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## Review

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# Isotopes as tracers of the sources of the lunar material and processes of lunar origin

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Ever since the Apollo programme, isotopic abundances have been used as tracers to study lunar formation, in particular to study the sources of the lunar material. In the past decade, increasingly precise isotopic data have been reported that give strong indications that the Moon and the Earth's mantle have a common heritage. To reconcile these observations with the origin of the Moon via the collision of two distinct planetary bodies, it has been proposed (i) that the Earth–Moon system underwent convective mixing into a single isotopic reservoir during the approximately  $10^3$  year molten disc epoch after the giant impact but before lunar accretion, or (ii) that a high angular momentum impact injected a silicate disc into orbit sourced directly from the mantle of the proto-Earth and the impacting planet in the right proportions to match the isotopic observations. Recently, it has also become recognized that liquid–vapour fractionation in the energetic aftermath of the giant impact is capable of generating measurable mass-dependent isotopic offsets between the silicate Earth and Moon, rendering isotopic measurements sensitive not only to the sources of the lunar material, but also to the processes accompanying lunar origin. Here, we review the isotopic evidence that the silicate–Earth–Moon system represents a single planetary reservoir. We then discuss the development of new isotopic tracers sensitive to processes in the melt–vapour lunar disc and how theoretical calculations of their behaviour and sample observations can constrain scenarios of post-impact evolution in the earliest history of the Earth–Moon system.

## 1. Introduction

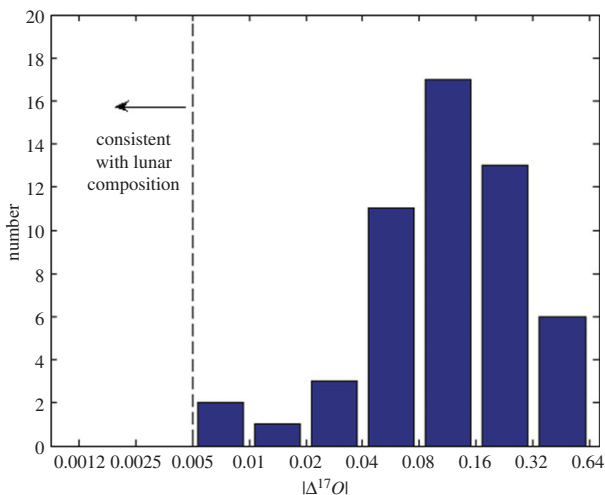
The origin of the Earth–Moon system is an unsolved problem. The process is generally thought to have been initiated by an off-centre collision of a planet-sized body with the proto-Earth towards the end of Earth accretion [1,2]. The ‘standard’ model of an impact of a Mars-mass body onto the proto-Earth can simultaneously explain the total angular momentum of the system and the lunar metal depletion and mass [3], but does not readily explain the isotopic homogeneity observed between silicate Earth and Moon [4–6]. The reasons are twofold. First, potential Moon-forming impacts that leave the system with approximately its present level of angular momentum [7–10] derive a major fraction of the proto-lunar disc (40–90%) from the less massive proto-planet. Second, the range of tracers that display isotopic homogeneity in the silicate Earth and Moon is such as to leave little doubt that the atoms composing these objects represent a single planetary reservoir (see §2).

Two scenarios have been proposed as solutions to the problem of isotopic homogeneity. First, it has been suggested that turbulent mixing in the approximately  $10^3$  year fluid epoch after the giant impact but before lunar accretion can isotopically equilibrate the Earth and proto-lunar disc into a single reservoir [11]. Second, it has been proposed that the Moon-forming impact was a high angular momentum event [12,13] that placed an Earth-mantle-like disc into orbit, but that the post-impact system subsequently lost most of its angular momentum via a resonance with the Sun [13,14]. One of the major goals of lunar origins research is to determine which, if any, of these scenarios most closely corresponds to the Moon-forming event. The equilibration scenario requires that the proto-lunar disc be characterized by efficient mixing across its radial extent such that the outermost disc can inherit the isotopic composition of the innermost disc (and post-impact Earth). The high angular momentum scenarios place no such requirement on the disc evolution. Such a distinction in the requirements for the post-impact evolution in the proposed scenarios suggests that determining the transport properties of the proto-lunar disc may help to clarify the solution to the problem of the ‘terrestrial’ lunar material.

Chemical constraints may be brought to bear on this problem, because the disc—through strong liquid–vapour partitioning—can potentially imprint distinct chemical signatures of its evolution onto the lunar-forming material (e.g. the moonlets) that form in its periphery [15]. Recently, it has become apparent that *isotopic* abundances can also be used to interrogate post-impact processes, because the isotopic composition of certain elements (e.g. silicon) is measurably different between a silicate liquid and its coexisting vapour [16]. Here, we present a model for calculating equilibrium liquid–vapour isotopic fractionation and discuss what observations of mass-dependent offsets can tell us about fractionation after the giant impact. In §2, we discuss evidence that the isotopic homogeneity between silicate Earth and Moon reflects derivation from a single *planetary* reservoir—here defined as a reservoir established via processes at planetary pressures (more than 1 GPa)—as opposed to a single *nebular* reservoir—one established via low-pressure processes alone. In §3, we present the fractionation model, its application to the fractionation of silicon isotopes, and possible interpretations of the data in the light of such calculations. In §4, we outline ways in which progress can be made in developing the isotopic constraints on the origin of the Earth–Moon system.

