

CHEMICAL AND ISOTOPIC  
CONSEQUENCES OF LUNAR  
FORMATION VIA GIANT IMPACT

Thesis by

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“We must trust the perfection of the creation so far, as to believe that whatever curiosity the order of things has awakened in our minds, the order of things can satisfy.”

– Ralph Waldo Emerson, Nature

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## ABSTRACT

There is near consensus in the planetary science community that the origin of the Moon can be traced to a massive interplanetary collision between a roughly Mars-sized object and the growing Earth towards the end of planetary accretion. Many in the geochemical community, however, have rightly expressed skepticism towards this hypothesis. The compositional signatures of the giant impact have never been clearly articulated, and no one has yet used the ideas of lunar origin to say something about the lunar composition that was not previously known, that is, to make a prediction. The work presented here seeks to develop the theory of lunar origin with two goals in mind: of reconciling the predictions of the dynamical scenario with the observed signatures in the lunar composition, and of making new predictions for the lunar chemical and isotopic composition that can test and further constrain the theory through comparison with observations.

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## *Chapter 1*

### INTRODUCTION

George Darwin, in 1879, put forward the idea that the Moon was derived from the rocky mantle of the Earth via a process of fission. He speculated that perhaps the Pacific Basin was the scar left from this ancient event. It is easy, with the hindsight gained from the discovery of seafloor spreading and plate tectonics, to look back on this idea as faintly amusing. But in fact, Darwin was doing something remarkable. He was not only trying to speculate about the problem of lunar origin, but was looking at the modern system for evidence that betrays the mechanism of formation.

Although largely ignored for nearly a decade after its proposal in the mid-1970s, the giant impact hypothesis of lunar origin has gained widespread support in the planetary science community. The idea is that a massive collision between two planetary-sized objects injected at least a lunar mass of material into Earth orbit — which could accrete into a single Moon — and spun the Earth up, yielding the primordial five hour day.

Among the successes of this hypothesis are its ability to account for the large amount of angular momentum in the Earth-Moon system, to preferentially remove metallic Fe from the lunar material, to generate the small, but non-zero inclination of the early lunar orbit relative to the early Earth's equator, and to account for the lunar mass. Furthermore, such massive collisions between planet-sized bodies are now thought to be the primary growth mode of the terrestrial planets, including the Earth. In this way,

just as planet formation is understood as a by-product of star formation, lunar formation can be regarded as a by-product of the planet formation process. In the words of one planetary scientist, the impact hypothesis “has a naturalness almost approaching inevitability”.

Enthusiasm for the giant impact hypothesis from the geochemistry community has been less apparent. In summarizing chemical data that bears on the question of lunar origin, one author writes, “Although none of these observations actually disproves the giant impact hypothesis, we find it disquieting that the obvious consequences expected of a giant impact are not observed to be fulfilled”. Part of the reason for this discord is that the compositional consequences of lunar formation via giant impact have never been articulated. The goal of the work presented here is to take a step in this direction.

## **1.1 Chapter 2 — The Equilibration Hypothesis**

In this chapter, we put forward the idea that the Earth-Moon system underwent a great homogenization event in the first thousand years after the giant impact. Central to this story is the fact that smooth-particle hydrodynamic (SPH) simulations of the Moon-forming impact generate melt-vapor circumterrestrial disks, not intact Moons. Due to computational limitations, such numerical simulations typically capture the first 24 hours after the impact event during which important processes such as the injection of mass and angular momentum into orbit via gravitational torques take place. In every simulation of this kind to date, the pre-dominant contribution to the proto-lunar disk, after the first 24 hours of evolution, is the mantle of the impacting planet rather

than the Earth. However, we do not yet have a scenario that starts with a hot, melt-vapor circumterrestrial disk, and follows the evolution, ending with a lunar-mass body.

Given that the post-impact evolution of such fluid disks is not well understood, the approach here is to use the cosmochemical signatures — in the chemical and isotopic composition of the Moon — as indicators of the operative physical processes. In this chapter, we argue that the very precise match of the oxygen isotopic character of the silicate Earth and Moon requires an episode of turbulent mixing to homogenize the molten post-impact Earth with the molten proto-lunar disk through exchange with a common vapor atmosphere.

Essential to this argument is the idea that lunar formation must be understood in the context of planet formation, and that we can learn about the probable composition of the Moon-forming impactor by studying the composition of other Solar System bodies. Mars, in particular, as a remnant of the population of lunar-to-Mars mass objects that collided to form the terrestrial planets, yields information about the compositional gradients that existed in the inner Solar System and hence about the probable composition of the Moon-forming impactor. Such an approach suggests that the impactor was compositionally distinct, and necessitates an episode of post-impact turbulent mixing to explain the isotopic homogeneity of the Earth-Moon system.

Hence, the modeling presented here is motivated by the observations with the goal of identifying the processes — such as turbulent mixing of fluids — that were involved during the molten-disk era of lunar formation. Even without detailed knowledge, we

can set constraints on the disk evolution. For example, the longest possible timescale for turbulent mixing of fluids is the cooling timescale, which is the  $\sim 10^3$  years required to radiate to space the enormous energy that is released in the giant impact event, after which, absent other energy sources, the lunar material begins to crystallize.

This thousand-year period, short relative to the timescales between giant impacts and close encounters with other planetary objects, but long relative to dynamical (orbital and/or shockwave crossing) times, is the maximum time interval that is available for imprinting the signatures of the processes of lunar formation. In this chapter, we show that with plausible assumptions, efficient turbulent mixing of the fluid post-impact Earth and melt-vapor lunar disk is possible. This turbulent mixing episode is now supported by observed similarities in other isotopic systems, notably tungsten and silicon.

This chapter was published in the journal *Earth and Planetary Science Letters* under the title, “Equilibration in the Aftermath of the Moon-forming Giant Impact”.

## 1.2 Chapter 3 — Chemical Fractionation

In this chapter, we cease studying the lunar composition from the standpoint of source tracers imprinted in the pre-planetary era (i.e.,  $\Delta^{17}\text{O}$ ) whose signals can only be erased through homogenization and begin studying indicators (i.e., chemical composition) whose signals in the lunar composition could have been generated during the lunar formation process. Fundamentally, this is due to the fact that different silicate phases in equilibrium have the same oxygen isotopic character ( $\Delta^{17}\text{O}$ ) but distinct chemical

compositions. Hence, instead of modeling homogenization of probable pre-existing isotopic differences, in this chapter we attempt to evolve inferred differences in the chemical composition of the silicate Earth and Moon. While such modeling is motivated by the observations, this approach is complicated by the fact that the lunar bulk composition is not known with any precision. Indeed, there exist contradictory views of the lunar composition in the lunar petrology and seismology literature, revealing the difficulty of its unambiguous determination.

Each approach has shortcomings. For example, the seismic stations that were placed on the Moon by the Apollo astronauts are mostly sensitive to the nearside interior, and it is known that the lunar interior exhibits lateral heterogeneity. The bulk density and moment of inertia carry information about bulk lunar interior, but the compositional inversion is non-unique. None of the samples returned by the Apollo astronauts and the Lunakhod robots, and none of the lunar meteorites in our collections, escaped the primordial lunar differentiation event of magma ocean crystallization. For this reason, petrologic reconstructions of the lunar bulk composition are model-dependent. Nevertheless, there is agreement among researchers that the Moon is composed of ultramafic silicates broadly similar to the terrestrial mantle. However, significant uncertainty exists regarding certain compositional features (i.e., the FeO/MgO ratio) of the Moon relative to Earth mantle, around which petrologic debates have raged for decades. The result is a range in the reconstructions of the lunar bulk composition.

Here we take a different approach. We ask what chemical compositions can be evolved from the partially vaporized Earth mantle via the process of liquid rainout. Since this is the first attempt at quantitative modeling of liquid-vapor fractionation during lunar formation, we focus on the relatively simple silicate vapor atmosphere of Earth, and neglect any fractionation that may have occurred in the proto-lunar disk with which such an atmosphere is in turbulent exchange.

The signal we are seeking to explain is the widely inferred elevated FeO/MgO ratio of the Moon relative to the silicate Earth. Given that FeO in silicate melts has a higher vapor pressure than MgO, rainout of liquid droplets can generate atmospheric parcels with enhanced FeO/MgO ratios relative to the Earth mantle. The goal of this chapter is to determine whether the magnitude of such a silicate Earth-Moon difference can evolve due to rainout in the silicate vapor atmosphere of the post-impact Earth. The main conclusion is that such a difference can evolve. However, since liquid-vapor fractionation involves separation of phases, rather than components, such a feature is accompanied by concomitant lunar depletions in refractory elements (i.e., CaO, Al<sub>2</sub>O<sub>3</sub>) excluding certain bulk compositions as products of fractionation from Earth mantle.

### **1.3 Chapter 4 — Isotopic Fractionation**

Having briefly made a foray into the subject of the lunar chemical composition, in this chapter, we revisit the question of the lunar isotopic composition. Here we examine those signals in the isotopic composition that, like the chemical composition, can be

generated during the lunar formation process. For example, we consider differences in the  $^{18}\text{O}/^{16}\text{O}$  ratio of the silicate liquid and co-existing vapor that could be expressed in a difference between silicate Earth and Moon depending on the degree to which these phases separated during lunar formation. Such isotopic effects have generally been overlooked because, at high temperatures, equilibrium isotopic differences between co-existing phases tend to zero, and the temperatures in the afterglow of the giant impact are among the highest encountered in the geosciences.

Nevertheless, high-temperature isotopic fractionation has, in recent years, been observed for elements whose bonding environment in various phases differs greatly. For example, the isotopes of silicon, due to the very different bonding environment experienced in metal and silicates, have been used to argue that silicon was fractionated during high-temperature core formation, and is one of the light elements in the Earth's core. Here, motivated by the fact that the bonding environment for rock-forming elements is very different in the liquid and vapor, we quantify the equilibrium isotopic fractionation for silicon, magnesium, iron, and oxygen at the temperatures encountered on the post giant-impact Earth, and find that they are not negligible. Indeed, the equilibrium liquid-vapor fractionation for some elements is quite substantial.

To translate an isotopic difference between silicate liquid and vapor to one between the silicate Earth and Moon requires a scenario of phase separation. The setting considered for such separation is the same as the chemical fractionation calculations of Chapter 3. In this way, the role of silicate vapor petrology in determining the lunar



composition can be constrained, not only via chemical differences, but also via small offsets in the stable isotope composition of the bulk silicate Earth and Moon.

Approximating the silicate Earth with only two components, the olivine end-members  $(\text{Fe,Mg})_2\text{SiO}_4$ , we make predictions for the isotopic offsets accompanying the chemical fractionation necessary to generate the widely inferred elevated FeO/MgO ratio of the Moon relative to the silicate Earth. Such a scenario is capable of generating a  $\sim 100$  ppm difference in the  $^{30}\text{Si}/^{28}\text{Si}$  ratio of the silicate Earth and Moon. At present no silicon isotope difference in the silicate Earth-Moon system can be resolved. Nevertheless, the calculation here presented underscores the importance of capturing the partial vaporization behavior of elements in the post-giant-impact environment, as well as the relative abundance of the species present in equilibrium in the silicate vapor for generating predictions of isotopic fractionation, both of which require more realistic thermodynamic models of the liquid solution. The principle conclusions from this chapter are that small mass-dependent isotopic differences between the silicate Earth and Moon may carry the signatures of the processes of lunar formation from a melt-vapor circumterrestrial disk and that a better understanding of the expected signatures requires a better understanding of high-temperature ( $T \sim 3,000$  K) magmas.

While the Moon is the most conspicuous planetary object from the Earth, and the only one yet visited by humans, strong connections between its mechanism of origin and observed characteristics have been elusive. This thesis is an attempt at strengthening such connections.

## THE EQUILIBRATION HYPOTHESIS

**Abstract**

Simulations of the moon-forming impact suggest that most of the lunar material derives from the impactor rather than the Earth. Measurements of lunar samples, however, reveal an oxygen isotope composition that is indistinguishable from terrestrial samples, and clearly distinct from meteorites coming from Mars and Vesta. Here we explore the possibility that the silicate Earth and impactor were compositionally distinct with respect to oxygen isotopes, and that the terrestrial magma ocean and lunar-forming material underwent turbulent mixing and equilibration in the energetic aftermath of the giant impact. This mixing may arise in the molten disk epoch between the impact and lunar accretion, lasting perhaps  $10^2$ – $10^3$  years. The implications of this idea for the geochemistry of the Moon, the origin of water on Earth, and constraints on the giant impact are discussed.

**2.1. Introduction**

The Moon is generally believed to have formed from the debris ejected from the impact of a Mars-sized body onto the forming Earth (Cameron and Ward 1976, Hartmann and Davis 1975). At present, the argument in favor of such a scenario is twofold: a single, off-center collision with a nearly formed Earth can account for the angular momentum present in the Earth-Moon system, as well as the bulk lunar iron depletion. The geochemical arguments for the giant impact, however, are less

compelling than dynamical ones, because the chemical consequences of the impact have not been fully explored, with the result that compositional Earth-Moon similarities and differences — to the extent that they trace the effects of the giant impact — have never been satisfactorily explained.

The similarity of the inferred lunar composition to that of the silicate Earth has been taken as evidence for the derivation of the lunar material from the Earth's mantle (Ringwood 1979). Hydrodynamic simulations of the giant impact (Cameron 2000, Canup 2004b, Canup and Asphaug 2001), however, ubiquitously derive the majority of the lunar material from the impactor. Hence, any elemental or isotopic similarity between the composition of the silicate Earth and Moon would have to be interpreted to be due to nebular mixing or planetary accretion processes. Here, we show that a compositional relationship between the silicate Earth and Moon may naturally arise in the aftermath of the impact event. The central idea is turbulent mixing of projectile and target material in the time between the giant impact and lunar accretion.

Two characteristics of oxygen make this element an ideal tracer for studying solar system formation processes. First, oxygen isotopes were distributed heterogeneously in the early solar system (Clayton 1993) and can therefore be used to trace the sources of planetary material. Second, the presence of three stable isotopes enables identification of heterogeneity that occurred in a mass-independent way. Such mass-independent heterogeneity in the solar system may have resulted from photochemical self-shielding of carbon monoxide in the solar nebula (Clayton 2002, Lyons and Young

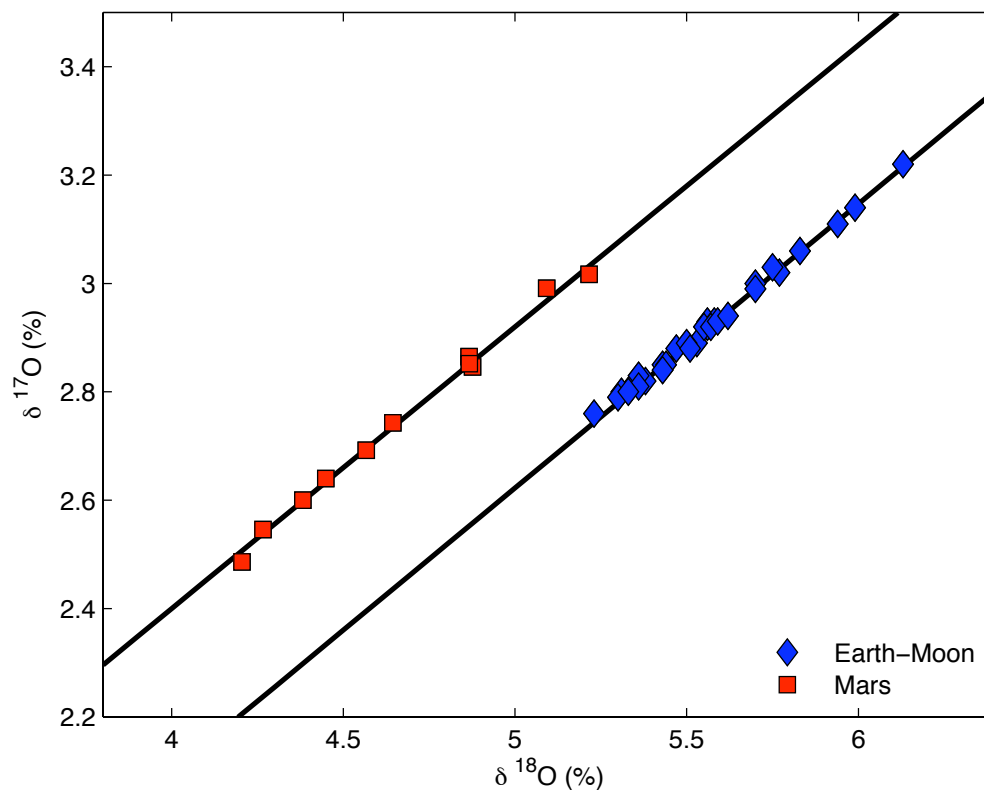
2005) or its parent molecular cloud (Yurimoto and Kuramoto 2004). However, no petrologic process is known to fractionate the isotopes in a mass-independent way, making it possible for samples to precisely reflect the isotopic character of the reservoirs from which they are derived. For this reason, to the extent that the sampled reservoirs are representative of the composition of the parent planets, the isotopic character of the sampled planets is known.

