Isotopic composition of the moon and the lunar isotopic crisis

The isotopic compositions of the Earth and the Moon are nearly identical for a variety of elements, while other solar system bodies show considerable variations. The isotopic similarity of the Earth and Moon places, together with the depletion in volatile elements, the density deficit, and the large size of the Moon relative to the Earth, strong observable constraints on lunar formation models. Currently, the paradigm of lunar formation, the Giant Impact model, is going through an "isotopic crisis" because it can only be reconciled with the isotope data when some ad hoc assumptions are made.

Origin of Isotopic Variations

Variations in isotopic composition can be of mass-dependent or mass-independent origin. The two types of isotopic variations are fundamentally different and are used to address different questions. Mass-dependent changes in isotope compositions are due to equilibrium or kinetic reactions that follow mass-dependent laws and can provide evidence for various nebular and planetary processes (e.g., condensation, evaporation, core formation, magmatic differentiation, alteration). Mass-independent isotope variations are of radiogenic (used for chronometry), nucleogenic and cosmogenic (used to determine exposure ages, erosion rates, impact gardening), or nucleosynthetic (used to study nucleosynthetic processes in stars and as marker for establishing genetic relationships between planetary bodies) origin and are also referred to as isotopic anomalies. In determining the degree of genetic relatedness of the Earth, Moon, and potential Moon-forming impactor, the isotope anomalies are of particular interest, because they are not affected by mass-dependent secondary processes and may provide direct constraints of the fraction the Moon derived from the proto-Earth and the impactor.

Mass-Independent Isotope Composition of the Moon

Oxygen: Oxygen has three stable isotopes (¹⁶O, ¹⁷O, and ¹⁸O) and was the first element for which isotope anomalies were observed on a bulk planetary scale. Initially interpreted as reflecting nucleosynthetic heterogeneities in the solar nebula, the anomalies are now thought to have formed by nebular photochemical reactions (Clayton 2003). In any case, the markedly different O isotopic compositions among most planetary bodies are inherited from a heterogeneous pre-accretionary solar nebula, which makes oxygen a prime tracer of planetary genetics. The total Δ^{17} O variation found in meteorites is about 7 ‰ (the deviation of the ¹⁷O/¹⁶O ratio of a sample from the terrestrial mass-fractionation line in per mil), while rocks from the Moon and the Earth have been found indistinguishable at the 0.02 ‰ level. A recent high-precision study on three lunar samples found a resolvable difference in Δ^{17} O of 0.012 ± 0.006 ‰, which is interpreted as the first isotopic evidence for a Moon-forming impactor or the modification of the Earth's mantle composition by a chondritic late veneer (Herwartz et al. 2014).

Titanium: Planetary-scale Ti isotope anomalies are of nucleosynthetic origin and record the incomplete mixing of presolar materials in the solar nebula. Among meteorite parent bodies, the anomalies span a range of ~6 ε^{50} Ti (parts per 10,000 deviation of the 50 Ti/ 47 Ti from the terrestrial standard after mass bias correction by internal standardization), and no Ti isotope anomalies are found between the Earth and the Moon at the ± 0.04 ε level. This was interpreted as evidence for the Moon being mainly made out of proto-Earth material (Zhang et al. 2012).

Chromium: Nucleosynthetic isotope anomalies in chromium are roughly correlated with the ones in titanium and span a range of ~2.4 ϵ^{54} Cr (parts per 10,000 deviation of the 54 Cr/ 52 Cr from the terrestrial standard after mass bias correction by internal standardization) in meteorites, while the Earth and Moon are indistinguishable at the ~0.1 ϵ level (Qin et al. 2010). Tungsten