## 2. Isotopes as nebular and planetary tracers

The striking cosmochemical similarity of silicate Earth and Moon has become recognized as a major constraint that must be explained in any scenario of lunar origin. While Earth-like signatures—including Earth-like oxygen isotopic abundances [17] and chemical abundances indicative of high-pressure core formation [18]—were observed in lunar samples soon after



**Figure 1.** Histogram of the oxygen isotopic offset between impactor and target planets is plotted for all giant impacts in a Chambers [24] simulation, calibrated to the Earth–Mars difference (0.32‰). The mean deviation of impactors’ compositions from the final planets is  $\langle |\Delta^{17}O_{\text{imp}} - \Delta^{17}O_{\text{planet}}| \rangle = 0.15\text{‰}$ . Compositional scatter among incoming impactors is comparable to the differences observed between the planets. None of the impactors in this simulation have a composition similar enough to the target planet (i.e. with an offset  $< 0.005\text{‰}$ ) to yield the Earth–Moon system. A linear gradient with heliocentric distance is here assumed, but similar results are obtained for different initial gradients for any scenario in which the source regions of the terrestrial planets overlap (figure 2 of [11]). (Online version in colour.)

the Apollo programme, decades of advances in analytical techniques have revealed a new array of observations that together constitute strong evidence that the lunar and terrestrial mantle material represent a single reservoir. Here, we review the isotopic evidence that bears on this question.

### (a) Oxygen

The refinement of laser fluorination techniques has revealed that silicate Earth and Moon are indistinguishable in their oxygen isotopic character ( $\Delta^{17}O$ ) at a 5–10 ppm level [5,19–21], whereas Mars’ offset from the Earth—resolved earlier—is 320 ppm [22,23]. Forward modelling of the isotopic offsets of impacting planetary embryos with planets during accretion—by assigning isotopic compositions to the initial embryos and calibrating the initial values to reproduce the Earth–Mars offset—predicts a distribution of isotopic offsets that peaks at approximately 100 ppm with very few impactors being as compositionally similar to the target planet as the Moon is to the silicate Earth (figure 1). This line of reasoning relies on the observation that—in all  $N$ -body simulations of terrestrial planet accretion—radial mixing causes the source regions of the Earth and Mars to overlap such that the heterogeneity observed between these two planets is expected to reflect heterogeneity in their source materials [25–29]. We note, however, that such a heterogeneous accretion scenario for oxygen isotopes implies either that the isotopic similarity between enstatite meteorites and the Earth [20,30] is a coincidence or that our present understanding of terrestrial planet formation is incomplete. This issue requires further attention. Moreover, ideas about heterogeneous accretion of terrestrial oxygen are primarily based on measurements of Mars and could be further tested via the return of samples from the surface of Mercury or the atmosphere of Venus, or the unambiguous identification of meteorites from these planets.

## (b) Titanium

New measurements of the mass-independent isotopic composition of titanium have revealed an Earth–Moon identity set against a background nucleosynthetic heterogeneity observed in the inner Solar System [6]. While the precision of titanium measurements—relative to the full range of isotopic heterogeneity observed in the Solar System—is not high as that of oxygen [31], these observations provide an important, unique constraint, because titanium is a refractory element and can be expected to be concentrated into liquid phases in the aftermath of the giant impact. Hence, if only the vapourized components undergo turbulent mixing and equilibration post-impact [11], titanium isotopes might be expected to display Earth–Moon heterogeneity, which they do not. Either the proto-Earth and impactor were more compositionally alike than suggested by models of planet formation [27], or post-impact turbulent mixing involved liquid–liquid exchange of droplets that were suspended and coupled to the common convecting vapour atmosphere [16], or there was direct injection of Earth–mantle-like material into orbit during the giant impact [12,13]. Applying new, high-precision analytical techniques to existing titanium isotope measurements for samples from Mars [32]—currently the benchmark for isotopic variability in the inner Solar System—would be desirable. As with oxygen, knowledge of the titanium isotope composition of Mercury and Venus will place the isotopic composition of lunar samples in a more instructive context.

