported by the Deep Carbon Observatory (Sloan Foundation), NSF, U.S. Department of Energy, Shell, the Carnegie Institution of Washington, and the University of California, Los Angeles. The complete data table for this study can be found in the supplementary materials.

SUPPLEMENTARY MATERIALS

www.sciencemag.org/content/351/6272/496/suppl/DC1

Materials and Methods

SupplementaryText

Figs. 51 to 57

Tables S1 to S4

References (42–67)

18 July 2015; accepted 13 December 2015

10.1126/science.aad5025