: No significant nucleosynthetic W anomalies have been found on a planetary-scale level, but W shows radiogenic variations in ¹⁸²W, due to the decay of short-lived ¹⁸²Hf ($T_{1/2}$ = 8.9 Ma). Chondritic meteorites, and by inference bulk planets, have an about uniform Hf/W ratio and bulk W isotopic composition. Planetary mantles, however, evolve with a

super-chondritic Hf/W because Hf is a lithophile (stays in the mantle) and W is moderately siderophile (partitions into the core). The mantles thus develop positive ¹⁸²W anomalies relative to chondrites, while planetary cores have a Hf/W of ~0 and negative ¹⁸²W anomalies relative to chondrites. The size of the W anomaly in a planetary reservoir depends on the timing and the conditions of metal-silicate separation and, especially for larger bodies, on the details of the accretion history, like the number and sizes of accreting bodies and the degree of equilibration of their metallic cores with the target mantle. Given the number of variables and the stochastic nature of planet formation, it is considered unlikely that any two differentiated bodies in the inner solar system ended up with the same ¹⁸²W anomaly in their mantles. The range of mantle anomalies observed in solar system bodies is in the order of 25 ϵ^{182} W (parts per 10,000 deviation of the ¹⁸²W/¹⁸³ W from the terrestrial standard after mass bias correction by internal standardization). However, the W isotope compositions of the lunar and terrestrial mantles are identical within ~0.2 ϵ^{182} W. Most recent high-precision W isotope measurements indicate an anomaly of ~ +0.2 ϵ in the lunar mantle that could be tracing the impactor or the late veneer of chondritic material onto the Earth (Kleine et al. 2014). Furthermore, the Hf/W ratios of the lunar and the terrestrial mantles are identical within uncertainty (27.8 ± 3.3 and 27.4 ± 4.2, respectively; Dauphas et al. 2014), adding yet another similarity that needs to be explained by formation models of the Moon (Table 1, Fig. 1).

Table 1

Isotopic anomalies of planetary bodies relative to the Earth's mantle composition

	Δ ¹⁷ Ο	ε ⁵⁰ Τi	ε ⁵⁴ Cr	ε ¹⁸² W
Moon	0.012 ± 0.006	-0.03 ± 0.04	0.05 ± 0.08	0.2 ± 0.1
Mars	0.3 ± 0.07	-0.77 ± 0.1	-0.17 ± 0.03	0.6 ± 0.2
Other bodies	-4.3 to 2.53	-1.3 to 4.2	-0.75 to 1.75	−2 to 25
Origin of anomaly	Photochemistry, nucleosynthetic	Nucleosynthetic	Nucleosynthetic	Radiogenic

Data sources: O (Clayton 2003; Herwartz et al. 2014), Ti (Zhang et al. 2012; Trinquier et al. 2009), Cr (Qin et al. 2010), W (Kleine et al. 2009; 2014)





Mass-independent isotope compositions of the Moon and Mars relative to the terrestrial mantle (≡0) and range observed in other planetary bodies

Relevance of Mass-Independent Isotope Variations for the Origin of the Moon

The Giant Impact hypothesis is the current paradigm for the formation of the Moon. It states that the Moon formed from the impact debris of a catastrophic collision between the proto-Earth and an about Mars-sized planetary embryo and naturally explains many of the observable constraints of the Earth-Moon system like angular momentum, lunar density deficit, large size of the Moon relative to its host, as well as the Moon's volatile depleted nature and relatively young age. Furthermore, accretion modeling indicates that collisions of protoplanets with planetary embryos are common and represent the final stage of planetary growth. However, these accretion models also imply that the planetary embryos forming the terrestrial planets are sourced from a relatively large feeding zone of the disk. Given these models and the large spread observed in the mass-independent isotope compositions among planetary bodies, it is generally assumed that the impactor and the proto-Earth had a different isotopic makeup. Numerical simulations of the canonical Giant Impact scenario imply that the majority of the Moon is derived from the mantle of the impactor, with the remaining fractions coming from the proto-Earth mantle and the impactor core. The putative isotopic anomalies of the impactor should thus be preserved in the Moon. For example, assuming that the impactor was not only Mars sized but would actually have been Mars, then the Moon should have clearly resolvable isotopic anomalies compared to the Earth (about 2/3 the size of the ones of Mars). However, no anomalies (beyond what could be accounted for by late veneer additions to the Earth and Moon) are observed in the Moon. To overcome this "lunar isotopic crisis," several possibilities are discussed, all of which require some ad hoc assumptions, however:

- 1. The lunar accretion disk forming after the Giant Impact equilibrated isotopically with the molten terrestrial mantle. Quantitative assessment of such a scenario is difficult. Gas-mediated equilibrium in the accretion disk may be possible for volatile elements (Pahlevan and Stevenson 2007), but the short lifetime of the disk renders complete mixing and equilibrium for refractory elements like Ti unlikely (Zhang et al. 2012). Isotopic equilibration is the only Giant Impact scenario that can explain the similarity in W isotopes between the modern lunar and terrestrial mantles, if one does not assume it to be a coincidence.
- 2. The Moon is mainly derived from the proto-Earth and the canonical Giant Impact is incorrect. Impact scenarios where the majority of the Moon is derived from the proto-Earth are possible (Ćuk and Stewart 2012), but they require very special parameters and violate angular momentum constraints. Also, even if 90 % of the Moon would derive from the proto-Earth, a Mars-like impactor would still lead to detectable anomalies in the Moon. In this scenario, as in any impact scenario without complete isotopic equilibration, the similarity in W isotopes between the modern lunar and terrestrial mantles would be a coincidence.
- 3. The Earth and the impactor had very similar isotope compositions after all, indicating that both bodies accreted from an inner disk uniform reservoir (IDUR) at about the same heliocentric distance. Such a scenario would allow for any type of impact to create the Moon, but suggests that our current planetary accretion models may be inaccurate.

It seems clear that whichever scenario applies, the Giant Impact hypothesis is best reconciled with the isotope data when the impactor had a similar isotope composition as the proto-Earth. Based on this observation, a carbonaceous chondrite-like impactor from the outer solar system can be excluded. Instead, most likely, the Moon-forming impactor was a large body that formed in close proximity to the proto-Earth, and thus, naturally the two bodies had very similar isotope compositions. The similarity in W isotope composition and Hf/W ratios of the terrestrial and lunar mantles remains puzzling, as these values are set during metal-silicate equilibration and core formation, which happened under different conditions in the two bodies.

Mass-Dependent Isotope Composition of the Moon

Mass-dependent isotope variations are generally reported in delta notation, which is the parts per 1,000 deviation of an isotope ratio in a sample relative to that of a standard $\delta A/B = [(A/B)_{sample}/(A/B)_{standard} - 1] \times 10^3$. By convention, A always refers to the heavier and B to the lighter isotope, so that a positive $\delta A/B$ indicates an isotopic composition of the sample that is heavier than the standard and a negative $\delta A/B$ an isotope composition that is lighter than the standard. The A/B used to obtain $\delta A/B$ for the elements discussed below are 7 Li/ 6 Li, $^{18}O/^{16}O$, 26 Mg/ 24 Mg, 30Si/ 28 Si, $^{34}S/^{32}S$, $^{37}Cl/^{35}$

CI, ⁴¹K/³⁹K, ⁵⁶Fe/⁵⁴Fe, ⁶⁶Zn/⁶⁴Zn, and ⁹⁸Mo/⁹⁵Mo. The mass-dependent isotope compositions in lunar basalts and soils are compared to the composition of chondrites and the Earth's mantle for each element, and potential fractionation mechanisms are discussed (Table 2).

	Lunar basalts	Lunar soil	Chondrites	Earth mantle	Uncertainty
δ ^{7/6} Li	4.9 ± 2.2	6.6 ± 3.1	3.1 ± 1.3	3.5 ± 0.5	2SD
δ ^{18/16} Ο	5.6 ± 0.3	5.6 ± 0.3	-4 to 17	5.5 ± 1	2SD
δ ^{26/24} Mg	-0.33 ± 0.29	-0.24 ± 0.13	-0.28 ± 0.06	-0.27 ± 0.07	2SD
δ ^{30/28} Si	-0.29 ± 0.03	-	-0.7 to -0.45	-0.30 ± 0.03	95 % C.I.
δ ^{34/32} S	0.57 ± 0.09	6.1 to 13.5	0.0 ± 0.2	-1.28 ± 0.33	95 % C.I.
δ ^{37/35} Cl	0 to 4.7	6 to 16	-0.3 ± 0.6	-0.2 ± 0.6	2SD
δ ^{41/39} K	0.5 ± 0.2	5 to 13	0.20 ± 0.14	0.28 ± 0.21	95 % C.I.
δ ^{56/54} Fe	0.05 to 0.22	-	0.005 ± 0.008	0.025 ± 0.025	95 % C.I.
δ ^{66/64} Zn	-5.4 to 1.9	2.6-5.6	0 ± 0.5	0.28 ± 0.05	95 % C.I.
δ ^{98/95} Mo	-0.05 ± 0.03	-	-0.16 ± 0.02	-0.1 ± 0.1	95 % C.I.