## (c) Tungsten

Through the presence of the short-lived radionuclide hafnium-182 and the decay reaction  $^{182}\text{Hf} \rightarrow ^{182}\text{W}$  ( $\tau_{1/2} = 9$  Myr), early Solar System reservoirs characterized by distinct chemical compositions (i.e. Hf/W ratios) developed distinct isotopic abundances (i.e. in the ratio of  $^{182}\text{W}/^{184}\text{W}$ ). Importantly, hafnium is expected to quantitatively partition into planetary silicates, whereas most inner Solar System tungsten is sequestered into metallic cores. The tungsten isotopic abundances of samples is therefore a chronometer for the establishment of these chemically distinct reservoirs [33]. The isotopic abundances measured in planets reflect the timing of core formation in precursor bodies, the timescale of accretion, the degree of tungsten partitioning into core metal and the amount of metal–silicate re-equilibration following collisions [34–37]. In this context, approximately 200 ppm excess of  $^{182}\text{W}$  measured in the Earth’s mantle—relative to undifferentiated meteorites [38–40]—is a signature that reflects both the timing and character of terrestrial core formation. Potential low-mass Moon-forming impactors—such as Mars—are expected to have experienced a more rapid accretion history [41] and—all else being equal—to have developed larger  $^{182}\text{W}$  excesses. In this context, the similarity of the lunar  $^{182}\text{W}/^{184}\text{W}$  to the Earth mantle value to within less than 20 ppm [4]—in spite of equal bulk silicate Earth and Moon Hf/W ratios to within tens of percent [42,43]—is surprising. Even if the proto-Earth and Moon-forming impactor had grown from similar starting materials, the distinct accretionary history of distinct planetary bodies renders the tungsten isotopic similarity of silicate Earth and Moon an unexpected observation that must be explained [44]. The tungsten isotopic observations [4] therefore provide evidence that the Earth’s mantle and Moon represent the outcome of a single accretionary history, either through direct injection of an Earth-like proto-lunar disc [12,13] and the isolation of metals from silicates during and after the Moon-forming event, or through vapour-mediated equilibration of tungsten isotopes in the energetic aftermath of the giant impact [11,16]. The latter may be aided via volatilization of tungsten in the highly oxidizing conditions prevalent in the silicate vapour atmosphere [45,46].

## (d) Silicon

An important new class of tracers that has been developed in recent years derives from precise measurements of mass-dependent isotopic compositions, most notably for silicon. While

physico-chemical processes may fractionate silicon isotopes, rendering samples compositionally distinct from the planetary reservoirs from which they are derived, for high-temperature magmatic processes, these effects have been shown to be small [47–49]. Importantly, the  $^{30}\text{Si}/^{28}\text{Si}$  of the silicate Earth is observed to be enriched relative to primitive meteorites and differentiated meteorites from Vesta and Mars by approximately 120–200 ppm [47,48,50], but identical to the silicate Moon to within about 30 ppm [51–53].

What is the origin of the silicon isotopic differences observed between silicate Earth–Moon and samples derived from Mars and the asteroid belt? There are two possibilities. First, it is possible that the material from which the Earth–Moon grew was characterized by distinct isotopic characteristics compared with materials from which Mars and the asteroids grew. Support for this view comes from *N*-body simulations of the evolution of the Solar System that suggest that a small fraction (less than 1–2%) of planetesimals originating in the outer terrestrial planet region (1.0–1.5 AU) is implanted into the asteroid belt, whereas an even smaller fraction (less than 0.01–0.1%) of primitive material originating in the inner terrestrial planet region (0.5–1.0 AU) is implanted into the belt and available for sampling via meteorites [54]. Such calculations suggest that ‘terrestrial chondrites’ [55]—the building blocks of the Earth—should not be well represented in our meteorite collections. As such, we cannot rule out nebular inheritance as the origin of the silicon isotopic data.

Nevertheless, a number of recent developments suggest a different possibility: that high-temperature, high-pressure core formation has sequestered light silicon isotopes into the Earth’s core [50]. The density deficit of the Earth’s outer core relative to a pure FeNi alloy implies the presence of one or more abundant light elements—such as hydrogen, carbon, oxygen, silicon or sulfur—in the core fluid. Forward modelling of the conditions of terrestrial core formation constrained by mantle abundances of siderophile elements suggests that significant silicon dissolution into core-bound metal is possible [56,57]. Theoretical calculations [50], experiments [58,59] and empirical observations [60] of metal–silicate partitioning suggest that this process is associated with a fractionation of the right sign and magnitude to account for the observed isotopic offset between silicate Earth and primitive meteorites if 5–10 wt% silicon entered the Earth’s core [47,48,50,53]. In general, if appreciable quantities of silicon are partitioned into the core, then the residual silicate portion of a planetary body will acquire a heavy silicon isotope signature. Critically, the partitioning of silicon into core-forming alloys depends on the pressure, temperature and oxygen fugacity of equilibration [61,62]. Hence, if core formation is the cause of the silicon isotopic offset between the silicate Earth and primitive meteorites, then a distinct isotopic signature would be expected for a distinct Moon-forming impactor. This expectation is borne out by observations of samples from Mars [47,50,53] and implies that the Moon inherited its silicon isotopic composition from the silicate Earth.