The oxygen isotopic character of the Earth and Moon are indistinguishable. Here, we outline the reasons why this observation is unexpected, present a mixing model as a resolution to this problem, and discuss the implications of this idea for the geochemistry of the Moon, the origin of water on Earth, and constraints on the giant impact.

## 2.2. The Problem

On a three-isotope plot ( $\delta^{17}\text{O}$  vs.  $\delta^{18}\text{O}$ ), samples from a well-mixed planetary body fall on a single fractionation line with slope  $\sim 0.5$ , reflecting mass-dependent planetary fractionation processes (Robert et al. 1992). As a consequence of the heterogeneity in the early solar system, samples from distinct planetary bodies generally fall on distinct, parallel fractionation lines, with the offsets from the terrestrial line measured by  $\Delta^{17}\text{O}$  ( $\equiv \delta^{17}\text{O} - 0.52 \times \delta^{18}\text{O}$ ) in parts per thousand. The isotopic signals represented by  $\Delta^{17}\text{O}$  are inherited by the planets from starting materials during accretion, and are impervious to subsequent geological processes. For example, the fractionation line for samples from Mars are offset from the Earth by  $\sim 0.32$  per mil (Franchi et al. 1999),

forming a benchmark for the length-scale and magnitude of oxygen isotope variations in planetary bodies in the inner Solar System (Figure 2.1).



**Figure 2.1.** Oxygen isotopes for the Earth-Moon system and Mars. Samples from Mars are offset from the Earth by 0.32 per mil, while lunar data are indistinguishable from the Earth at the level of 0.005 per mil. Data from (Franchi et al. 1999, Wiechert et al. 2001)

By contrast, precise measurements on lunar samples reveal that the lunar fractionation line is indistinguishable from the terrestrial line to within the analytical uncertainties (Wiechert et al. 2001). Any difference between the Earth and Moon must be less than

0.005 per mil, which translates to a few percent of the difference between Earth and Mars. The Earth and Moon are isotopically indistinguishable to a very high level of precision, at least with respect to those parts of these bodies for which we have samples.

In the context of the standard giant impact scenario (Canup 2004a, Stevenson 1987), the measured lunar composition places severe constraints on the composition of the impactor. The reason for this is that smooth-particle hydrodynamic (SPH) impact simulations that are successful in forming the Moon suggest that most ( $\sim 80\%$ ) of the material that is injected into orbit is derived from the mantle of the impactor rather than the Earth (Cameron 2000, Canup 2004b, Canup and Asphaug 2001). Hence, even small isotopic differences between the silicate proto-Earth and impactor should have left an observable Earth-Moon difference because the impactor-derived lunar material escapes the diluting effects of mixing with the largest reservoir in the system, the Earth. Although these SPH calculations have their limitations, there is no basis to suppose that they are grossly inaccurate in this prediction. Indeed, this predominance of projectile material injected into orbit is readily understood in terms of the angular momentum of the material upon impact and the role of gravitational torques in raising the periapse of ejecta. These considerations make such an impact different from the extensively analyzed, conventional crater-forming impact events on planets. In any case, as shown below, even a 50-50 mixture would lead to difficulty in explaining the Earth-Moon similarity.

The standard explanation for the precise Earth-Moon match is that the proto-Earth and impactor formed from the same source regions. We can evaluate this possibility in the context of planet formation models and their sampling modes. Present scenarios of planet formation suggest that the process occurs in three stages: the growth of dust grains in the preplanetary disk into kilometer-sized planetesimals, the runaway growth of these planetesimals into lunar- to Mars-sized planetary embryos, and the final accretion of the planets through giant impact events (Chambers 2004).

During the process of runaway growth, embryos rapidly accrete all of the material in their feeding zone on  $\sim 10^5$ – $10^6$  year timescales. The feeding zones are typically only about 0.01 AU wide (Weidenschilling et al. 1997), and hence planetary embryos up to about Mars size — the size inferred for the impacting protoplanet — tend to record the oxygen isotope signature of their immediate vicinity in the disk. The formation of Earth and Venus, by contrast, requires an extended stage of planetary accumulation lasting  $\sim 10^7$ – $10^8$  years and characterized by giant impacts, a stage with a very different mode of sampling compared to that of the precursor embryos. In this last stage of growth, planetary embryos are scattered away from their places of birth. Thus, this stage of the accumulation process is accompanied by significant radial mixing. The planets that undergo giant impacts in this last stage sample material from a broad region of the protoplanetary disk. For example, the material that collects to form the

Earth has significant contributions from regions interior to Mercury and exterior to Mars (Chambers 2001).

In this sense, the provenance of the Earth and Venus is the entirety of the inner solar system, and the composition of Earth does not reflect the composition of material at 1 AU. Hence, even if the impactor were a runaway embryo that sampled material from an annulus  $\sim 0.01$  AU wide centered at 1 AU, or grew near Earth orbit at one of the Lagrange points (Belbruno and Gott 2005), a proto-Earth-impactor difference may be expected. In particular, the Earth collects a substantial fraction ( $> 10\%$ ) of its mass from the region of Mars, which is known to have a composition clearly distinct from the Earth. If the impactor accreted a few percent more or less material from the region of Mars than did the Earth, an Earth-Moon difference would have been observed. Stochastic, large-scale sampling, together with large-scale heterogeneity evinced by the Earth-Mars difference, strongly argues for heterogeneity among planetary embryos.

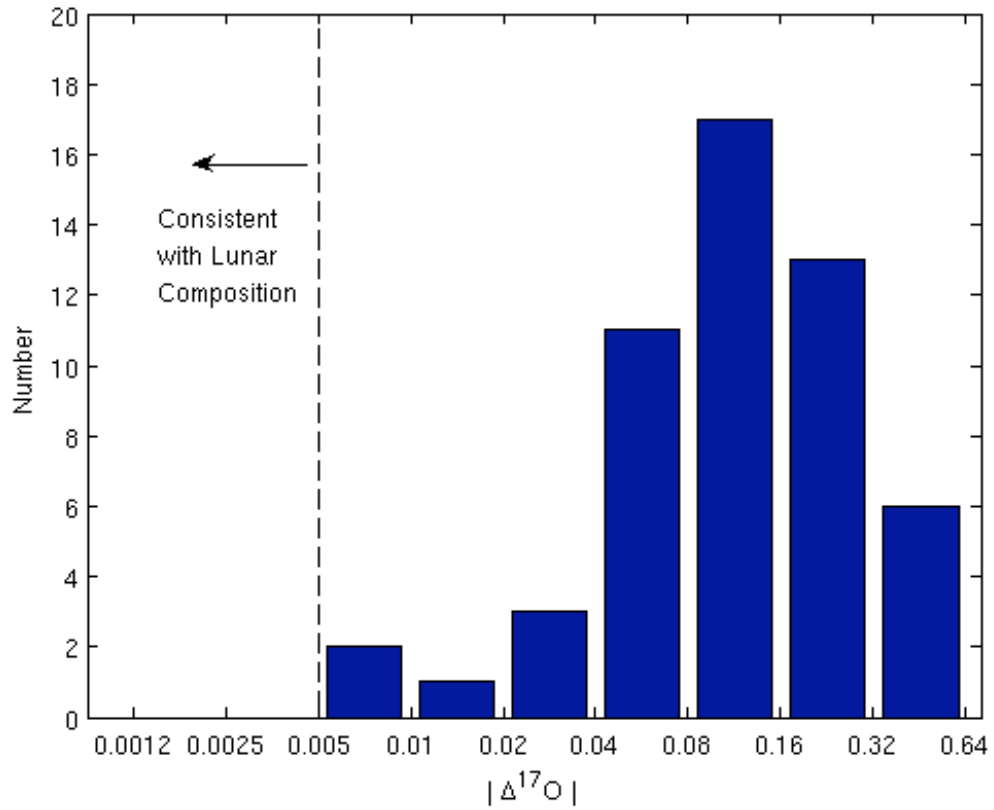
To quantify this argument, we can take the accretion simulations of Chambers (Chambers 2001) and forward model the composition of the impactors onto the forming planets. In this procedure, we take the starting embryos in the simulations and assign values of  $\Delta^{17}\text{O}$  based on heliocentric distance. We then follow the accretion through collisions and trace the provenance of the planets and the impactors that



contribute to their formation. In this way, we can make statements about the compositional scatter of the embryos that participated in giant impacts with the Earth during its formation. We do not know what the isotopic gradients in the inner solar system looked like. However, we do know that there was heterogeneity on the scale of planets, and any proposed initial profile must be consistent with this constraint. The simplest assumption is that there was a linear gradient with heliocentric distance in the inner planet region:

$$\Delta^{17}O(r) = c_1 \times r + c_2. \quad (2.1)$$

One advantage with this assumption is that there are only two free parameters, both of which can be calibrated so that, at the end of the accretion simulation, the third planet from the Sun has the composition of Earth ( $\Delta^{17}O = 0\text{‰}$ ) while the next planet out has the composition of Mars ( $\Delta^{17}O = +0.32\text{‰}$ ). For this purpose, we choose a simulation from (Chambers 2001) that yields four terrestrial planets at its conclusion. The result of this calculation is a histogram of the compositional scatter of impactors onto the forming planets, calibrated to the Earth-Mars difference (Figure 2.2).



**Figure 2.2.** Histogram of the composition of impactors onto the planets in Chambers' [18] simulation 21, calibrated to the Earth-Mars difference. The mean deviation of the impactors' compositions from the final planets is  $\langle |\Delta^{17}\text{O}_{\text{imp}} - \Delta^{17}\text{O}_{\text{planet}}| \rangle = +0.15\%$ . Compositional scatter among incoming impactors is comparable to the differences observed between the planets. None of the impactors in this simulation had a composition similar enough to the target planet to yield the Earth-Moon system. A linear gradient with heliocentric distance is assumed.

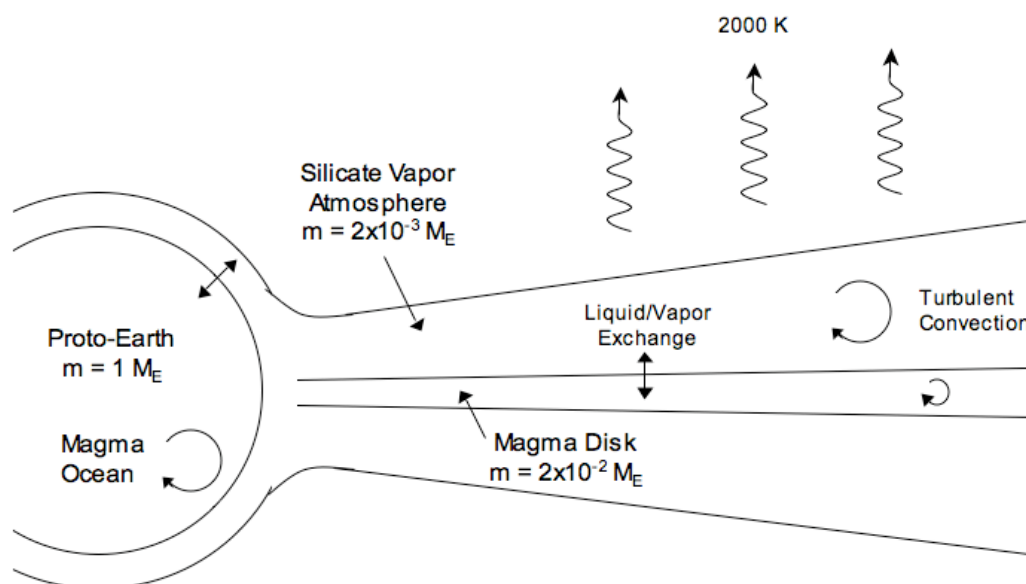
In order to overcome small-number statistics, we include the compositional scatter of impactors onto all four final planets. The main conclusion from this approach is that the scatter among the impactors onto the planets is comparable to the observed differences between the planets. In particular, none of the planetary impactors in this simulation has an isotopic composition similar enough to the final planet to yield the Earth-Moon system.

There are several questions raised by this approach that must be addressed. First, since the oxygen isotope composition of the gas (in CO and H<sub>2</sub>O) may be different from that of the solids (in silicates and oxides), assigning an isotopic composition to a heliocentric distance is only meaningful if the solids are isotopically disconnected, i.e., no longer equilibrating with the gas, and one is referring only to the solids. Second, the oxygen isotope composition of Vesta ( $\Delta^{17}\text{O} = -0.22\text{‰}$ ) (Wiechert et al. 2004), at its present heliocentric distance of 2.4 AU, is inconsistent with a monotonic radial variation in the early solar system. However, a recent model for the formation of differentiated asteroids suggests that Vesta formed in the terrestrial planet region and was later scattered into the asteroid belt (Bottke et al. 2006). Since the orbits of the less massive minor planets can be relatively easily shifted through gravitational scattering, the composition of Vesta is not a strong argument against an initial monotonic gradient in the inner planet region. In any case, both because of its mass and its proximity, we believe that the composition of Mars is a better guide to the gradients that prevailed in the terrestrial planet region during Earth formation.

To summarize, the present composition of the Earth reveals the average composition of contributing impactors, and approximates the composition of the inner solar system as a whole. In the standard picture of planet formation, Mars is a remnant of a population of planetary embryos that collided to form the Earth and Venus. The precise match between the composition of the Earth and Moon is difficult to reconcile with the heterogeneity observed between the terrestrial planets and present scenarios of accretion. The question we now address is whether post-impact mixing processes could have homogenized the Earth-Moon system, reducing any pre-existing isotopic heterogeneity to undetectable levels.

### **2.3. Model**

Immediately after the giant impact, the Earth-Moon system is largely molten and partially vaporized (Canup 2004a). The silicate Earth melts and forms a deep magma ocean, the proto-lunar material forms a circumterrestrial magma disk, and a common silicate-vapor atmosphere links the disk to the planet (Figure 2.3).