Table 2
Mass-dependent isotope compositions of chondrites, the Earth mantle, lunar basalts, and lunar soil/regolith

Only bulk rock measurements have been used in the data compilation. Data sources: Li (Pogge von Strandmann et al. 2011), O (Clayton 2003), Mg (Teng et al. 2010; Sedaghatpour et al. 2013), Si (Armytage et al. 2012; Dauphas et al. 2014), S (Day and Moynier 2014 and ref. therein), Cl (Sharp et al. 2013, K (Humayun and Clayton 1995), Fe (Craddock et al. 2013 and ref. therein), Zn (Day and Moynier 2014 and ref. therein), Mo (Burkhardt et al. 2014)

Lithium

: Little variation is found in the isotopic composition of the lithophile element Li between chondrites, the Earth and the Moon, implying insignificant fractionation during lunar formation and subsequent magmatic processes. Lunar soils and regolith samples and, to a lesser degree, lunar basalts show some variation and tend toward heavier $\delta^{7/6}$ Li than chondrites, terrestrial basalts, and peridotites. The heavier isotope composition of the lunar soil and regolith samples are explained by ion sputtering on the lunar surface by solar wind and galactic cosmic rays, assisted by regolith gardening due to micrometeorite bombardment, leading to the preferential loss of the lighter isotope (⁶Li) from the system. As all lunar basalt samples are collected from the surface regolith, some of the higher $\delta^{7/6}$ Li in these samples may also be caused by ion sputtering or by contamination from the regolith.



Oxygen

: While chondrites display a wide variation in $\delta^{18/16}$ O, the compositions of the terrestrial mantle, lunar basalts, and the lunar regolith are homogenous at ~5.5 ‰, showing no sign of fractionation by either the Moon-forming process or lunar magmatic differentiation. Ion sputtering is also affecting oxygen in lunar soils; however, as a major constituent of the crustal minerals (and in nonvolatile covalent bonding environments), the effect is not resolvable in bulk rock measurements.



Magnesium

: Like for Li and O, the Mg isotopic compositions of chondrites, the terrestrial mantle, and lunar samples are similar. Within lunar basalts, the high-Ti suite has on average a lower $\delta^{26/24}$ Mg than the high-Ti suite, which is explained by Mg isotope source heterogeneity produced during fractional crystallization of the lunar magma ocean, with ilmenite having a lighter Mg isotopic composition than olivine and pyroxene. The weighted average Mg isotopic composition of the Moon ($\delta^{26/24}$ Mg = -0.26 ± 0.16 ‰) is indistinguishable from the Earth ($\delta^{26/24}$ Mg = -0.27 ± 0.07 ‰) and chondrites ($\delta^{26/24}$ Mg = -0.28 ± 0.06 ‰), suggesting a homogeneous distribution of Mg isotopes in the solar system and no Mg isotope fractionation during the formation of the Moon.



Silicon: The Si isotope compositions of the terrestrial and lunar mantles are identical and significantly heavier than the ones of chondrites. The difference in Si isotope composition between the Earth's mantle and chondrites is interpreted as reflecting equilibrium isotope fractionation between metal and silicate during core formation and, thus, evidence of Si partitioning into the Earth's core. The presence of Si in the Earth's core could also account for the core's density deficit relative to pure FeNi metal and the super-chondritic Mg/Si ratio of the Earth's mantle. Under the redox conditions of terrestrial core formation, Si only partitions into metal under high pressures. Core formation in planetary embryos like Mars or in asteroids like Vesta is therefore not expected to result in a significant Si core partitioning, consistent with the chondritic Si isotope composition measured in meteorites from these bodies. Given these observations, the heavy Si isotope composition of the lunar mantle is unexpected in the framework of the Giant Impact, which suggests that the Moon is made mainly out of impactor mantle material (with chondritic Si isotopic composition). The Si isotopes in the lunar mantle are thus interpreted as reflecting isotopic equilibration of the lunar disk with the terrestrial mantle after core formation or that the Moon is made mainly out of proto-Earth material (Armytage et al. 2012).