Whether of nebular or planetary origin, the recent discovery of the indistinguishable silicon isotopic signature of silicate Earth and Moon—distinct from primitive meteorites and samples from other differentiated bodies—yields additional diversity to the geochemical evidence pointing to a common source for the silicate Earth and Moon [51–53]. Scenarios invoking direct generation of an Earth-like silicate disc [12,13] require limited post-impact high-*P*–*T* metal–silicate equilibration to preserve the silicon isotopic similarity of the silicate Earth and the proto-lunar disc, whereas turbulent inheritance scenarios [11,16] require liquid–vapour equilibration with limited phase-separation and associated liquid–vapour isotopic fractionation (see §3).

In summary, new high-precision isotopic observations of oxygen, titanium, tungsten and silicon in lunar and terrestrial samples have failed to detect any evidence for a distinct impacting planet. Even the recently detected oxygen isotopic offset between the silicate Earth and Moon [20] may be explained by small quantities of post-formation accretion. While variations in oxygen and titanium isotopes trace nebular processes, tungsten and (perhaps) silicon isotopes trace planetary processes and record planetary (i.e. core formation) signatures. The uniformity in such a diverse range of isotopic tracers—in the context provided by samples from Mars and the asteroid belt—argues that silicate Earth and Moon represent one planetary reservoir, a first-order

observation that must be explained in any scenario of lunar origin. Further insights into questions of provenance posed by meteoritic and lunar data may have to await the return of samples from Venus or Mercury.

### 3. Isotopes as tracers of post-impact process

We now turn from a discussion of isotopes as markers of heritage to isotopes as tracers of post-impact process. Why are we interested in process? First, distinct proposals for generating Earth–Moon homogeneity have distinct implications for post-impact processes: equilibration requires efficient radial mixing [11], whereas direct injection via high angular momentum impacts [12,13] do not. Mass-dependent isotopic signatures—to the extent that they are linked to post-impact process—have the potential to subject proposed scenarios to critical tests. Second, that the lunar material derives from the Earth’s mantle necessitates explanation for any *chemical* differences observed between these two reservoirs. Here, we illustrate the potential of isotopes to trace processes by focusing on signatures accompanying the development of chemical differences. Three such differences have been discussed in the literature.

First, a striking depletion in the abundances of the most volatile elements, epitomized by lunar potassium, has been observed since Apollo [63]. Thermodynamic calculations have been conducted to interpret the volatile abundances [64], but no quantitative physical–chemical scenario for the removal of volatile elements has yet been developed. Second, since Apollo, the lunar abundances of refractory elements have often been inferred to be greater than the Earth’s mantle. Recently, a downward revision in the inferred thickness of the lunar crust—a major reservoir for refractory elements—has shifted the inferred lunar abundances to approximately terrestrial values [65]. Finally, the FeO content of the silicate Moon has been inferred to be similar to [66] or significantly elevated relative to [67] the silicate Earth. Recent modelling supports the prevailing view that the composition of the lunar magma ocean was somewhat more FeO-rich than bulk silicate Earth [68]. Such a chemical difference between silicate Earth and Moon—despite the derivation of one from the other—prompts the question of its origin. We discuss several possibilities.

First, it is possible that pre-impact silicate differentiation resulted in FeO enrichment in shallow regions of silicate Earth and/or the impactor that are preferentially injected into orbit [8] and that initial differences between the lunar disc and Earth mantle survived the subsequent liquid–vapour evolution (Shun Karato 2013, personal communication). To test such a possibility, it would be necessary to identify trace element or isotopic signatures of crystal–liquid fractionation that might be indicative of such an origin.

Second, it is possible that the lunar FeO is partly generated in the proto-lunar disc through a chemical reaction. Impacts typically generate disks that are composed of several per cent Fe-rich metal derived from the cores of the impacting planets [8–10,12,13]. Such an injection is thought to ultimately lead to the formation of the lunar core [69]. However, reactions between metallic Fe and other chemical components in the disc, e.g.  $\text{Fe(l)} + \text{H}_2\text{O(v)} \Rightarrow \text{FeO(l)} + \text{H}_2\text{(v)}$ , might reduce the initial metal/silicate ratio while increasing the FeO content of disc silicates. What are the observable signatures of such a process? One signature relates to tungsten isotopes and arises from the expectation that silicates and metals that undergo chemical reaction in the proto-lunar disc will also chemically equilibrate. The tungsten isotopic composition of metals in the early Solar System is expected to be distinct from—and complementary to—that of silicates [33]. Such a reaction in the proto-lunar disc—and the associated metal–silicate equilibration—is therefore expected to result in the development of an isotopic offset in the tungsten isotope composition of terrestrial and lunar material, which is not observed [4]. Assuming Earth-like Hf/W partitioning for precursor planets, the precision of the isotopic measurements limits the increase of the FeO content of lunar silicates via reaction with core metals to less than 1 wt%. We conclude that oxidation of Fe-rich metals derived from planetary cores is not a viable process for increasing the FeO content of lunar silicates relative to Earth mantle.