**Figure 2.3.** Schematic of Earth and proto-lunar disk immediately after the giant impact. High radiative heat loss guarantees convection in the silicate Earth, disk, and atmosphere. Liquid/vapor exchange with a common silicate vapor atmosphere makes it possible for the two massive liquid reservoirs to equilibrate. Convection within the Earth allows the entire terrestrial silicate reservoir to be tapped.

The terrestrial magma ocean and the proto-lunar magma disk, as well as the enveloping silicate vapor atmosphere, are vigorously convective due to the high heat flow needed to match radiative losses from the photosphere of the planet and disk. Here we show that under such conditions, mixing and equilibration of the Earth's mantle with the proto-lunar disk is possible, and that the terrestrial and lunar material may have approached diffusive equilibrium with respect to their isotopic composition.

The gravitational energy released during the giant impact is large. The timescale to eliminate this heat — and hence to condense the silicate vapor atmosphere — is determined by radiative cooling:

$$\tau_{cool} = \frac{GM_E m_I}{\sigma T_e^4 4\pi R_E^3}. \quad (2.2)$$

An effective photospheric temperature of  $\sim 2,000$  K (Thompson and Stevenson 1988) and an impactor mass  $\sim 0.1 M_E$  (Canup and Asphaug 2001) yields a cooling timescale for the Earth of  $\sim 3 \times 10^3$  years. The corresponding timescale for the proto-lunar disk will be shorter than this estimate because (1) the surface area of the impact-generated disks are typically greater than that of the Earth and (2) only a fraction of the energy of impact is partitioned to the orbiting material. Hence, the cooling timescale for the lunar material will be somewhat shorter, perhaps  $10^2$ – $10^3$  years. In this respect, it is important to emphasize that the thermal energy deposited as heat in the orbiting material — although enough to partially vaporize it — is small relative to the latent gravitational energy that may be gradually released if the disk viscously evolves (Thompson and Stevenson 1988). We will refer back to this point later.

The extended disk atmosphere is contiguous with the silicate vapor atmosphere of Earth and can therefore act as an exchange medium, communicating isotopic signals between the two liquid reservoirs with which it is in contact. Although constituting only a fraction (maybe 10%) of the lunar disk by mass, and an even smaller fraction of

the Earth, the vapor atmosphere may process enough material to equilibrate the massive liquid reservoirs through continuous exchange. Since the silicate vapor atmosphere exists for a finite interval, any diffusive mixing must occur within such a timescale. We adopt the conservative point of view that there is negligible direct transport between the liquid in the disk and the terrestrial magma ocean, consistent with (Thompson and Stevenson 1988). Below, we attempt to estimate the rates of various mixing processes, and to show that they are fast in comparison with the cooling timescale.

### 2.3.1. Convection Within the Earth, Disk, and Common Atmosphere

The energy released during the giant impact will heat both the Earth and the projectile by many thousands of degrees (Canup 2004b). Large-scale motions will be turbulent and even small-scale turbulence will be possible because the silicate melt will be hot and de-polymerized. The heat flux from the system will be limited by radiation from an atmosphere with a photospheric temperature of  $\sim 2,000$  K (Thompson and Stevenson 1988). A crude estimate for the convective velocities required to accommodate these heat fluxes can be derived from mixing length theory (MLT):

$$V_{conv} = \left( \frac{FL}{\rho H} \right)^{1/3}. \quad (2.3)$$

Here  $F$  is the convective flux (equal to the radiative flux in steady-state),  $\rho$  is the density of the convecting medium,  $H$  is the temperature scale height of the system, and  $L$  is

the “mixing length” which represents the length scale associated with the largest eddies. In stellar convection, where MLT has found common application, the mixing length is often taken to be some significant fraction of the scale height of the system. Hence,  $L/H$ , and especially  $(L/H)^{1/3}$  will be of order unity. We take  $L/H = 0.1$ . Using this approach, we can estimate the convective velocity knowing only the temperature at the disk photosphere and the density of the convecting liquid or vapor. For a silicate liquid with  $\rho \sim 3 \times 10^3 \text{ kg/m}^3$ , the convective velocity is  $\sim 3 \text{ m/s}$  whereas a silicate vapor with density  $\rho \sim 3 \text{ kg/m}^3$  (Thompson and Stevenson 1988) carrying the same heat flux requires a convective velocity of  $\sim 30 \text{ m/s}$ . The flux decreases to zero at the disk mid-plane, but this will not affect these estimates for the largest-scale eddies. Rotation may inhibit the length-scales somewhat, through the Coriolis effect, but if one chose  $L$  so that  $v/\Omega L \sim 1$  where  $\Omega$  is the Keplerian rotation, then this predicts a smaller velocity by a factor of only a few.

The corresponding turnover timescales ( $\equiv L/v$ ) are: a *week* for the Earth’s mantle, and several *hours* in the magma disk and vapor atmosphere. Turnover timescales turn out to be much faster than the timescales for other processes, discussed below. Vertical mixing *within* the Earth, disk, and vapor atmosphere is fast compared to the cooling timescale, and is unlikely to be the rate-limiting step in Earth-Moon equilibration. Such rapid turnover makes it possible for material in each reservoir to be tapped for exchange through continuous exposure to liquid/vapor interfaces.



### 2.3.2. Liquid/Vapor Exchange

In this section, we attempt to estimate the timescale for the evaporative exchange of atoms between the liquid and vapor phases, both at the Earth-atmosphere interface, and the disk-atmosphere interface. This timescale is important because the vapor phase is the main carrier of isotopic signals between Earth and disk, but represents only a fraction, (maybe 20%) of the disk mass, and an even smaller fraction of an Earth mass. Hence, for the signals to be successfully communicated between the liquid reservoirs, there must be continuous, efficient liquid-vapor exchange.

In thermal equilibrium and with a slow change in mass fraction of the co-existing phases, the flux of atoms across the phase boundary is nearly the same in either direction. Evaporative exchange from the gaseous phase to the liquid can be estimated using the kinetic theory of gases. Aside from a constant numerical factor, the flux of gas molecules incident on the liquid surface is simply the product of the number density and the average thermal velocity. To get the exchange rate, this kinetic rate must be multiplied by a condensation coefficient, which represents the fraction of molecules impinging on the liquid surface that enter the liquid phase. Assuming ideal gas behavior for the vapor, the timescale to exchange the mass of the magma disk with the atmosphere is given by:

$$\tau_{ex} = \sigma V_t / P \alpha_c. \quad (2.4)$$

where  $\sigma$  is the surface mass density of the magma,  $V_t$  is the molecular thermal velocity,  $P$  is the vapor pressure, and  $\alpha_c$  is the condensation coefficient. For the most abundant silicate mineral in planets ( $\text{Mg}_2\text{SiO}_4$ , forsterite), its numerical value is  $\sim 0.1$  (Inaba et al. 2001). For a  $\sim 2$  lunar-mass disk extending out to  $\sim 5$  Earth radii,  $s \sim 5 \times 10^7 \text{ kg/m}^2$ . The vapor pressure of silicates at temperatures of  $\sim 3,000 \text{ K}$  is  $\sim 10\text{--}100$  bars (Thompson and Stevenson 1988). Finally, for a forsterite vapor composed of  $\text{MgO}$ ,  $\text{SiO}$ , and  $\text{O}_2$  (Stevenson 1987), the mean molecular weight is  $\sim 40$  amu, which yields a thermal velocity of  $\sim 1 \text{ km/s}$ . These parameters, which apply to the Earth-atmosphere interface as well as the disk-atmosphere interface, suggest that the exchange of several lunar masses of material across the phase boundary requires a timescale of the order of a week.

However, rapid exchange across a liquid-vapor interface does not guarantee rapid equilibration of the phases. The reason is that in the absence of diffusion or fluid motions within each phase, the *same* atoms are exchanged across the phase boundary. In this respect, it is important that the exchange is occurring in a two-phase medium (the liquid is interspersed with vapor bubbles, and the vapor with liquid droplets) that enhances the surface area for evaporative exchange compared to a smooth liquid/vapor interface.

Although the disk may undergo phase separation, allowing the liquid to settle (Machida and Abe 2004), the viscous evolution of the disk liberates enough energy to vaporize the disk (Canup 2004a). Indeed, as emphasized by (Thompson and Stevenson 1988),

the disk will be in a thermally regulated state such that the viscous self-heating balances the radiative cooling. Hence, in addition to the vapor that condenses at high levels in the atmosphere, generating clouds and droplets, part of the liquid magma vaporizes, generating bubbles. Since the timescale for the rainout of droplets may be as short as a week (Machida and Abe 2004), advective transport between liquid and vapor may be determined by the rate at which the vapor condenses into droplets via radiative cooling. The timescale to condense the mass of the vapor atmosphere, and hence to advect the vapor composition to the liquid disk is:

$$\tau_{rain} = L\sigma_v / F. \quad (2.5)$$

where  $L$  is the latent heat of condensation for silicates,  $\sigma_v$  is the surface density of the vapor atmosphere, and  $F$  is the radiative flux. For  $L \sim 10^7$  J/kg,  $\sigma_v \sim 10^7$  kg/m<sup>2</sup> corresponding to a disk composed of  $\sim 20\%$  vapor, and  $F$  determined by an effective radiating temperature of  $\sim 2,000$  K, this timescale turns out to be of order one year. As mentioned earlier, the latent gravitational energy gradually liberated by the disk viscously exceeds its thermal energy, allowing many rainout cycles to take place before the disk cools and condenses. Thus, the continuing process of phase separation amounts to a rapid, vertical advective transport between the liquid and the vapor, and may be instrumental in equilibrating the two phases.

In summary, the liquid/vapor exchange across the phase boundary is fast — it occurs on a timescale of a week — but this does not guarantee phase equilibration.

Liquid/vapor exchange is facilitated enormously by the fact that the process is taking place in a two-phase medium. As an example, air/sea exchange on the present Earth occurs much faster than would be expected due to the presence of bubble plumes near the ocean surface (Asher et al. 1996). An analogous process in the lunar disk might enable equilibration of the liquid and vapor on a timescale of years. Hence, liquid/vapor exchange is unlikely to be the rate-limiting step in the equilibration of the Earth and Moon.

### 2.3.3. Exchange from the Earth to Disk

Although the common atmosphere surrounding the Earth and disk is continuous, it nevertheless can be dynamically distinguished into two distinct regimes. The silicate vapor atmosphere surrounding the post-impact Earth is mainly supported against gravity by pressure gradients, whereas the disk atmosphere is supported by pressure gradients in the vertical direction, but mainly supported by nearly Keplerian rotation in the radial direction. Since the Earth will be rotating significantly slower than breakup velocity, there will be a velocity shear of several kilometers per second that separates these two dynamical regimes in the common vapor atmosphere.

The shear instability that results from this velocity difference is likely to facilitate a constant exchange across this dynamical interface. However, the gas density in this region may be lower than elsewhere because the atmospheric scale height is much smaller than the planetary radius. For the present, we make the assumption that is

most favorable to the mixing hypothesis, namely, that the exchange across this region is faster than elsewhere.

#### 2.3.4. Radial Mixing Within the Disk

We have argued above that the processes necessary for Earth-Moon equilibration through exchange with a vapor atmosphere: convection, liquid/vapor exchange, and exchange across a dynamical interface, are possibly fast in comparison with the cooling timescale. If this is indeed the case, then the rate-limiting step for Earth-Moon equilibration will be radial mixing through the proto-lunar disk. The reason for this is that the Moon forms from the outer-most disk material (Ida et al. 1997), and so it is important to quantify the extent to which the inner regions of the disk can communicate their terrestrial isotopic signals to the regions from which the Moon forms.

We assume that the liquid disk and its vapor atmosphere are turbulent, and that the fluid motions can be characterized by an eddy diffusivity (Tennekes and Lumley 1972).

We can then write Fick's Law:

$$\vec{J} = -\rho f_v D \vec{\nabla} c. \quad (2.6)$$

where  $J$  [ $\text{kg m}^{-2} \text{s}^{-1}$ ] is the mass flux,  $\rho$  is the density of the two-phase fluid,  $f_v$  is the vapor fraction,  $D$  is the turbulent diffusivity of the vapor, and  $c$  is the mass fraction of a passive tracer. Here, we have assumed that the liquid is stationary while the vapor is

diffusive because the vapor will be undergoing more vigorous convective motions than the liquid (Section 2.3.1). This equation can nevertheless describe changes in the composition of the liquid if there is rapid vertical equilibration of the liquid and vapor phases, i.e., the signals carried by the vapor are communicated to the liquid (Section 2.3.2). We take the divergence of equation (2.6) and combine it with the continuity equation to get:

$$\frac{\partial(\rho c)}{\partial t} = \bar{\nabla} \cdot (\rho f_v D \bar{\nabla} c). \quad (2.7)$$

For simplicity, we only consider a static disk, so that the density will be time-independent and can be taken out of the time-derivative. This assumption is valid as long as we consider timescales shorter than the timescale for the evolution of the disk, which may be  $10^2$ – $10^3$  years. Finally, because very little mass lies above the radiative photosphere, most of the disk will participate in the convective fluid motions. Hence, to a good approximation, we can integrate equation (2.7) in the direction perpendicular to the disk plane to yield:

$$\sigma \frac{\partial c}{\partial t} = \bar{\nabla} \cdot (\sigma f_v D \bar{\nabla} c). \quad (2.8)$$

where  $\sigma$  [ $\text{kg m}^{-2}$ ] is the total surface density. We can solve this equation in cylindrical coordinates with two boundary conditions. (1) The composition at the inner boundary of the disk is taken to be equal to the terrestrial composition, and constant with time,

i.e.,  $c(r = R_E, t) = 0$ . Even though  $c$  represents a mass fraction, we can shift the terrestrial composition to zero because the diffusion equation is linear. The time-independence of this boundary condition reflects the circumstance that convection within the Earth (Section 2.3.1), liquid-vapor exchange of terrestrial silicates (Section 2.3.2) and vapor exchange at the Earth-disk interface (Section 2.3.3) are efficient processes, enabling the entire terrestrial magma ocean to be tapped. This condition is satisfied to good approximation as long as the mass of the post-impact Earth that participates in the equilibration is much greater than the mass of the lunar disk. (2) There is zero net-flux at the outer boundary of the disk, i.e.,  $\partial c / \partial r(r = R_{out}, t) = 0$ . This condition stems from the assumption that all fluid parcels that reach the outer disk boundary reflect back and continue to participate in the turbulent motions. In effect, we neglect condensation and moonlet formation from the outer edge of the disk, possibly a valid assumption as long as we consider timescales shorter than the cooling time.