Alternatively, it was suggested that the difference in $\delta^{30/28}$ Si between the Earth and chondrites (and among chondrites) is of nebular origin. Indeed, in $\delta^{30/28}$ Si vs. Mg/Si space, the bulk silicate Earth plots on a nebular fractionation trend defined by chondrites, and this trend is indistinguishable from the core partitioning trend (Dauphas et al. 2014). It is thus conceivable that the high Mg/Si and heavy $\delta^{30/28}$ Si of the Earth's mantle are inherited from the more refractory precursor material from which the Earth accreted and that is not represented by any known type of chondritic meteorite. If the Moon-forming impactor accreted from the same materials, the similarity of the Earth and Moon in $\delta^{30/28}$ Si is explained in any Giant Impact scenario, and no isotopic equilibration is required.



Sulfur

: Sulfur is a volatile and chalcophile element. The $\delta^{34/32}$ S of the terrestrial mantle is slightly lighter than that of chondrites, possibly due to S isotope fractionation during terrestrial core formation (Labidi et al. 2013). Lunar basalts have within error indistinguishable $\delta^{34/32}$ S compared to chondrites, while lunar soils and regolith samples are significantly heavier because of ion sputtering and preferential loss of light S isotopes. The heavy $\delta^{34/32}$ S values of the lunar basalts relative to the terrestrial mantle are in agreement with forming the Moon mainly out of the mantle of a Mars-like impactor with chondritic S isotope composition.



Chlorine

: The volatile element CI is isotopically uniform in chondrites and the terrestrial mantle suggesting insignificant fractionation in the solar nebula and during planetary accretion. Lunar basalts show a range of $\delta^{37/35}$ CI from chondritic to slightly heavier values, while lunar soil and regolith samples are significantly heavier. The latter is attributed to ion sputtering and impact gardening on the lunar surface, the former to the volatilization of CI as metal halites and loss of CI during magmatic degassing (Sharp et al. 2013 and ref. therein).



Potassium

: Despite very different bulk K concentrations, the isotopic composition of the moderately volatile element K is homogeneous among chondrites, Earth and lunar basalts, suggesting no resolvable K isotope fractionation effects during planetary-scale volatile element depletion processes. Lunar soil and regolith samples are isotopically heavy due to ion sputtering on the lunar surface.



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Iron

: The iron isotope composition of lunar basalts is heavy compared to chondrites and the terrestrial mantle. Initially, this difference has been attributed to the loss of light Fe during the Giant Impact. However, as for Mg isotopes, the low-Ti and high-Ti basalts have distinct $\delta^{56/54}$ Fe (0.073 ± 0.018 ‰ and 0.191 ± 0.020 ‰, respectively), suggesting Fe isotope source heterogeneity produced during fractional crystallization of the lunar magma ocean, as well as isotope fractionation during partial melting. The $\delta^{56/54}$ Fe observed in lunar basalts may thus not represent the lunar mantle. Thus, at the moment it is unclear if the $\delta^{56/54}$ Fe of the lunar and terrestrial mantles are different or not.



Zinc

: The volatile element Zn shows only small isotopic variations in terrestrial magmatic rocks and chondrites, but a considerable range of about 8 ‰ in $\delta^{66/64}$ Zn in lunar basalts (as well as in meteorites from the differentiated asteroid Vesta). It was suggested that the $\delta^{66/64}$ Zn of the lunar mantle is best estimated by the heavy basalts and that this is evidence for the volatile loss during the Giant Impact. However, given the data, it cannot be stated with confidence whether the lunar mantle Zn isotope composition is different from the Earth, especially since the variations in $\delta^{66/64}$ Zn in lunar (and Vesta) basalts are readily explained by variable enrichments and depletions in condensed vapor phases (e.g., ZnCl), as was suggested to explain the lunar Cl isotope data.