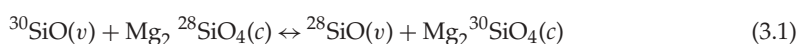
Finally, the enhanced FeO/MgO ratio of lunar silicates relative to Earth's mantle might derive from liquid–vapour fractionation. This possibility arises from distinct vapourization behaviours of distinct components, with FeO having a greater propensity for vapourization than MgO [70]. Hence, an enhanced lunar FeO/MgO relative to Earth mantle would require an episode of vapour enrichment of the lunar material divorced from the episode of vapour loss that led to the volatile depletion. Is such an episode of liquid–vapour fractionation possible? Recently, Pahlevan *et al.* [16] explored the extent to which phase separation ('rainout') within a terrestrial silicate vapour atmosphere can alter the composition of the atmosphere relative to the magma ocean from which it is sourced. Such calculations are relevant to the lunar composition if the proto-lunar disc inherits the composition at the top of terrestrial vapour atmosphere through turbulent exchange as has been proposed to explain the isotopic homogeneity of the Earth–Moon system [11]. Such a scenario is attractive because it has testable consequences, and illustrates both the opportunities and challenges of forging a connection between the formation process and remnant isotopic observables.

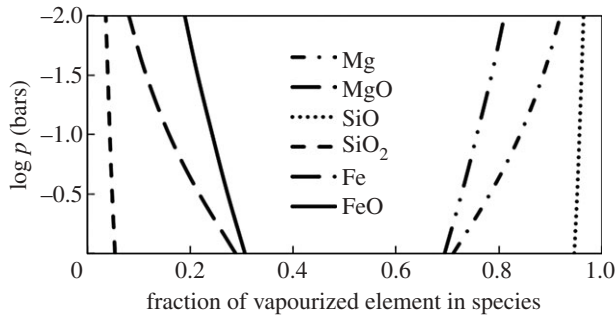
Consideration of isotopic fractionation following the Moon-forming impact has generally been restricted to kinetic processes, such as the kinetics of evaporation [71–73], because equilibrium isotopic fractionation between different phases has been assumed to be negligible at the relevant conditions. Such an assumption derives from the fact that equilibrium isotopic fractionation tends to zero at high temperatures [74]. This proverb of stable isotope geochemistry has been challenged in recent times as high-temperature processes such as crystal–liquid [75], metal–silicate [50,59] and liquid–vapour [16] equilibrium have been shown to measurably fractionate the isotopes. In general, significant high-temperature isotopic fractionation is possible—at thermodynamic equilibrium—when the bonding environment for an element is sufficiently distinct in coexisting phases owing to changes in bonding partners, valence and/or coordination. Here, we review what is known about equilibrium liquid–vapour isotopic fractionation in high-temperature silicate systems by way of example. This section is a compact version of [16].

### (a) Equilibrium isotopic partitioning

Because vapourization of silicates involves decomposition reactions, distinct differences in bonding environment between liquid and vapour exist for a number of elements. Silicon isotopes are attractive in this regard as a diagnostic for liquid–vapour fractionation for several reasons. First, the speciation for silicon between the liquid and vapour is known to be distinctly different, making significant high-temperature fractionation possible. Silicon in the melt exists in silica tetrahedra ( $\text{SiO}_4^{-4}$ ), whereas silicon monoxide (SiO) dominates the speciation of silicon in silicate vapour for the full range of conditions after the giant impact (figure 2). Second, silicon has been observed to display minimal isotopic fractionation during igneous processes [48,49] rendering the isotopic composition of samples potentially diagnostic of the composition of source reservoirs. Third, high-precision measurements of silicon isotopes in lunar and terrestrial rocks and meteorites have been made [47,48,50–53]. The original impetus for these measurements was the fractionation of Si isotopes owing to high-pressure terrestrial core formation and as tracers of the sources of the lunar material (§2*d*). However, it has become apparent that high-precision measurements constrain liquid–vapour fractionation and can transmit isotopic signals that *evolve* in the energetic aftermath of the giant impact.

We can estimate the magnitude of the isotopic fractionation between the vapour and liquid by considering the corresponding fractionation between vapour and crystalline forsterite. The rationale behind this approach is that the bonding environment for silicon in the crystal approximates that in the liquid, consistent with the observation that suites of igneous rocks display relatively uniform silicon isotope compositions [48,49]. To quantify the fractionation, an isotope exchange reaction and the corresponding equilibrium constant are evaluated





**Figure 2.** Equilibrium metal-bearing vapour species in coexistence with liquid droplets in the silicate vapour atmosphere of Earth.  $\text{SiO}(v)$ ,  $\text{Mg}(v)$  and  $\text{Fe}(v)$  dominate the speciation over  $\text{SiO}_2(v)$ ,  $\text{MgO}(v)$  and  $\text{FeO}(v)$  for the full range of conditions encountered on the post-giant-impact Earth. While lower temperatures in the upper atmosphere favour the formation of molecules, lower pressures favour dissociation into atomic forms and overwhelm the temperature effect.  $\text{SiO}(v)$  dominates the silicon speciation in silicate vapours for the full range of conditions encountered. The predominance of  $\text{SiO}(v)$  in the vapour dictates a distinct bonding environment than silicon in the liquid ( $\text{SiO}_4^{-4}$ ) and makes high-temperature isotopic fractionation possible. Monatomic  $\text{Si}(v)$  is included in the calculations but appears in negligible quantities (less than 3 ppm). Based on calculations described in Pahlevan *et al.* [16].