To solve this equation, we need to know the vapor fraction,  $f_v$ , and also something about the mass distribution,  $\sigma(r)$ . One possible approach uses the results from the impact simulations, which yield disk vapor fractions of  $\sim 20\%$  (Canup 2004b) and show that  $\sigma(r)$  decreases roughly as  $\sim 1/r$  (pers. comm., Robin Canup). To estimate the vigor of turbulent mixing, we parameterize the diffusivity in terms of the alpha model and present our results in terms of the alpha parameter. Later, we use mixing

length theory to estimate a value for alpha that may be realistic. The diffusivity can be written as:

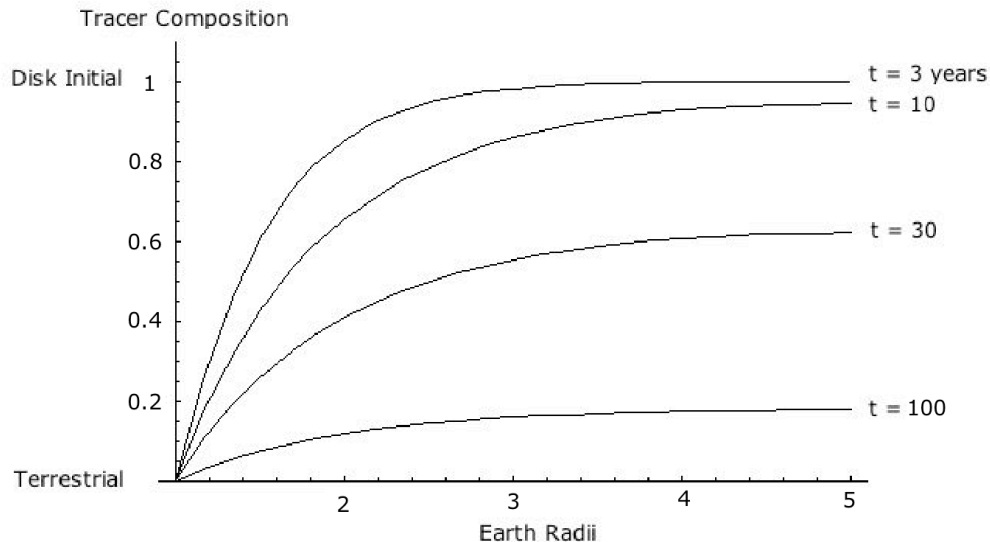
$$D = \alpha c_s H \quad (2.9)$$

where  $c_s$  is the gas sound speed, which, for a temperature of  $\sim 2,500$  K and a mean molecular weight of  $\sim 40$  amu for silicate vapor is  $\sim 1$  km/s.  $H$  is the pressure scale height of the disk atmosphere, which corresponds to  $\sim 10^3$  km in the inner regions of the disk and increases as  $\sim r^{3/2}$  in our model, as expected for a roughly isothermal disk.  $\alpha$  is a dimensionless number that parameterizes the vigor of the turbulent motions. This parameter is often introduced in the context of “viscous” disk evolution (Lynden-Bell and Pringle 1974, Shakura and Sunyaev 1973) but it is important to understand that we are here using it for mixing, not net mass transfer. Both processes may occur, but the net mass transfer could be zero and our model still work. In fact, the ability of turbulence to redistribute angular momentum is questionable (Ji et al. 2006).

## 2.4. Results

In the previous section, we have argued that the rate-limiting step for Earth-Moon equilibration is radial mixing through the proto-lunar disk. Here, we present results of calculations of radial mixing subject to the assumptions described above. Figure 2.4 shows snapshots of the disk composition at various times.

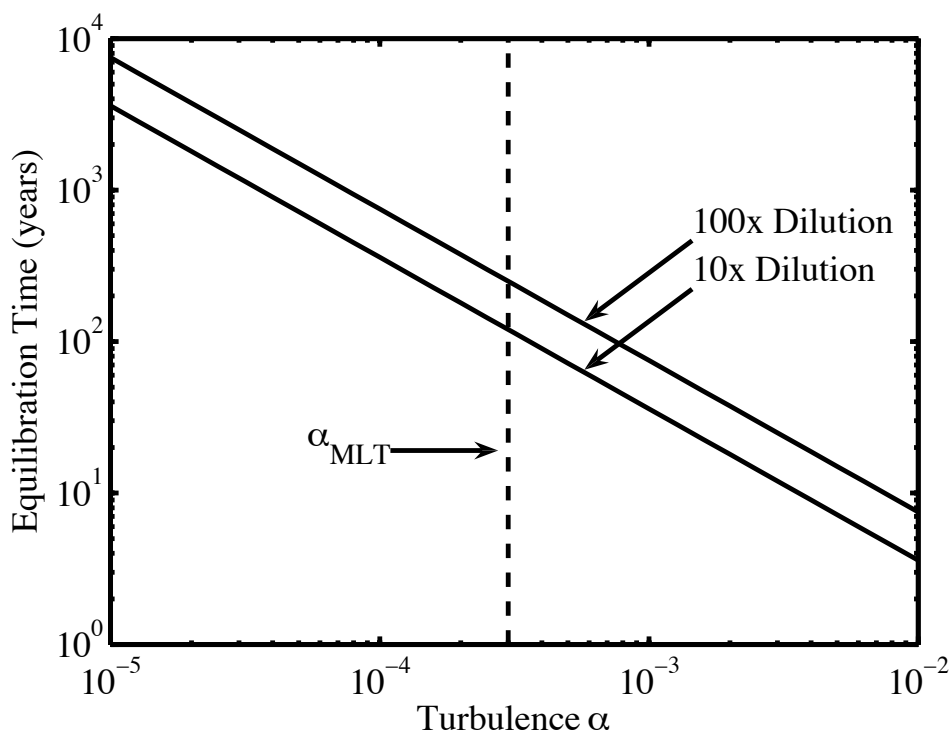




**Figure 2.4.** Snapshots of the solution to the diffusion equation, with the value of the tracer composition plotted against the cylindrical radius. The Earth's tracer composition is defined as zero and is unchanged by mixing; the initial composition of the disk is unity. Such mixing applies to passive tracers that readily partition between the liquid and vapor.

Initially, exchange with the Earth causes the inner regions of the disk to become contaminated with terrestrial composition. As the diffusion proceeds, the composition of the disk becomes progressively more Earth-like. Turbulent mixing may proceed for a time period comparable to the cooling timescale, after which diffusive exchange between the Earth and disk halts due to the condensation of the vapor into the liquid phase. The mean composition of the Moon is then obtained by integrating the composition of the outer half of the disk.

The longer the turbulent diffusion proceeds, the greater is the dilution of the Earth-Moon difference from post-impact levels. We can define an equilibration time as the timescale to reduce the Earth-lunar disk difference by a factor of 10–100. (From Figure 2.2, the majority of impactors require dilution of such magnitude to yield the measured lunar composition). Figure 2.5 displays the quantitative trend of how the vigor of turbulence reduces the equilibration time. The main result from these calculations is that for timescales of  $10^2$ – $10^3$  years, efficient mixing between the Earth and the lunar-forming material requires alpha values of  $10^{-3}$ – $10^{-4}$ .



**Figure 2.5.** Timescale to dilute the Earth-Moon isotopic difference as a function of the diffusive turbulence alpha parameter. The lunar composition is obtained by

integrating the composition of the outer half of the disk. Mixing length theory gives a  $\sim 3 \times 10^{-4}$  corresponding to 100x dilution in  $\sim 250$  years. The equations for the two lines are  $T(\text{years}) = 0.75/\alpha$  and  $T(\text{years}) = 0.36/\alpha$ .

What is a realistic value for alpha? To estimate the vigor of turbulence in the lunar disk, we must have some idea of the physics that underlies the instability that leads to turbulence. If we assume that thermal convection is the primary source of turbulence, we can calculate the diffusivity as the product of the convective velocity, derived from mixing length theory, and the length scale associated with the convection:

$$D = V_c L. \tag{2.10}$$

Here,  $L$  is the “mixing length”, which represents the size of the largest convective eddies, and is typically taken to be some significant fraction of the scale height of the system. Here we take  $L/H = 0.1$ . For such a diffusivity, we get an alpha value of  $\sim 3 \times 10^{-4}$  suggesting that efficient turbulent mixing across the extent of the lunar disk is possible. This simple estimate ignores the effects of rotation, which may inhibit radial diffusion, and should be taken as an upper limit. As noted previously, modestly smaller length scales (i.e.,  $L \sim 10$  km) may not change the velocity estimate much but in equation (2.10) such a small eddy size might prevent our mechanism from working.

## 2.5. Discussion

These calculations suggest that extensive mixing between the Earth and the lunar disk is possible. However, there are unresolved questions that prevent a more definitive conclusion. For example, since the Moon forms from the outermost disk material, it may not fully participate in the diffusion occurring between the inner regions and the Earth. In particular, the outermost regions of the disk cool faster, perhaps freezing and cutting off a fraction of the proto-lunar material from isotopic exchange. Furthermore, it is not yet clear whether efficient exchange of material between the terrestrial and disk atmospheres occurs. Despite these uncertainties, it is possible that the Moon will form with a significantly more Earth-like oxygen isotope signature than the impactor that triggered its formation.

Current scenarios of planet formation suggest that the Earth and the impactor are unlikely to have had the same composition to within the analytical measurements. Here, we have explored the possibility that such formation theories are correct, and that the Earth-Moon system equilibrated in terms of oxygen isotopes in the aftermath of the giant impact. However, it is also possible that current scenarios of late-stage planet formation are incomplete, and that the predictions they make regarding radial mixing are incorrect. In particular, there are processes, such as non-accretionary collisions, dynamical friction with a sea of small bodies, and interaction with a small amount of residual nebular gas, that are not fully incorporated in present dynamical simulations, and that may be important in determining the final provenance of the terrestrial planets.

This raises the possibility that Mars is anomalous, that is, the Earth-Mars difference is not representative of the scatter between the embryos that collided to form the Earth. In the present formation scenarios, the source regions of the Earth and Mars overlap, and the Earth accretes a significant amount of material from the Mars region, with compositions that presumably match that of Mars. However, the same dynamical simulations are unable to produce planets with masses as low as Mars or Mercury (Chambers 2001). It has been recognized that the depletion in mass from the region of Mars may be the tail end of the depletion of the asteroid belt, and may not be a feature that arises from late-stage accretion. In this regard, it is worthwhile to attempt to track the fate of material originating in the region of Mars. In particular, while > 10% of the planetary embryos in the asteroid belt that are removed by mean-motion resonances collide with the terrestrial planets, those embryos that are removed by the secular resonance at 2.1 AU are dynamically excited so rapidly that they almost always collide with the Sun (Chambers and Wetherill 2001). It is important to continue to consider the fate of Mars-like material in order to clarify the meaning of oxygen isotopes for planet formation.

Although oxygen isotope measurements are at present not available for Venus and Mercury, the dynamical scenarios predict that rocks from Venus, which also sampled a wide region of the inner solar system, will fall on a fractionation line close to, but not identical with, that of the Earth-Moon system. Similarly, the scenario outlined here, whereby it is assumed that the innermost solar system exhibits heterogeneity in oxygen

isotope abundances, suggests that Mercury, which was the product of a few runaway embryos, can be expected to have an oxygen isotope anomaly comparable in magnitude to that of Mars. The identification of meteorites or the successful completion of sample return missions from these planets may one day enable us to test these predictions.

## 2.6. Implications

### 2.6.1 Lunar Geochemistry

What are the implications of the proposed model for the geochemistry of the Moon? The turbulent mixing and equilibration that is invoked to explain the Earth-Moon similarity in oxygen isotopes is not restricted to the element oxygen, but may include other tracers of terrestrial mantle composition, for example, silicon (Georg et al. 2007). If the chemical composition of the liquid and vapor were the same, then isotopic homogeneity through turbulent mixing between the silicate Earth and Moon would necessarily imply chemical homogeneity as well. However, equilibrium thermodynamics dictates elemental fractionation between the liquid and vapor. For example, it has been experimentally determined (Nagahara et al. 1994) that fayalite ( $\text{Fe}_2\text{SiO}_4$ ) has a higher vapor pressure than forsterite ( $\text{Mg}_2\text{SiO}_4$ ). For this reason, it is likely that the silicate vapor will have a higher Fe/Mg ratio than the silicate liquid with which it is in contact. This can cause a compositional difference between silicate Earth and Moon even in a closed system where no vapor escapes to infinity. Although a detailed treatment of the chemical consequences of equilibration is beyond the scope of this chapter, we merely note that melt-vapor equilibrium includes isotopic, as well as

elemental fractionation. Hence, major-element chemical differences between the silicate Earth and Moon (Jones and Palme 2000) will, in this model, be accompanied by mass-dependent isotopic differences. Determining the expected magnitude of such equilibrium isotopic fractionation will be the topic of Chapter 4.

### 2.6.2. Origin of Water on Earth

Among the chief differences between Earth and Moon is the stark depletion of volatile elements on the Moon, including water. The model we have put forward suggests that the Earth should have transmitted a volatile-element signal to the lunar material. However, the lunar rocks are strongly depleted in volatile elements relative to the terrestrial mantle (Ringwood 1979). The resolution to this dilemma may be the consideration of open-system processes such as hydrodynamic escape. Hydrogen in the lunar disk will be unbound (Stevenson 1987), and it is well known that a hydrodynamic wind of light elements is capable of entraining heavy elements (i.e., Na, K) in the outflow that would not escape of their own accord (Hunten et al. 1987). Whether or not a particular element significantly escapes depends on its volatility, abundance, and atomic mass. To determine whether the proposed mixing scenario can be reconciled with the lunar depletion of volatile elements, it will be necessary to take such considerations into account. Here, we merely note that if the scenario that we have outlined is correct, the lunar depletion of volatile elements may require the Earth to transport hydrous materials to the lunar disk to drive an outflow, a constraint that requires the Earth to have accreted significant amounts of water before the moon-forming giant impact.

### 2.6.3 Constraints on the Giant Impact

Among the most striking differences between the Earth and Moon is the bulk lunar depletion of iron (by  $\sim 3x$  from cosmic composition). The present explanation for this depletion is the differentiation of the impactor prior to the giant impact, and the preferential injection of impactor mantle into circumterrestrial orbit. However, in the scenario that we have outlined here, turbulent mixing and equilibration with the terrestrial mantle may remove iron from the orbiting disk, obviating the necessity for the giant impact to directly account for this fundamental Earth-Moon difference. Although not demonstrated here, it may be possible to relax this constraint on giant impacts capable of producing an iron-depleted Moon. At the same time, the necessity of equilibrating oxygen isotopes may require an additional constraint. Current impacts place roughly an equal amount of material interior and exterior to the classical Roche limit (Canup 2004b) defined by the lunar bulk density at 2.9 Earth radii. Inside this radius, tidal forces prevent the disk material from aggregating. Although a small amount of vaporization will greatly reduce the density and move the Roche radius outward, outside of the classical Roche radius, pure melts/solids may accrete when they collide. For this reason, a more massive, Roche-interior initial disk may be a more conducive starting condition for equilibration.

## 2.7. Conclusions

Dynamical simulations of terrestrial planet formation suggest that the Earth and the moon-forming impactor did not have identical source regions. The heterogeneity implied by the oxygen isotope difference between Earth and Mars suggests that the



impactor may have been isotopically distinct. The model we have put forward suggests that in the aftermath of the giant impact, the proto-Earth and the proto-lunar disk may have approached diffusive equilibrium, reducing any pre-existing differences in oxygen isotope composition, and perhaps eliminating any primary heterogeneity in the Earth-Moon system. This model has testable consequences for the geochemistry of the Earth and Moon. Unraveling the oxygen isotope story in the inner solar system, for example, by sampling Venus and Mercury, may help to resolve the long-standing problem of the provenance of the terrestrial planets. The possibility explored here is a first step towards understanding the meaning of oxygen isotopes for lunar formation.