Molybdenum

: Molybdenum is a refractory and moderately siderophile element that shows little mass-dependent isotope variations among chondrites but can be significantly fractionated between metal and silicate liquids during core formation at temperatures below 3,000 °C. The $\delta^{98/95}$ Mo of the terrestrial mantle is not well defined but likely similar to the chondritic value, given the high temperatures associated with terrestrial core formation. The Mo isotope composition of lunar basalts is resolvably lighter than that of chondrites, which could reflect core formation in the Moon at about 1,800 °C or an inherited signature of the core formation in the impactor.



Relevance of Mass-Dependent Isotope Variations for the Origin of the Moon

Geologically speaking, the Moon is a fairly simple system compared to the Earth. It does not have plate tectonics or an atmosphere, and once the lunar rocks have been formed by magmatic processes, they were not obstructed by recycling into the mantle, metamorphism, or biotic processes. Mass-dependent isotope fractionations in the Moon thus only record a limited number of processes like evaporation/condensation in the aftermath of the putative giant impact, core formation, magma ocean crystallization, partial melting, magmatic differentiation, or loss of volatile elements by degassing. Nevertheless, using isotope fractionation to pinpoint specific processes remains challenging and often depends on model assumptions, because more than one process might lead to the observed isotope fractionation and in many cases it is unclear what the starting (and bulk) compositions of the Earth, Moon, and impactor reservoirs were (e.g., lunar basalts are not always representing the isotope composition of the lunar mantle).

From the above compilation, it is evident that mass-dependent isotope variations between lunar and terrestrial rocks provide valuable constraints on lunar evolution and its relation to the Earth, but up to now they do not represent a "smoking gun" for a specific Moon-formation scenario. In most cases the isotope composition of the lunar basalts is indistinguishable from the terrestrial mantle and chondrites (Li, O, Mg, Cl, K, Zn), and where it is not, the variations can be ascribed to core formation on the Earth (Si, S) and on the Moon (Mo), volatilization at the lunar surface (Cl, Zn), and magmatic source heterogeneity and partial melting (Fe), so that there is currently no compelling evidence for any significant Giant Impact-induced mass-dependent isotope fractionation. This does not mean that there was no Giant Impact, but rather that this putative event must have involved high temperatures and caused only little evaporative loss into open space.

Future Directions

Nearly half a century after the Apollo landings, first-order questions about lunar formation, composition, nature of volatile depletion, and relation to the Earth are still not satisfactorily answered. Isotopes provide key constraints on these

questions and show that the Earth and the Moon are closely related. It remains to be seen if the relatedness amounts to a "fission" of the Moon from the Earth, or is due to isotopic equilibration in the magma disk after the Giant Impact, or is the sign of an isotopically uniform inner disk reservoir from which both the proto-Earth and the impactor formed.

So far, only a handful of elements have been analyzed at high precision. Expanding the analysis of mass-independent isotope variations to planetary samples not yet analyzed (in particular ungrouped meteorites and ideally samples from Venus or Mercury) and to other elements (e.g., ultra-refractory elements like Ca and the REEs) could provide important clues on the isotopic homogeneity in the inner solar system and the feasibility of a postimpact isotope equilibration scenario. Likewise, extending the mass-dependent isotope work to other differentiated planetary bodies and other elements will aid to our understanding of the processes that led to the presence or absence of isotope variations in the Earth-Moon system. Of particular interest in this respect is the question whether the indistinguishable Si isotope signature of the Earth and the Moon is due to terrestrial core formation (which would imply the Moon to be mainly out of proto-Earth material or isotopic equilibration of the mantle and the Moon-forming disk), or if it is a nebular feature of the inner solar system (which would indicate that the proto-Earth and the impactor formed from similar materials and thus places no restrictions on the impact process). There remains enough to do for a new generation of lunar scientists.

Cross-References

- Lunar Geochemistry
- Giant Impact Hypothesis
- Interior
- Interaction with Solar Wind and Cosmic Rays

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Further Reading

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