and

$$K_{\text{eq}} = \frac{Q(\text{Mg}_2^{30}\text{SiO}_4)}{Q(\text{Mg}_2^{28}\text{SiO}_4)} \bigg/ \frac{Q(^{30}\text{SiO})}{Q(^{28}\text{SiO})} \quad (3.2)$$

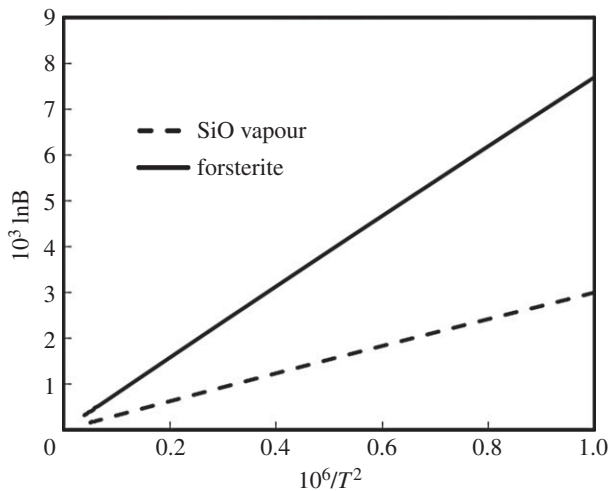
where  $Q$  is the reduced partition function of the isotopologues in the phase of interest. For the condensate, the  $B$  factor (or reduced partition function ratio) of silicon in crystalline forsterite is calculated using density functional theory and assuming harmonic vibrations [76]. For the vapour, as discussed, thermodynamic equilibrium calculations show that the  $\text{SiO}$  molecule dominates the speciation of silicon (more than 94% of silicon-bearing molecules) for the full range of conditions encountered after the giant impact. Silicon—alone among the major elements—has a vapour speciation that can be well approximated with a single molecule (figure 2). Following [74], the partitioning of isotopes is calculated by evaluating the ratio of partition functions for isotopically substituted and normal populations, assuming harmonic vibrations:

$$\frac{Q'}{Q} = \prod_i \frac{\nu'_i e^{-U'_i/2} (1 - e^{-U_i})}{\nu_i e^{-U_i/2} (1 - e^{-U'_i})} \quad (3.3)$$

where  $\nu$  represents the vibrational frequency of the normal isotopologue (e.g.  $^{28}\text{Si}^{16}\text{O}$ ) and is determined via spectroscopy and adopted from standard sources [77],  $\nu'$  represents the vibrational frequency of the substituted isotopologue ( $^{30}\text{Si}^{16}\text{O}$ ) calculated from  $\nu$  and the known dependence of the vibrational frequency on the reduced mass, and  $U$  is the dimensionless mode energy ( $\equiv h\nu/kT$ ). With this approach, we can calculate the  $B$ -factor for silicon in the  $\text{SiO}$  molecule, which quantifies the preference of heavy isotopes for this vapour molecule (and, for an isotope exchange reaction involving the exchange of a single atom, is simply equal to  $Q'/Q$ ).  $B$ -factors for  $^{30}\text{Si}/^{28}\text{Si}$  as a function of temperature in the liquid and vapour are plotted in figure 3.

Two points are worth noting. First, in equilibrium, the isotopic composition of the vapour will be enriched in the lighter isotopes of silicon relative to the liquid at all temperatures. Second, the magnitude of the isotopic fractionation is quite large. Using the fact that the equilibrium constant





**Figure 3.** The silicon isotope fractionation factors—for  $^{30}\text{Si}/^{28}\text{Si}$ —in forsterite, a proxy for silicon in the liquid, and for  $\text{SiO}(\text{v})$ , the dominant Si-bearing vapour molecule. As expected for the high-temperature limit, the fractionation factors decrease as  $1/T^2$ . At a given temperature, the difference between the two plotted lines yield the difference in  $\delta^{30}\text{Si}$  values between the phases at equilibrium. Hence, at  $10^3$  K, the isotopic fractionation  $\Delta$  ( $\equiv \delta_{\text{l}} - \delta_{\text{v}}$ ) between crystalline forsterite and co-existing vapour is approximately 5 per mil. Such a large fractionation renders silicon isotopes sensitive tracers of the post-impact evolution. For  $^{28}\text{SiO}$ , a fundamental vibrational frequency of  $1241 \text{ cm}^{-1}$  was used.