## CHEMICAL FRACTIONATION

**Abstract**

Despite its importance to questions of lunar origin, the chemical composition of the Moon is not precisely known. In recent years, however, the isotopic composition of lunar samples has been determined to high precision, and found to be indistinguishable from the terrestrial mantle, despite widespread isotopic heterogeneity in the Solar System. In the context of the giant impact hypothesis, a high level of mass-independent isotopic homogeneity can be generated if the proto-lunar disk inherits the isotopic character of the post-impact Earth through turbulent mixing while the system is extensively molten and partially vaporized. In the absence of liquid-vapor separation, such a model leads, in addition, to the lunar inheritance of the Earth mantle chemical composition. Hence, the turbulent mixing model raises the question of how chemical differences arose between the silicate Earth and Moon. Here we explore the chemical consequences of liquid-vapor separation in one of the settings relevant to the lunar composition: the transient, silicate vapor atmosphere of the post giant-impact Earth. We show that liquid droplets suspended in the vapor atmosphere of Earth can equilibrate with the intervening vapor on a timescale short relative to convective turnover timescales, motivating calculations using equilibrium thermodynamics. We quantify the extent to which removal of liquid droplets by rainout can enrich the upper atmosphere in the residual vapor, and show that plausible parameters can generate the widely postulated  $\sim 2x$  enhancement in the FeO/MgO

ratio of the silicate Moon relative to Earth mantle. We quantify the extent to which such an enhancement in the vapor depletes the lunar material in refractory elements and use our results to determine the range of lunar compositions consistent with inheritance from the post impact silicate vapor atmosphere of Earth.

### **3.1. Introduction**

The Moon is generally thought to have formed from the debris generated by the off-center collision of a Mars-sized proto-planet with the proto-Earth towards the end of accretion (Cameron and Ward 1976, Hartmann and Davis 1975). Such a scenario can explain the angular momentum of the Earth-Moon system, the lunar metal depletion (Cameron 2000, Canup 2004b, Canup 2008, Canup and Asphaug 2001), and the terrestrial isotopic character of the lunar material (Pahlevan and Stevenson 2007). However, no quantitative model exists that can explain the chemical composition of the silicate Moon and its relationship to high-temperature processes that must have followed a giant impact.

A weakness of the giant impact hypothesis has been that its predictions regarding lunar chemistry have never been clearly articulated. The reasons are twofold. First, smooth-particle hydrodynamic (SPH) impact simulations consistently derive the initial disk of material orbiting the Earth primarily from the mantle of the impactor (Cameron 2000, Canup 2004b, Canup 2008, Canup and Asphaug 2001) whose composition cannot be independently known. Second, we do not yet have a complete scenario of lunar formation starting with the impact event and ending with a fully formed Moon (Canup

2004a, Stevenson 1987). In particular, the SPH simulations generate a hot, melt-vapor circumterrestrial disk on a timescale of hours while it may take  $\sim 10^3$  years of cooling before lunar accretion sets in, a time during which the lunar-forming material may have been processed and altered. The compositional signatures of the giant impact may have been imprinted while the lunar material existed in the form of such a melt-vapor disk (Machida and Abe 2004, Thompson and Stevenson 1988), or even during lunar accretion (Abe et al. 1998), important stages of the evolution that have received limited attention. At present, it is not clear to what extent the lunar composition represents a snapshot of the mantle of the impacting planet or subsequent processes immediately following the giant impact and prior to the formation and closure of the Moon.

The passage of the lunar-forming material through a high-temperature partially vaporized disk, an era lasting up to  $\sim 10^3$  years, makes possible processing of the lunar material through turbulent exchange with the Earth's post-impact atmosphere (Pahlevan and Stevenson 2007), hydrodynamic escape of vapor to infinity (Genda 2004, Genda and Abe 2003), and precipitation of liquid droplets (Machida and Abe 2004), processes that have the potential to determine the chemical and isotopic composition of the resulting Moon. Turbulent mixing of the Earth-Moon system in the fluid aftermath of the giant impact is supported by similarities between the silicate Earth and Moon in the isotopes of oxygen (Wiechert et al. 2001), an element that exhibits mass-independent heterogeneity in the solar system and whose isotopic composition can therefore be used to recognize genetic relationships between planets. Tungsten isotopes, sensitive to the timescale of accretion and core-formation in

planets (due to the decay of lithophile  $^{182}\text{Hf}$  to siderophile  $^{182}\text{W}$ ), have recently been observed to exhibit homogeneity in the silicate Earth-Moon system (Nimmo et al. 2010, Touboul et al. 2007, Touboul et al. 2009). Due to the asymmetric nature of the giant impact, and the fact that more massive planets take longer to accrete, such an isotopic homogeneity is unexpected (Nimmo et al. 2010), and likely requires turbulent mixing of W isotopes in the fluid aftermath of the giant impact. W isotopes can equilibrate if — in the oxidizing environment of the giant impact — tungsten becomes a volatile element and partially partitions into the vapor. However, this is not necessary. W isotopes in the silicate Earth-Moon system may also become homogenized if W quantitatively partitions into the liquid, but the droplets into which it partitions remain coupled to the exchanging turbulent vapor. This is the scenario explored in this chapter (and further discussed in Section 3.5). The question of W equilibration is an important one because the tungsten isotopic homogeneity of the silicate Earth-Moon system is observed despite the fact that these two silicate reservoirs appear to have distinct Hf/W ratios. Hence, the equilibration of W isotopes provides an internal Earth-Moon isochron that yields the most precise limits on the timescale of Earth accretion. W isotopes provide evidence for turbulent mixing, but they also provide an example of how the question of turbulent mixing can have far-reaching implications for the meaning of the lunar chemical and isotopic composition (in this case as a precise chronometer for terrestrial accretion). In addition, the hypothesis that the lunar material acquired its composition from a partially vaporized Earth mantle through turbulent exchange is attractive because it has testable consequences.

One consequence of the equilibration hypothesis is that liquid-vapor equilibrium and partial separation may have played a central role in lunar formation. At sufficiently high temperature, the isotopic fractionation between co-existing phases approaches zero (Urey 1947). Chemically, because silicate mantles are multi-component systems, the composition of a silicate liquid and its co-existing vapor will, in general, be distinctly different. This behavior of high temperature equilibrium — of similar isotopic but different chemical composition of co-existing phases — makes it a prime candidate for explaining isotopic similarities and chemical differences in the silicate Earth-Moon system. Here, we explore a scenario in which liquid-vapor fractionation in the post giant-impact environment can *evolve* chemical differences even as it eliminates isotopic heterogeneity via large-scale mixing.

### **3.2. The Role of Liquid-Vapor Fractionation**

There are multiple settings in which liquid-vapor fractionation may have taken place, each with different consequences for the composition of the Moon. First, there is phase separation (“rainout”) in the Earth’s post-impact atmosphere. This is relevant to lunar composition if the proto-lunar disk exchanges material with the Earth’s silicate vapor atmosphere and ultimately inherits its composition, as has been proposed to account for the terrestrial oxygen isotopic character of lunar matter (Pahlevan and Stevenson 2007). In such a setting, any fractionation leads to vapor enrichment in the lunar composition, as rainout removes liquid droplets from ascent to the upper atmosphere that Earth exchanges with the proto-lunar disk. Second, fractionation is

possible in the proto-lunar disk itself, the precipitation of droplets towards the mid-plane separating the liquid from the vapor. However, due to our poor understanding of the disk evolution, we do not yet know if phase-separation in the disk ultimately enhances the lunar material in the liquid or vapor. Finally, fractionation is possible via outgassing from a lunar magma ocean and escape of the resulting transient atmosphere from the lunar gravity field, or from precursor liquid moonlets. Such fractionation would enhance the lunar material in liquid through the elimination of vapor.

The lunar bulk composition is not well known. There are mutually exclusive viewpoints on the bulk lunar FeO/MgO ratio and refractory element abundances, for example. One of the goals of this work is to demonstrate that not all proposed lunar compositions can be derived from the Earth mantle via liquid-vapor fractionation. As we show below, the behavior of the most abundant components (FeO-MgO-SiO<sub>2</sub>) is tied to the fate of more refractory (i.e., CaO, Al<sub>2</sub>O<sub>3</sub>) as well as more volatile (i.e., Na<sub>2</sub>O, K<sub>2</sub>O) elements. Partitioning Earth mantle material into a liquid and complementary vapor, a single stage enhancement of vapor via partial removal of liquid leads to a composition with a higher FeO/MgO ratio, a depletion of refractory elements, and an enhancement in volatile elements. Hence, a one-stage model producing a higher lunar FeO/MgO ratio (discussed below) is incapable of generating an enrichment of refractory elements or the volatile element depletion of the lunar material starting from Earth mantle composition.

Large depletions of volatile elements may, nevertheless, occur via partial vaporization or incomplete condensation and removal of the most volatile fraction of the material, for example, during the lunar magma ocean and molten disk stage, respectively. Since extreme depletions of volatile elements are observed, such an episode of fractionation must be taken seriously. However, the process responsible for the volatile-element depletion may have been de-coupled from the major-element fractionation, leaving the lunar FeO/MgO ratio essentially unchanged. No researcher has claimed that the silicate Moon is *depleted* in its FeO content relative to Earth mantle. Hence, if the lunar material was derived from the Earth's mantle via liquid-vapor fractionation, then the process responsible for the volatile element depletion was evidently not effective at depleting the most volatile major-element component, FeO. The volatile element depletion may have been restricted to elements less abundant than the major elements, for example, if the process responsible for the depletion was energy-limited.

Here, we restrict ourselves to fractionation that occurs via rainout in the post giant-impact silicate vapor atmosphere of Earth. We focus on a major-element compositional feature: the FeO/MgO ratio of the silicate Moon, a ratio sometimes inferred to be significantly higher than (Hood and Jones 1987, Mueller et al. 1988, Ringwood 1977), and sometimes inferred to be essentially identical with (Warren 2005), the terrestrial mantle. We choose this chemical tracer for several reasons. First, both iron and magnesium are major elements in silicate mantles, and their lunar abundances are therefore constrained — even in unsampled regions — by geophysical measurements. Second, these oxides — and their corresponding silicates — have



significantly different behavior during vaporization, FeO being much more volatile than MgO (Nagahara et al. 1988), making the FeO/MgO ratio a sensitive tracer of liquid-vapor separation. Third, thermodynamic data for major elements exist at the temperatures of relevance ( $T = 2,500\text{--}3,500$  K). The question we ask is whether an elevated lunar FeO/MgO ratio can be evolved from the partially vaporized magma ocean of Earth via liquid rainout in the convective vapor atmosphere, and what the consequences of such a process would be for the abundances of refractory elements in the Moon. In this way, we determine the range of lunar bulk compositions that can be derived from the Earth mantle via liquid-vapor fractionation.

### 3.3. Mantle Model

The composition of the Earth's mantle is constrained by direct samples from the mantle, the composition of basalts generated by partial melting of the mantle interpreted with the insights of experimental petrology, and seismology. Through these methods, it has been determined that the Earth's upper mantle has an FeO content of  $\sim 8$  weight percent and a molar Fe/Fe+Mg ratio of  $\sim 0.1$  (O'Neill and Palme 1998). A compositional difference between the upper mantle and deep mantle cannot be excluded but is not compelled by any geochemical or geophysical argument. Furthermore, the Earth's upper mantle has an Mg/Si ratio that places its composition (in the MgO-SiO<sub>2</sub>-FeO system) between olivine (Fe,Mg)<sub>2</sub>SiO<sub>4</sub> and pyroxene (Fe,Mg)SiO<sub>3</sub>. Because we are interested in investigating the FeO/MgO ratio, we approximate the terrestrial mantle composition as a solution of ferromagnesian olivine with an Fe/Fe+Mg ratio of  $\sim 0.1$ .

Determining the lunar bulk composition is more difficult. The Moon is a highly differentiated object and unambiguously determining its composition from samples is not possible. There are several reasons for this. First, the crust is a major reservoir for some elements (i.e., aluminum) such that uncertainties in the thickness and compositional stratification of the crust result in major uncertainty in determining the lunar bulk composition. Second, post-formation mixing of the lunar interior via mantle convection has been weak or absent, as evinced by the radiogenic isotopic heterogeneity (i.e., Sr isotopes) of samples derived from distinct regions of the lunar mantle via partial melting (Turcotte and Kellogg 1986). Such isotopic heterogeneity implies that the chemical heterogeneity generated during the primordial lunar differentiation has also survived. Finally, it is not yet clear how deep the source regions of the samples represented on the surface are, and the deep lunar mantle, in particular, may be unsampled.

Nevertheless, petrologic studies have concluded that the sampled lunar mantle — in particular the source region for mare basalts — is significantly enhanced in FeO relative to the terrestrial mantle (Ringwood 1977). Geophysical measurements have also been brought to bear on the question. In particular, interior models must simultaneously satisfy the density, moment of inertia, and seismic velocity constraints. Geophysical constraints tend to corroborate the suggestion from lunar petrology that the lunar FeO content is somewhat elevated relative to Earth mantle (Hood and Jones 1987, Mueller et al. 1988). However, the uncertainties are large, and estimates for the

bulk lunar FeO content and FeO/MgO ratio range from values close to Earth mantle (Warren 1986, Warren 2005) to significant enhancements ( $\sim 13\%$  FeO by weight,  $\text{Fe}/\text{Fe}+\text{Mg} \sim 0.2$ ) relative to the silicate Earth (Taylor et al. 2006). Both compositions can be reproduced in the context of the present model, albeit with different consequences for the refractory element abundances of lunar matter. We model the silicate Moon as an olivine solution with an Fe/Fe+Mg ratio of 0.1–0.2. The question we ask is whether such a compositional feature could have been derived from a partially vaporized Earth mantle via fractionation in the aftermath of the giant impact, and what the concomitant consequences for lunar composition would be.

### 3.4. Thermodynamic Model

The low-pressure form of the most abundant silicate mineral in planets is olivine  $(\text{Mg,Fe})_2\text{SiO}_4$ . For the purposes of this study, we have chosen to take this mineral composition to represent the silicates, the only compositional parameter being the Fe/Mg ratio. Experiments have shown that olivine, as liquid or crystal, evaporates congruently (Mysen and Kushiro 1988, Nagahara et al. 1988), at least at the temperatures relevant to the solar nebula ( $T < 2,000$  K). The congruence refers to the fact that two di-valent cations (iron or magnesium) enter the vapor phase for each silicon atom, but the vapor, despite having olivine composition, has a different Fe/Mg ratio than the coexisting condensate. Here, we assume that this vaporization behavior of olivine extends to the higher temperatures encountered on a post giant-impact Earth, and that the only components are the olivine end-members. This assumption can be tested by the extension of thermodynamic models of multi-component liquids

(Ghiorso et al. 2002, Ghiorso and Sack 1995) to the temperatures of relevance ( $T = 2,500\text{--}3,500\text{ K}$ ), or by performing an experiment in this temperature range.

We consider only two phases: liquid and vapor. The temperatures here encountered are above the liquidus temperature of olivine (2160 K). As such, solids are assumed to be absent. For the liquid, we assume an ideal solution between olivine end-members. We take the vapor to be a mixture of ideal gases, and include atomic, monoxide, and dioxide metal-bearing species, as well as oxygen in monatomic and molecular form. The thermodynamic data for phase equilibrium calculations come from standard compilations (Chase et al. 1985, Robie et al. 1978). Following (Fegley and Cameron 1987), we fit the standard state Gibbs free energy of reaction with a constant entropy and enthalpy. In some cases, this procedure represents a significant approximation. The thermodynamic data for liquid fayalite, in particular, only exists up to 1800 K and its application here therefore requires a considerable extrapolation. A summary of the data used is given in Table 3.1.

**Table 3.1** The standard entropy and enthalpy of reactions ( $\ln K = \Delta G^\circ/RT$ ,  $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ ) that determine the vapor pressure and speciation in equilibrium with liquid olivine.

Reaction	$\Delta S^\circ$ (J/mol.K)	$\Delta H^\circ$ (kJ/mol)	Reference
$Mg_2SiO_4(l) = 2 MgO(v) + SiO_2(v)$	490	1888	30
$Fe_2SiO_4(l) = 2 FeO(v) + SiO_2(v)$	412	1500	30,31
$MgO(v) = Mg(v) + \frac{1}{2}O_2(v)$	24.1	77.4	30
$FeO(v) = Fe(v) + \frac{1}{2}O_2(v)$	52.6	174	30
$SiO_2(v) = SiO(v) + \frac{1}{2}O_2(v)$	76.6	197	30
$SiO(v) = Si(v) + \frac{1}{2}O_2(v)$	67.7	557	30
$O_2(v) = 2 O(v)$	134	509	30

For vaporization reactions, for example, of forsterite, we have:



where the left-hand side is equivalent to  $Mg_2SiO_4(l)$ , but is written such that the exchange of a single atom describes the difference between the liquid components. This choice of component makes it possible to describe the liquid as an ideal solution ( $a_i = x_i$ ) where  $a_i$  and  $x_i$  are the activity and mole fraction of the  $i$ th component in the liquid (Navrotsky 1987). The statement of chemical equilibrium for a two-phase system is the equality of chemical potentials for each component in both phases. For the evaporation reaction above, the equilibrium constant can be written:

$$K_1 = \frac{P(\text{MgO})^2 \times P(\text{SiO}_2)}{x_{\text{Fe}}^2} = \exp(-\Delta G_1^\circ / RT) \quad (3.2)$$

where we have additionally assumed that the vapor species behave as ideal gases ( $f_i = P_i$ ) where  $f_i$  and  $P_i$  are the fugacity and partial pressure of the  $i$ th gaseous species. An equation of this kind is written for each reaction in Table 3.1, relating the partial pressures and liquid mole fractions to the standard-state Gibbs free energy of the reaction. Knowledge of the congruent vaporization behavior of olivine is incorporated by requiring that the vapor have olivine composition, i.e.,  $(\text{Fe}+\text{Mg})/\text{Si} = 2$ ,  $\text{O}/\text{Si} = 4$ .

$$P(\text{FeO}) + P(\text{Fe}) + P(\text{MgO}) + P(\text{Mg}) = 2 \times \sum_i P_i^{\text{Si}} \quad (3.3)$$

$$2P(\text{O}_2) + P(\text{O}) = 4 \times \sum_i P_i^{\text{Si}} \quad (3.4)$$

where  $P_i^{\text{Si}}$  is the sum over Si-bearing vapor species,  $P(\text{SiO}_2) + P(\text{SiO}) + P(\text{Si})$ . The partial pressure of  $\text{O}_2$  is counted twice because we are counting atoms. By the Gibbs phase rule ( $f = 2 + c - \phi$  where  $f$  is the number of independent variables,  $c$  is the number of components, and  $\phi$  is the number of phases), a two-phase, two-component system is di-variant (olivine end-members are the only components because we incorporate the knowledge that olivine vaporizes congruently). However, specifying two parameters in a di-variant system allows one to solve for the intensive properties (i.e., specific entropy, composition) of the phases present, not their relative amounts.

Because we are interested in studying parcels with varying degrees of vapor, finding solutions requires that we specify an extra parameter such as the specific entropy of the parcel that constrains the degree of vaporization. This calculation is completely analogous to calculations of isentropic melting in the modern mantle (Asimow et al. 1997).

Parcel calculations require expressions for the specific entropy of the phases present, which — for an ideal solution and a mixture of ideal gases — can be related in a straightforward manner to the entropy of the constituents as pure substances. For an ideal liquid solution, we have:

$$\bar{S}_L(T, P) = \sum_i x_i \bar{S}_i(T, 1) - 2R \sum_i x_i \ln x_i \quad (3.5)$$

where  $S_L$  is the entropy of the liquid per mole of Si atoms,  $x_i$  is the mole fraction of the  $i$ th component in the melt,  $S_i$  the entropy of the  $i$ th component as a pure liquid, and  $R$  the universal gas constant. The first term is a sum over the components as pure liquids, and the second term is the entropy of mixing term, the factor of two resulting from the substitution of two atoms between olivine end-members. We assume that the pressure is sufficiently low as to not affect the liquid structure. Such an approximation should be fairly accurate since we are only concerned with two-phase regions of the Earth, and the calculations here indicate that the critical pressure at which vapor begins to co-exist with the liquid ( $< 0.1$  GPa) is much less than the bulk modulus of liquid silicates ( $\sim 100$  GPa). For a mixture of ideal gases, we have:

$$\bar{S}_v(T, P) = \left( \sum_i x_i \bar{S}_i(T, 1) - R \sum_i x_i \ln x_i - R \ln P \right) \times \frac{1}{f_{Si}} \quad (3.6)$$

with the first term in parenthesis the sum over species of the entropy of the gas molecules as pure gases at standard pressure (taking into account the entropy from rotational and vibrational degrees of freedom), the second term an entropy of mixing term arising from the fact that the vapor is a mixture of randomly distributed gas molecules, and the third term a pressure correction for ideal gases, which relates to the volume available to each molecule. The expression in parenthesis is the entropy per mole of gas molecule. Therefore, for consistency with the expression for the entropy of the liquid, we divide by  $f_{Si}$ , the fraction of gas molecules that are silicon-bearing ( $f_{Si} = [P_{SiO_2} + P_{SiO} + P_{Si}] / P$ ) which results in an expression for the entropy of the vapor per mole of Si atoms. The data used for the pure liquids and gases are listed in Table 3.2.



**Table 3.2** Entropy data for pure liquids and vapors at 1 bar ( $S = A.\ln T + B$ )

Substance	A (kJ/mol.K)	B (kJ/mol.K)	Reference
Mg <sub>2</sub> SiO <sub>4</sub> (l)	189	-992	30
Fe <sub>2</sub> SiO <sub>4</sub> (l)	192	-905	30,31
SiO <sub>2</sub> (v)	59.8	-120	30
SiO (v)	36.8	-2.1	30
Si (v)	22.1	+41.5	30
MgO (v)	48.5	-51	30
Mg (v)	21.7	+23.8	30
FeO (v)	38.5	+17.9	30
Fe (v)	25.2	+35.7	30
O <sub>2</sub> (v)	37.5	-15	30
O (v)	21.2	+40.1	30

Finally, we assume that we are dealing with a pure system, i.e., no other species are present besides those accounted for explicitly. We therefore have expressions for the purity of the liquid and vapor solutions:

$$\sum_i x_{i,L} = 1 \quad (3.7)$$

$$\sum_i P_i = P \quad (3.8)$$

For the liquid, the greatest correction to this model approximation comes from the presence of pyroxene (i.e., an [Fe+Mg]/Si ratio < 2) as well as the oxide components

CaO and Al<sub>2</sub>O<sub>3</sub>, each of which have abundances of several percent. We later consider the fate of these refractory oxides under the assumption that they partition quantitatively into the liquid as passive tracers (Section 3.8). For the vapor, the greatest impurity may be metallic iron from the impactor's core that gets emulsified as droplets, remaining suspended in the Earth's magma ocean after the giant impact, and vaporizing along with the silicate liquid upon ascent. For typical impactor masses (0.1–0.2 Earth mass) and core mass fractions ( $\sim 0.25$ ) and partial emulsification (0.3–0.8) of impactor core material, such metal constitutes a few weight percent of the well-mixed terrestrial magma ocean, and may be the source of the lunar core. A potentially important correction for the vapor comes from the fact that we are using the ideal gas law, and near the critical point, the density of the vapor approaches the density of the liquid and intermolecular forces cannot be neglected. Such refinements will be the subject of future studies. Finally, closed-system behavior of parcels requires statements of mass balance and entropy additivity:

$$X = f_v X_v + (1 - f_v) X_L \quad (3.9)$$

$$\bar{S} = f_v \bar{S}_v + (1 - f_v) \bar{S}_L \quad (3.10)$$

where  $f_v$  is the mole fraction of Si atoms (or olivine units) that are vaporized,  $X$  and  $S$  are the composition ( $=\text{Fe}/\text{Fe}+\text{Mg}$ ) and specific entropy of the atmospheric parcel, and  $X_L$  and  $X_v$  are the composition of the liquid and vapor phases, respectively. Equation (3.2) and six analogous equations (one for each reaction in Table 3.1), and equations (3.3)–(3.10) constitute the constraints in this problem. Once the

thermodynamic data (Tables 3.1, 3.2) are specified, there are eighteen variables and fifteen constraints. We must therefore specify three variables to fully determine the system of equations: the parcel composition ( $X = 0.1$ ), the parcel specific entropy ( $S = 10 \text{ k}_B/\text{atom}$ ) and the total pressure ( $P = 0.01\text{--}1 \text{ bar}$ ). The chosen values for the specific entropy and total pressure are discussed in Sections 3.7 and 3.8, respectively. We simultaneously solve for the temperature ( $T$ ), the vapor fraction ( $f_v$ ), the specific entropy ( $S_L, S_V$ ) and composition ( $X_L, X_V$ ) of the liquid and vapor phases, and the partial vapor pressure of each of nine vapor species ( $P_i$ ) by simultaneously solving the described system of coupled, non-linear equations using the MAPLE software package.

### 3.5. Dynamical Model

With a thermodynamic model of liquid-vapor silicates, we can construct one-dimensional models of the convective magma ocean of Earth and the transition to the overlying silicate vapor atmosphere under certain assumptions about the relevant dynamics. In the absence of phase changes, the energy released due to the impact of a  $\sim 0.1$  Earth mass impactor onto the proto-Earth generates a mean temperature increase:

$$\Delta T = \frac{0.1GM_E}{R_E C_P} = 4,000 \text{ K} \quad (3.11)$$

with  $C_p = 1,400 \text{ J/kg.K}$  appropriate to the high-temperature, Dulong-Petit limit. For a  $\sim 0.2$  Earth mass giant impactor (Canup 2008), the mean temperature rise is correspondingly twice as great. In all cases, however, vaporization contributes negligibly to the energy budget of Earth because — as discussed in Section 3.4 — only the outer, low-pressure regions can undergo vaporization. For this reason, a mean temperature increase for the Earth of several thousand degrees is inevitable and it is nearly guaranteed that the post-giant-impact silicate Earth is a magma ocean enveloped by a vapor atmosphere. Heat loss via radiation from a  $\sim 2,500 \text{ K}$  photosphere (Thompson and Stevenson 1988) drives vigorous convection throughout the system.

We cannot calculate the chemical consequences of turbulent Earth-Moon mixing without an understanding of the relevant dynamical regime in such a strongly driven system. One dynamical possibility is that of a “settled” magma ocean, a smooth liquid-vapor interface, and a separately convective vapor atmosphere for both the Earth and the proto-lunar disk, with material exchange between the terrestrial and lunar reservoirs restricted to elements that partition into the vapor atmosphere. This was the picture originally discussed in connection with the equilibration hypothesis (Pahlevan and Stevenson 2007). However, motivated, in part, by observations of refractory element isotopic homogeneity (i.e., W, Cr) in the silicate Earth-Moon system and, in part, by the attractiveness of deriving even the liquid in the proto-lunar disk from the well-mixed terrestrial magma ocean (Warren 1992), we develop the chemical consequences of a different variant of the equilibration hypothesis, namely, that of “unsettled” material exchange between the terrestrial magma ocean and the proto-

lunar disk. In such a case, a single convective column nominally characterizes the silicate Earth from deep regions where only liquid is present, through a critical pressure where two phases become distinguishable to the upper regions of the silicate vapor atmosphere where exchange with the melt-vapor disk presumably takes place. Similarly, a single convective column is assumed to characterize the vertical structure in the proto-lunar disk from the mid-plane up to the rarified photosphere where heat and entropy are radiated to space. Such a scenario can homogenize the relative abundances and isotopic composition of refractory elements through advection of the liquid into the vapor atmosphere and exchange of droplets coupled to the turbulent vapor. Furthermore, this scenario is testable because it predicts a high-level of mass-independent isotopic homogeneity in the silicate Earth-Moon system for all elements irrespective of volatility. As an example, the chromium isotopic homogeneity observed in the silicate Earth-Moon system (Lugmair and Shukolyukov 1998, Trinquier et al. 2008) should extend to high precision.

For the purposes of this chapter, we calculate the composition at the top of the terrestrial atmosphere and assume that it is inherited by the proto-lunar disk and expressed in the lunar bulk composition without further fractionation. In the absence of phase separation (“rainout”), the composition of a parcel (liquid and vapor) at the top of the atmosphere reflects that of the well-mixed terrestrial magma ocean. Hence, such an “unsettled” dynamical state can generate lunar parcels isochemical with the terrestrial mantle. In the next section, we consider the consequences of partial rainout on evolving compositions distinct from the terrestrial mantle. We note that in this

chapter we are only exploring one of a number of possible dynamical scenarios, each of which will have different consequences for lunar composition.

### 3.6. Equilibrium Approximation

Before we can use thermodynamics to calculate elemental partitioning, we must ask whether thermodynamic equilibrium is actually attained (or approached) between the liquid and vapor in the scenario under consideration. As discussed above (in section 3.5), we only consider the case where a single convective column describes both the terrestrial magma ocean and silicate vapor atmosphere and neglect the possibility that the liquid and vapor settle into a magma ocean and a separately convective vapor atmosphere. In such a case, the liquid exists as suspended droplets throughout most of the two-phase column, and equilibration of liquid and vapor is potentially rate-limited by diffusion through (1) the liquid droplets and (2) the intervening vapor. We consider the kinetics of each of these processes in turn. Both depend on the typical size of droplets, which can be calculated with the aid of a microphysical cloud model. For the purposes of this argument, we consider the maximum droplet size, determined by the stabilizing effect of surface tension against hydrodynamic fission (Prandtl 1952):

$$a_{\max} = \left( \frac{C_D \gamma}{\rho_L g} \right)^{1/2} = 3 \text{ mm} \quad (3.12)$$

where  $\gamma$  is the surface tension of silicates,  $\rho_L$  is the density of the liquid,  $g$  is the surface gravity, and  $C_D$  is a constant of order unity. The maximum size for silicate droplets in the silicate vapor atmosphere of Earth is not very different from raindrops in the

modern terrestrial atmosphere, because the surface tension ( $\sim 0.3 \text{ J/m}^2$ ) (Walker and Mullins 1981) and density ( $\sim 3,000 \text{ kg/m}^3$ ) of silicate liquids are greater than that of liquid water by an approximately constant factor. For diffusion through liquid droplets, we have:

$$\tau_L = \left(\frac{a}{\pi}\right)^2 \frac{1}{D_L} = 10^2 \text{ sec} \quad (3.13)$$

for a maximum droplet size of 3 mm and atomic liquid diffusivity of  $\sim 10^{-8} \text{ m}^2/\text{s}$  in the high-temperature limit (de Koker 2008). Hence, maximally sized droplets equilibrate with nearby vapor on a timescale of minutes; smaller droplets will equilibrate even faster. Similar considerations apply for diffusion through the intervening vapor, the length scale of relevance being the average spacing between droplets. To within a factor of order unity, the diffusion time through the vapor can be written:

$$\tau_V = f_V^{2/3} a^2 \left(\frac{\rho_L}{\rho_V}\right)^{2/3} \frac{3}{l_{mfp} V_{th}} = 60 \text{ sec} \quad (3.14)$$

for a vapor fraction  $f_V = 0.1$ , the average size of droplets  $a = 3 \text{ mm}$ , the density of liquid  $\rho_L = 3,000 \text{ kg/m}^3$  and vapor  $\rho_V = 3 \text{ kg/m}^3$ , a mean free path  $l_{mfp} = 1 \text{ um}$  for diatomic molecules (with cross-section  $\sigma = 5 \times 10^{-15} \text{ cm}^2$ ), and thermal velocity of  $\sim 1 \text{ km/s}$ , this timescale also turns out to be about a minute, comparable to the timescale for diffusion through the liquid. This calculation holds in the limit where the liquid dominates the mass ( $f_V \ll 1$ ) but the vapor dominates the volume ( $f_V \gg \rho_V/\rho_L$ ). The droplet size enters because at fixed vapor fraction, smaller droplets mean *more* droplets

and a shorter distance for a vapor molecule to diffuse before entering a droplet's sphere of influence. We can compare these timescales to the timescale for convective turnover ( $=H/v_c$ ), which, for a convective velocity of  $\sim 30$  m/s and an atmospheric scale height of  $\sim 100$  km is  $\sim 3 \times 10^3$  seconds (Pahlevan and Stevenson 2007). Furthermore, heat generally diffuses faster than atoms, so chemical equilibrium also implies thermal equilibrium between the liquid droplets and vapor. We conclude that thermodynamic equilibrium is a good approximation, even in this rapidly convective system, and partitioning between the liquid droplets and intervening vapor reflects that of equilibrium at ambient conditions along atmospheric ascent/descent paths.