is nearly equal to unity [ $\Delta = (K_{\text{eq}} - 1) \times 10^3$ ], and the fact that the vapour speciation does not appreciably change throughout the range of relevant conditions, we can write the fractionation of  $^{30}\text{Si}/^{28}\text{Si}$  between forsterite and coexisting vapour:

$$\Delta_{L-V}^{\text{Si}} = 5 \times \left( \frac{10^3}{T} \right)^2 \text{‰}. \quad (3.4)$$

This expression is accurate in the temperature range encountered after the giant impact ( $T = 2500 - 3500$  K) to better than 10%. A 5‰ difference in the  $^{30}\text{Si}/^{28}\text{Si}$  of liquid and vapour at  $10^3$  K is enormous. For comparison, isotopic fractionation between forsterite and quartz at the same temperature ( $10^3$  K) is less than 0.5‰ [3,76]. This calculation suggests that, in conditions where silicon undergoes partial vapourization, its isotopes are very sensitive tracers of phase separation.

## (b) Liquid–vapour fractionation model

To translate such calculations for isotopic differences between silicate liquid and vapour into statements about silicate Earth and Moon requires a physical scenario for the post-impact evolution that describes the separation of phases. Thus far, a physical scenario has been developed for only one setting potentially relevant to the lunar composition: the silicate vapour atmosphere of the post-giant impact Earth [16]. Here, we describe the chemical thermodynamic and dynamical model used to conduct these calculations.

In brief, silicate Earth and proto-lunar disc are approximated with olivine composition,  $(\text{Fe,Mg})_2\text{SiO}_4$ , the only compositional parameter being the FeO/MgO ratio, which is well-defined for the bulk silicate Earth [78] and is constrained but less well defined for silicate Moon, ranging from essentially identical with the Earth mantle [66] to nearly twice the terrestrial mantle value [67]. The thermodynamic model is of a two-phase, two-component system, and describes the liquid as a binary olivine solution and the vapour as a mixture of ideal gases, as expected in the dilute gas limit with interatomic distances much greater than atomic dimensions. The

dynamical model is of a single isentropic column extending from deep regions in the convective terrestrial magma ocean where a single phase is present through a level where two phases become distinguishable to the top of the silicate vapour atmosphere. Such an ‘unsettled’ two-phase column may be possible because of the vigour of the convective motions necessary to match radiative losses at photospheric temperatures of approximately 2500 K [79].

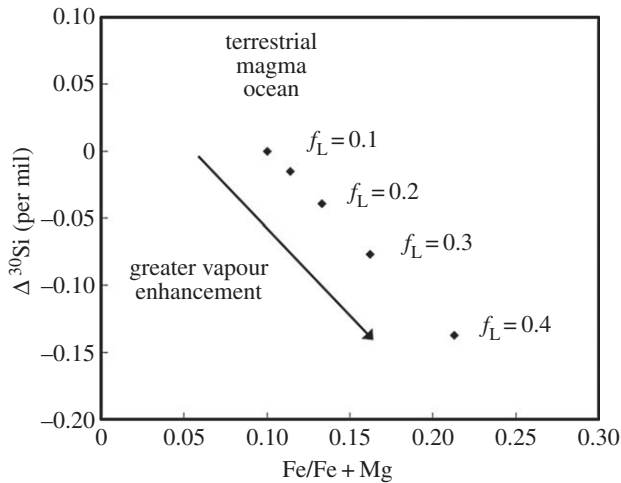
In such a setting, any fractionation leads to vapour enrichment in the lunar composition, as rainout removes liquid droplets from ascent to the upper atmosphere that Earth may exchange with the proto-lunar disc. While such a scenario—without phase separation—is capable of generating chemical compositions for the silicate Moon that are identical with Earth’s mantle, it is the possibility of removal of MgO-rich droplets and enrichment of the FeO/MgO ratio in the silicate vapour atmosphere that makes this setting interesting from the point of view of generating the chemical differences in the Earth–Moon system.

Rainout of silicate droplets generates both chemical and isotopic fractionation. Removal of heavy silicon in liquid droplets shifts the isotopic composition of the upper atmosphere towards that of the vapour relative to the terrestrial magma ocean. However, because the degree of liquid rainout is not well constrained, a range of outcome for the composition of the upper terrestrial atmosphere is possible. One constraint on the degree of rainout is the less than two times enhancement in the FeO/MgO ratio of lunar silicates relative to the Earth’s mantle [67]. For the degree of phase separation that would generate such a difference, the model predicts an approximately 140 ppm difference in the  $^{30}\text{Si}/^{28}\text{Si}$  ratio of terrestrial and lunar silicates to arise, at least for thermal conditions generated in the ‘standard’ giant impact (figure 4). As discussed previously (§2d), any silicon isotope offset between the silicate Earth and Moon is constrained to be less than approximately 30 ppm [51–53], suggesting minimal phase separation. In the absence of phase separation, liquid droplets may remain fully suspended up to high levels in the Earth’s silicate vapour atmosphere and the proto-lunar disc that would result from turbulent inheritance would be isochemical with the terrestrial magma ocean. However, *to the extent that the lunar composition is distinct from the bulk silicate Earth*, an isotopic offset in the silicate Earth–Moon system is expected in the context of this model.