### 3.7. Thermal State

In analogy with modern planetary atmospheres, we assume that the convective part of such an “unsettled” magma ocean and vapor atmosphere is isentropic. We can make an estimate of the post giant-impact mantle entropy knowing something about the state of the pre-impact Earth and the entropy production due to giant impact heating:

$$S_{final} = S_{initial} + \Delta S \quad (3.15)$$

where  $\Delta S$  is the entropy production due to heating. We cannot know the precise state of the pre-impact Earth. However, a nearly formed Earth in the late stages of accretion will have experienced multiple giant impacts, and cooling via solid-state convection is inefficient over the timescales of planet formation. Hence, we expect the pre-impact terrestrial mantle to be hot but at least partly solid. As a first

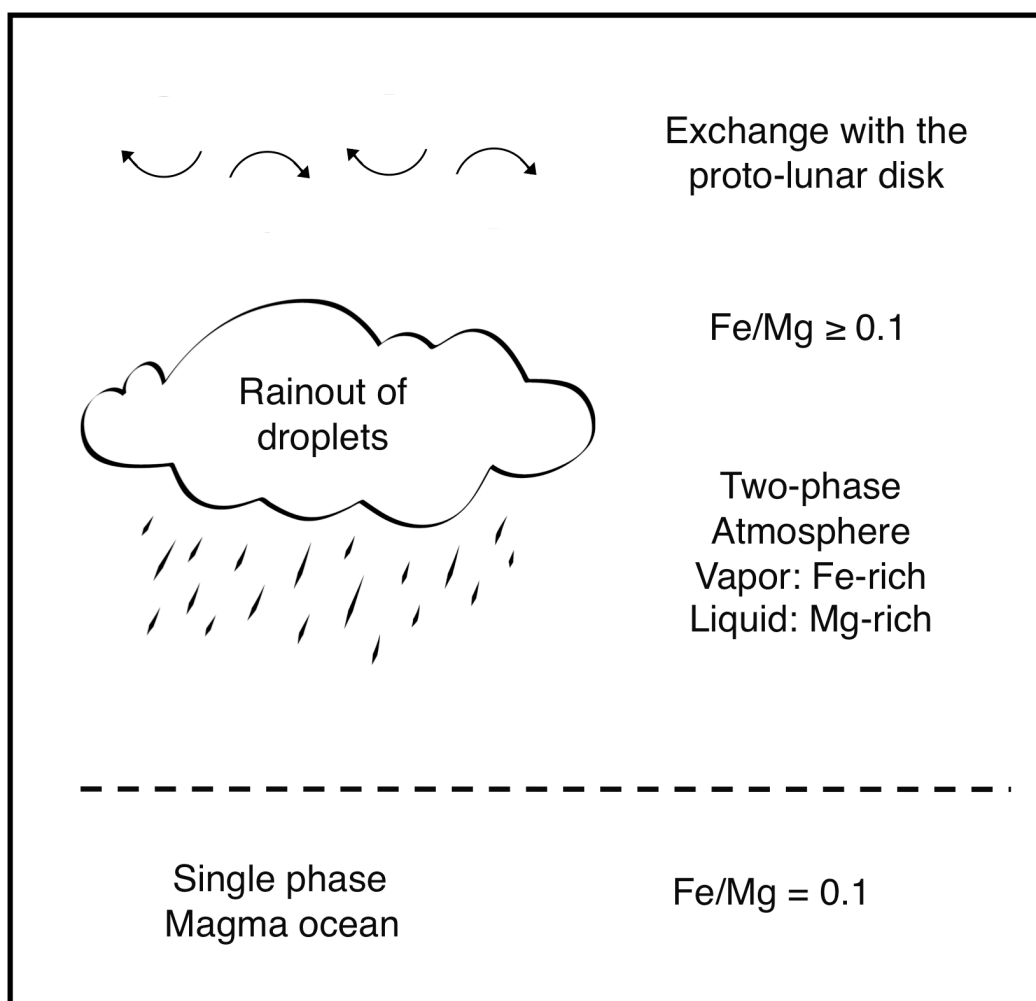


approximation, we take the modern mantle value for the entropy of the pre-impact Earth,  $\sim 6 k_B/\text{atom}$  (Asimow et al. 2001), where  $k_B$  is Boltzmann's constant. For the entropy production due to giant impact heating, we have:

$$\Delta S = \int_{T_{\text{init}}}^{T_{\text{final}}} C_p \frac{dT}{T} = \frac{3k_B}{m} \times \ln(T_{\text{final}} / T_{\text{init}}) \quad (3.16)$$

where  $m$  refers to the mean atomic mass ( $\sim 20$  amu). For initial temperatures of 2–3000 K and an average impact heating  $\Delta T = 4,000$  K, the value of the natural logarithm is nearly unity. Hence, the entropy production due to a Mars-mass giant impact is about equal to  $C_p$ , which is  $3k_B/\text{atom}$  in the high-temperature, DuLong-Petit limit. Note that we can neglect the entropy change due to melting because it is small on this scale ( $\sim 0.5 k_B/\text{atom}$ ). A two Mars-mass impactor would cause an average temperature increase  $\Delta T = 8,000$  K and an entropy increase of  $\sim 5k_B/\text{atom}$ . Hence, a reasonable estimate of the entropy of the post giant-impact Earth is  $10 k_B/\text{atom}$ . However, this estimate of the entropy is an upper limit because the isentropic assumption may be inapplicable to the immediate post-impact environment, since the giant impact may preferentially deposit energy (and entropy) in the upper layers of the Earth, causing an inversion layer. Some time may have to pass after the giant impact for the upper layers to cool such that calculations of a fully convective, isentropic Earth have relevance. Once the Earth becomes well mixed and fully convective, however, one parameter — the specific entropy — specifies the thermal structure of the silicate Earth during the course of its cooling history. With knowledge of the thermal structure, we proceed to calculate the range of compositions that can be

derived from the magma ocean in the silicate vapor atmosphere via rainout of droplets (Figure 3.1). Such a scenario is analogous to the process of condensation and rainout that results in a dry stratosphere ( $< 3 \text{ ppm H}_2\text{O}$ ) in the modern terrestrial atmosphere.



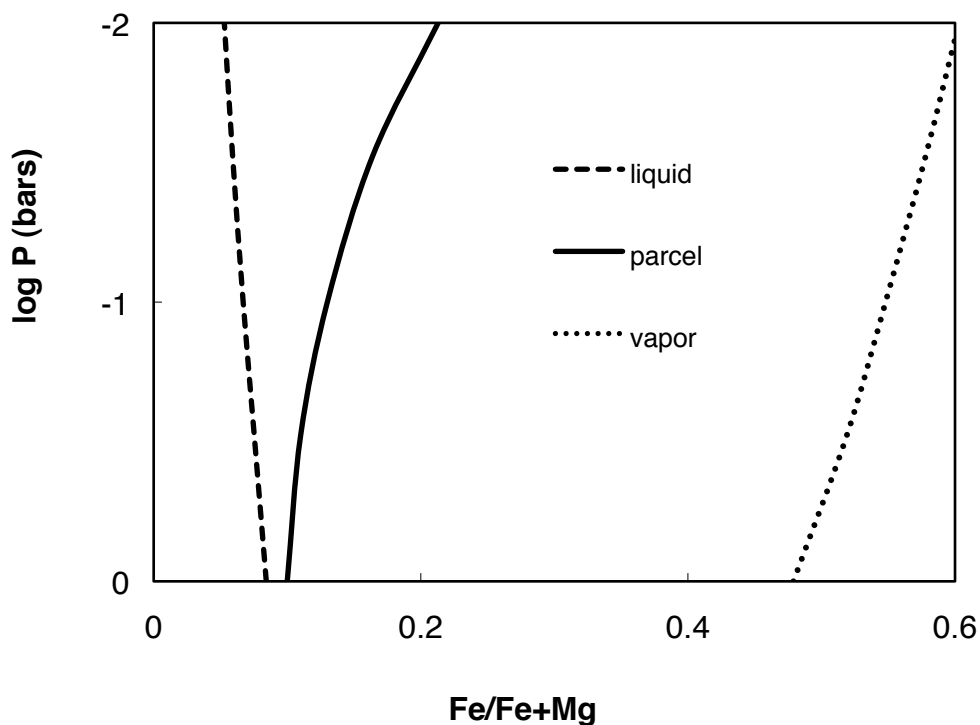
**Figure 3.1.** Chemical fractionation via liquid rainout. A single convective column characterizes the Earth from the deep magma ocean, where only one phase is present, through the top of the two-phase atmosphere. Rainout of Mg-rich droplets in ascending parcels shifts the composition of the upper atmosphere towards the vapor composition. The degree of rainout in these models is a free parameter.

### 3.8. Chemical Fractionation

Fractionation calculations in the silicate vapor atmosphere of Earth require two steps: a closed-system step, described above (Section 3.4), whereby the liquid and vapor equilibrate at a new pressure, and an open-system step, whereby the newly-equilibrated liquid partially rains out, shifting the properties of the parcel (entropy, composition) toward that of the vapor. At each altitude, we assume that a fraction,  $f_L$ , of the liquid is removed via rainout. We treat  $f_L$  as a free parameter, and explore the consequences of varying it for the resulting lunar bulk composition inherited from the silicate Earth. When the liquid is partially removed, the vapor fraction in the remaining parcel increases, and is calculated according to mass balance:

$$f_{V-new} = \frac{1}{1 + (1 / f_{V-old} - 1) \times (1 - f_L)} \quad (3.17)$$

Using the new value of the vapor fraction and equations (3.9) and (3.10), we calculate the entropy and composition of the parcel after rainout. Subsequent episodes of droplet-vapor equilibration at a lower pressure — representing adiabatic ascent — and partial liquid removal make it possible to calculate the compositional structure of the silicate vapor atmosphere undergoing varying degrees of rainout. This procedure is exactly analogous to the calculation of “pseudoadiabats” in atmospheric science.



**Figure 3.2.** Chemical structure of the silicate vapor atmosphere of Earth. The parcel represents the composition of the atmosphere (liquid and vapor) and shifts toward that of the vapor as liquid droplets separate via rainout. This calculation assumes that a fraction  $f_L$  ( $\approx 0.4$ ) of the liquid is removed via rainout every threefold decrease in pressure, and that the parcel entropy before rainout is  $10 k_B/\text{atom}$ . A twofold enhancement of the FeO/MgO ratio — comparable to the silicate Earth-Moon difference — evolves.

Plotted in Figure 3.2 is the result of a sample calculation with initial (“pre-rainout”) parcel entropy of  $10 k_B/\text{atom}$ . The parcel entropy is a key parameter because it

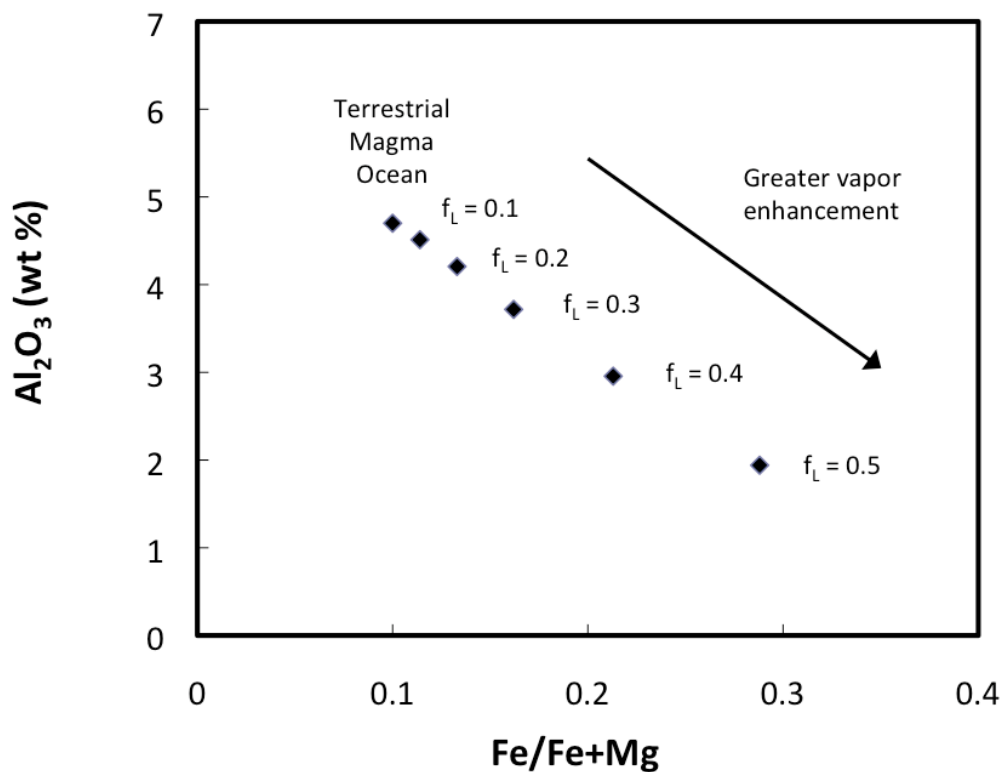
determines the thermal structure of the atmosphere, specifically, temperature (T) and vapor fraction ( $f_v$ ) as a function of pressure. This particular value of entropy corresponds to a temperature of 3310 K and a vapor mass fraction of 4 percent at the reference pressure of 1 bar. This calculation assumes 40 percent liquid removal via rainout ( $f_L = 0.4$ ) every threefold decrease in pressure (roughly every scale height), starting at a pressure of 1 bar. Partial removal of Mg-rich droplets over two orders-of-magnitude of pressure release can re-produce the widely postulated  $\sim 2x$  enhancement of the lunar FeO/MgO ratio.

In addition to the major elements, we are interested in following the behavior of tracers during rainout. However, for this purpose, we must know the partitioning behavior of elements between liquid and vapor, which requires a solution model that yields reliable activity coefficients for trace elements at the temperatures of relevance ( $T = 2,500 \text{ K} - 3,500 \text{ K}$ ). At present, no such solution model exists. However, we can still calculate the behavior of elements in certain limiting cases. For elements that quantitatively partition into the liquid, we have:

$$X_{new}^R = X_{old}^R \times \frac{(1 - f_L)}{f_{V-old} + (1 - f_L) \times (1 - f_{V-old})} \quad (3.18)$$

where  $X^R$  represents the mole fraction of the refractory tracer in the liquid before and after rainout. We use this approach to follow the fate of major-element refractory oxides (i.e., CaO, Al<sub>2</sub>O<sub>3</sub>) in the context of rainout scenarios just discussed under the

assumption that these oxides partition quantitatively into the liquid, and compare the results with inferred abundances in lunar bulk composition models (Figure 3.3).