### (c) Interpretation of predictions versus observations

We have described a model that suggests that—if the FeO/MgO of the silicate Moon was elevated owing to liquid–vapour fractionation in the silicate vapour atmosphere of Earth—a measurable silicon isotopic offset between silicate Earth and Moon should have evolved, an offset that is not observed. What is the interpretation? There are several possibilities. First, it is possible that the liquid–vapour separation occurred at higher temperatures than estimated in [16], for example, if the entropy and energy deposition during the giant impact occurred preferentially in the Earth’s shallow regions [8,9] or if the Moon-forming event was a more energetic impact than the standard Mars-mass impact model [12,13]. Second, calculations for predicting isotopic fractionation to date have employed a binary olivine thermodynamics for silicates, whereas the Earth’s mantle and Moon are characterized by  $\text{Mg}/\text{Si} < 2$  [78] necessitating more realistic thermodynamic models of high-temperature silicate liquids to accurately capture the behaviour of major elements in such settings. Improved thermodynamic models may exhibit distinct partial vapourization behaviour for silicon in a way that mutes its isotopic fractionation relative to predictions based on olivine thermodynamics. Third, it is possible that crystal–liquid fractionation before the giant impact, rather than liquid–vapour fractionation in its aftermath, was responsible for the major element differences between silicate Earth and Moon, and that such a signature survived the subsequent post-impact evolution. Finally, it is possible that the viewpoint that silicate Moon is nearly isochemical with the silicate Earth [66] is correct.

Despite the formation of the Moon from a melt–vapour disc [79,80], clear chemical evidence for liquid–vapour fractionation [63,81], and potentially large accompanying isotopic fractionations [16], no mass-dependent offsets between silicate Earth and Moon have been unambiguously established, an observation that is perhaps surprising. Nevertheless, that quantifiable scenarios



**Figure 4.** The chemical and isotopic composition at the top of the Earth's silicate vapour atmosphere is plotted as a function of the degree of phase separation ( $f_L$  is the fraction of liquid that is removed via rainout per scale height). Complete liquid suspension ( $f_L = 0$ ) yields silicate vapour atmospheres that are isochemical with the underlying magma ocean from which they are sourced. Moderate degrees of rainout ( $f_L = 0.4$ ) can generate greater FeO/MgO ratios—as often inferred for the silicate Moon—but the removal of liquid in such a model leads to an enrichment in light silicon isotopes for the lunar material, which has not been observed. Concomitant chemical and isotopic differences between silicate Earth and Moon is a consequence of this model. To the extent that chemical differences between these reservoirs exist, mass-dependent isotopic offsets are expected (fig. 6 of [16]).

produce measurable isotopic signals renders existing isotopic data capable of excluding certain scenarios and guiding theoretical developments of the post-impact evolutionary sequence. The interpretation of the isotopic observations in terms of evolutionary processes requires further work.

#### 4. Future works

Forging quantitative connections between the formation process and isotopic abundances presents several unique challenges, each of which leads to new avenues of research. First, more accurate multi-component thermodynamic models of silicate liquids at the temperatures of relevance ( $T = 2500 - 3500$  K) are needed to accurately capture the partial vapourization behaviour of elements of interest. While vapourization experiments in this temperature range have been rare, *ab initio* computational techniques may permit a thermodynamic description of silicate liquids at the high temperatures encountered during lunar origin (Burkhardt Miltzer 2012, personal communication). Second, better geophysical characterization of the Moon—for example, via a lunar seismic network—would permit a more precise determination of the lunar bulk composition. While samples can—in certain cases—accurately reflect the isotopic composition of the lunar magma ocean, direct connections between the *chemical* composition of samples and the bulk Moon are more elusive. A better knowledge of the lunar bulk composition—in particular whether significant differences with the major element composition of the bulk silicate Earth exist—would clarify the constraints posed by the lunar composition for scenarios of origin. Third, physical models of fractionation in settings other than the silicate vapour atmosphere of the Earth (e.g. in the melt-vapour proto-lunar disc) are required in order to develop a better understanding of the lunar formation process. In particular, developing models to interpret the meaning of the lunar volatile depletion—epitomized by the lower K/U ratio of lunar silicates relative to the silicate Earth [63,81]—in terms of a physical process requires

new modelling efforts. A major question is whether such a process of liquid–vapour separation also imparted measurable signatures to the lunar isotopic composition. While no signatures have been detected for elements—such as potassium [82]—whose isotopes have negligible high-temperature equilibrium fractionation (Edwin Schauble 2013, personal communication), candidate isotopic offsets between silicate Earth and Moon have recently been observed [83]. Lastly, determining the stable isotope composition of silicate Earth and Moon to higher precision and for new elements will open new windows to the lunar formation process. The unambiguous identification of such isotopic signals will provide the raw materials for crafting the next generation of lunar origin scenarios.

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