**Figure 3.3.** FeO has a preference for the vapor relative to MgO. Hence, rainout of liquid droplets generates upper atmospheres with compositions shifted towards higher Fe/Fe+Mg relative to the underlying magma ocean. Al<sub>2</sub>O<sub>3</sub> partitions strongly into the liquid, and rainout therefore depletes the upper atmosphere in alumina (and other refractory elements) relative to the terrestrial magma ocean. An alumina abundance of 4.7 weight percent is assumed for the Earth mantle.

First, we note that compositions derived from the terrestrial mantle *enhanced* in FeO/MgO through liquid rainout are *depleted* in refractory elements. Bulk composition models featuring both an elevated FeO/MgO ratio and an enhancement in the refractory element abundances in the bulk silicate Moon can therefore be ruled out as compositions capable of being evolved from the terrestrial mantle by liquid-vapor fractionation. Second, the co-variance of the evolved FeO/MgO ratio and refractory element abundances suggests that, in the context of this scenario, knowing the value of the FeO/MgO ratio determines the abundances of the refractory elements, and vice-versa. In this context, it is noteworthy that refractory element abundances essentially identical with Earth mantle are commonly inferred. However, given that even the abundances of Al<sub>2</sub>O<sub>3</sub> and CaO in the terrestrial mantle are only known to tens of percent, a precise comparison is not possible.

There are several parameters in these calculations, only some of which are constrained. The maximum pressure at which phase separation can, in principle, occur is dictated by thermodynamics as the pressure above which the material exists as a single phase, and is therefore well-constrained. The minimum pressure at which phase separation may occur, however, is not well known. In particular, we do not know at what altitude exchange with the proto-lunar disk takes place (or, indeed *if* efficient exchange takes place), because it depends on the poorly understood dynamics. This is an area where numerical fluid-dynamical simulations can shed significant light on this problem. For our purposes, we consider pressure levels as low as  $\sim 10$  millibar, because the silicate vapor atmosphere of Earth may be convective to such altitudes (Thompson and

Stevenson 1988). We have taken the fraction of the liquid,  $f_l$ , which rains out at each altitude as a free parameter to explore the range of compositions that can be derived from the Earth via liquid-vapor fractionation, and merely note that this value may be constrained with a microphysical cloud model because only the largest droplets may have a chance to undergo rainout.

### 3.9. Discussion

There is a certain similarity between the FeO/MgO ratio of the silicate Earth and Moon. In this chapter, we have explored the possibility that the major element composition of the lunar material was inherited via turbulent exchange from a partially vaporized silicate Earth in an “unsettled” state during the afterglow of the giant impact. In the absence of phase separation, this scenario predicts homogeneity in the chemical composition of the silicate Earth-Moon system. However, various degrees of rainout along atmospheric ascent paths can evolve compositions distinct from the bulk silicate Earth. Furthermore, petrologic and geophysical observations suggest up to a  $\sim 2x$  enhancement in the FeO/MgO ratio in lunar silicates relative to Earth mantle, suggestive of one or more episodes of chemical fractionation. Both the direction and magnitude of the required fractionation are consistent with liquid-vapor fractionation in the silicate vapor atmosphere of Earth. For the purposes of this chapter, we have adopted the point of view that the composition at the top of the silicate vapor atmosphere is inherited by the proto-lunar disk and is expressed in the lunar bulk composition without further fractionation. This is clearly an over-simplification, as at least one subsequent stage of fractionation is required to explain the lunar volatile



depletion. For the scenario presented here to have predictive power in terms of the lunar composition, the episode of volatile element depletion must have been divorced from the fractionation of major elements. Below, we discuss several additional chemical tracers that may be used to shed light on the fractionation processes during this earliest period of lunar pre-history.

### 3.9.1 Olivine/Pyroxene Fractionation

Congruent vaporization of olivine end-members has been demonstrated experimentally at the temperatures relevant to the solar nebula ( $T < 2,000$  K). Such congruent vaporization may break down at the much higher temperatures encountered here, and the vapor co-existing with liquid olivine may deviate from olivine composition. In particular, Si/(Mg+Fe) fractionation may take place. Such fractionation is rendered more likely on the post-giant-impact Earth because the mantle is not composed of pure olivine ( $\text{Si}/[\text{Mg}+\text{Fe}] > 1/2$ , pyroxene is also present), and enstatite has been experimentally shown to vaporize *incongruently*, with the vapor enriched in silica (Mysen and Kushiro 1988). Therefore, rainout on the actual post-impact Earth may have resulted in a certain degree of Si/(Mg+Fe) fractionation in addition to the Fe/Mg fractionation here explored. Such fractionation, if inherited by the proto-lunar disk, would be expressed in an olivine/pyroxene ratio for the lunar mantle distinct from the Earth, a feature that is, in fact, found in certain lunar bulk composition models (Ringwood 1977). A better determination of the lunar bulk composition, as well as detailed thermodynamic data for high temperature silicate

liquids would permit the lunar olivine/pyroxene ratio to serve as a quantitative constraint on liquid-vapor fractionation scenarios like the one here explored.

### 3.9.2 Volatile Trace Elements

The one-stage scenario explored in this chapter is one where the silicate Moon acquires its major-element composition by being preferentially enriched in terrestrial vapor, and, in the absence of other processes, would be *enhanced* in volatile elements relative to Earth mantle. This is contrary to the observations. In particular, elements that condense from the solar nebula at temperatures below 1200 K (i.e., Na, K) are *depleted* in lunar samples, as observed in the lunar basalts (Ringwood and Kesson 1977). Therefore, the scenario explored here is, at best, an incomplete story. Such a scenario can be reconciled with the lunar volatile depletion by considering additional episodes of fractionation during lunar formation distinct from that which occurred in the silicate vapor atmosphere of Earth. At present, the settings and physical processes involved in the lunar volatile depletion are not clear. Volatile element depletion may have occurred during the disk phase, due to liquid rainout in the protolunar disk (Machida and Abe 2004) followed by elimination of the residual vapor through thermal escape in a hydrodynamic wind (Genda 2004, Genda and Abe 2003) or inward radial diffusion of the vapor-enriched parcels toward the inner regions of the proto-lunar disk that eventually accrete onto the Earth. In this process, analogous to the turbulent redistribution of water vapor in the solar nebula followed by condensation past the ice line (Stevenson and Lunine 1988), the silicate Earth is the reservoir complimentary to the lunar volatile depletion. Conversely, the separation and loss of volatile elements

may have occurred after the disk phase, during the process of lunar accretion (Abe et al. 1998), or even due to outgassing from a naked magma ocean followed by hydrodynamic escape of the transient vapor atmosphere. Future work must aim to identify the physical setting(s) for the volatile element depletion so that scenarios that explore the meaning of the magnitude (and incomplete nature) of the volatile element depletion can be developed.

### **3.10. Conclusions**

The equilibration hypothesis presents us with an opportunity. Progress in developing and testing the giant impact hypothesis has been hampered by an inadequate knowledge of the composition of the impactor that triggered lunar formation. That the lunar isotopic composition is identical with the terrestrial mantle to high precision raises the possibility that the lunar material was thoroughly processed through the Earth's post-impact vapor atmosphere and underlying magma ocean. In such a scenario, and without liquid-vapor separation, the lunar mantle would be expected to be isochemical with the Earth mantle. Therefore, observed chemical differences in the silicate Earth-Moon system require explanation. Here, we have explored the possibility that chemical fractionation in the silicate vapor atmosphere of Earth is solely responsible for any major-element differences in the silicate Earth-Moon system. Our results demonstrate that an enhancement — relative to Earth mantle — of the FeO/MgO ratio must be accompanied by a depletion of refractory element abundances, permitting only certain lunar bulk compositions to be inherited from the partially vaporized silicate Earth. Progress in developing the lunar origin scenario

therefore requires better determination of the lunar chemical composition through gravity data, a seismic network, and other geophysical characterizations.

## ISOTOPIC FRACTIONATION

**Abstract**

In the last several years, the isotopic composition of lunar samples has been determined with unprecedented precision, making possible unprecedented inquiries into signatures of the lunar formation process. A high level of mass-independent isotopic homogeneity in the silicate Earth-Moon system argues for system-wide turbulent mixing in the energetic, melt-vapor aftermath of the giant impact. While such a scenario is capable of generating chemical compositions for the silicate Moon that are identical with the Earth's mantle, observed chemical differences between these two reservoirs motivate a study of liquid-vapor fractionation as a process that generates chemical differences. We have previously shown that inferred differences in the major-element composition of the bulk silicate Earth and Moon can be derived by liquid rainout in the silicate vapor atmosphere of the post-impact Earth. Here we show that, in addition to chemical differences, liquid-vapor fractionation can generate significant mass-dependent isotopic offsets, even at the high temperatures encountered after the giant impact. We calculate the isotopic fractionation for the major-elements silicon, magnesium, iron, and oxygen and quantify the evolution of isotopic offsets between the silicate Earth and Moon due to varying degrees of rainout in the hot, silicate vapor atmosphere of Earth. We identify the precision with which the isotopic composition of planetary reservoirs must be determined to be sensitive to the high-temperature processes of lunar formation and find that they are comparable to

precisions that can be achieved with modern analytical techniques. We then use existing measurements to conclude that either a two-stage model is required to evolve the major-element composition of the silicate Moon or that the minority viewpoint that the silicate Moon is isochemical with the terrestrial mantle may be correct.

#### **4.1. Introduction**

The Moon is generally imagined to have formed from the debris generated by the off-center collision of a Mars-sized proto-planet with the proto-Earth towards the end of accretion (Cameron and Ward 1976, Hartmann and Davis 1975). This scenario can explain the angular momentum of the Earth-Moon system and the lunar metal depletion (Cameron 2000, Canup 2004b, Canup 2008, Canup and Asphaug 2001), and releases enough energy to fully melt and partially vaporize the proto-Earth and surrounding proto-lunar disk. The post-impact stage of the evolution is of interest because processing in the hot, fluid aftermath of the giant impact may imprint the cosmochemical signatures of lunar formation. For example, the high level of homogeneity in the oxygen isotopic character of the Earth-Moon system (Wiechert et al. 2001) provides evidence for fluid dynamical turbulent mixing in the thousand years immediately following the giant impact, a time during which the silicate vapor atmosphere in equilibrium with the terrestrial magma ocean may have been in turbulent exchange with the melt-vapor proto-lunar disk (Chapter 2), imprinting the chemical and isotopic signatures of the terrestrial mantle on the lunar material. In addition, while a physical scenario has never been developed, post-impact liquid-vapor separation is likely responsible for the lunar volatile element depletion, and this is

especially true if the lunar material acquired its isotopic composition from the terrestrial mantle, a process that — by itself — requires liquid-vapor equilibration. The goal of this chapter is to determine whether liquid-vapor fractionation in the post-giant-impact environment, a process evinced by possible major-element differences in the chemical composition of the silicate Earth and Moon (Chapter 3) and the lunar volatile element depletion, also imparted measurable signatures in the lunar isotopic composition.

#### 4.2. Isotopes as Tracers

Isotopes may be used in several ways to shed light on the lunar formation process. First, they may be used as source tracers, i.e., tracers used to identify the sources of planetary material. For example, following dust-gas separation in the solar nebula, the triple isotope composition of oxygen ( $\Delta^{17}\text{O}$ ) in the pre-cursor planetary dust is fixed, the only factor determining the oxygen isotopic character of planetary reservoirs being the material from which they are sourced. Nucleosynthetic anomalies (e.g., in the abundance of the  $^{54}\text{Cr}$  isotope) serve a similar role. Second, the relative abundances of isotopes may be used as chronometers for the processes of lunar formation. For example, since the siderophile elements are depleted in the silicate Moon, and since the degree of depletion correlates with increasing siderophile nature of the elements, the material comprising the silicate Moon must have experienced equilibration with metal. Tungsten isotopes, through radiogenic siderophile  $^{182}\text{W}$  production from lithophile  $^{182}\text{Hf}$  decay ( $t \sim 9$  Myrs), provide information on the timing of this equilibration. Likewise, strontium isotopes, through radiogenic  $^{87}\text{Sr}$  production from volatile  $^{87}\text{Rb}$

decay ( $t \sim 47$  Gyrs) provide information on the timing of the lunar volatile depletion. Finally, isotopes, as witnesses to the formation event, may serve as process tracers, i.e., the relative abundances of the isotopes may be sensitive to the processes of lunar formation. It is this final possibility that we explore in this chapter.

Consideration of isotopic fractionation following the Moon-forming giant impact has been restricted to kinetic processes, such as the kinetics of evaporation (Humayun and Clayton 1995, Poitrasson et al. 2004, Pritchard and Stevenson 2000), 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 (Urey 1947). This proverb of stable isotope geochemistry has been challenged in recent times as high-temperature processes such as partial melting and core formation have been shown to measurably fractionate the isotopes. Here, we show that equilibrium partitioning between silicate liquid and co-existing vapor — even at the temperatures encountered after the giant impact — can generate measurable isotopic fractionation. Following the approach from Chapter 3, we calculate the isotopic fractionation that occurs due to liquid rainout in one of the settings relevant to lunar origin: the Earth's post-impact silicate vapor atmosphere. We quantify the correspondence between the chemical and isotopic composition of the silicate Moon if liquid-vapor fractionation in the silicate vapor atmosphere of Earth was the sole setting that determined its major-element composition. In such a setting, any fractionation leads to vapor enrichment in the lunar composition, as rainout removes liquid droplets from ascent to the upper



atmosphere that Earth exchanges with the proto-lunar disk. Hence we quantify the consequences of vapor enrichment for the isotopic composition of silicon ( $\delta^{30}\text{Si}$ ), magnesium ( $\delta^{26}\text{Mg}$ ), iron ( $\delta^{56}\text{Fe}$ ) and oxygen ( $\delta^{18}\text{O}$ ) in the silicate Moon relative to Earth mantle. We then use existing isotopic measurements to argue that either a second stage of fractionation — distinct from the one that occurs in the silicate vapor atmosphere of Earth — must have been involved in determining the major-element composition of the silicate Moon or the minority view that the silicate Earth and Moon are isochemical, or nearly so, in terms of major-element chemistry may be correct.

### 4.3. Atmospheric Model

The compositional model, thermodynamic model, and dynamical model used to conduct these calculations are the same as those used to carry out chemical fractionation calculations in Chapter 3. In brief, the silicate Earth and Moon are approximated with olivine composition,  $(\text{Fe,Mg})_2\text{SiO}_4$ , the only compositional parameter being the Fe/Mg ratio, which is well-defined for the bulk silicate Earth (O'Neill and Palme 1998) and is constrained but less well-defined for the silicate Moon, ranging from essentially identical with the Earth mantle (Warren 2005) to nearly twice the terrestrial mantle value (Khan et al. 2007). The thermodynamic model is of a two-phase, two-component system, and describes the liquid as an ideal solution and the vapor as a mixture of ideal gases. The dynamical model is of a single isentropic column extending from deep regions in the convective magma ocean where only one phase is present through a critical pressure where two phases become distinguishable

to the top of the silicate vapor atmosphere. Such an “unsettled” two-phase isentropic column is possible because of the vigor of the convective motions necessary to match radiative heat loss at photospheric temperatures of  $\sim 2,500$  K. Such a state has no analogue in the modern Solar System because the only modern body that has heat fluxes comparable to the post giant-impact Earth, the Sun, is composed of a single-phase fluid. Here, we develop the consequences liquid rainout and quantify the correspondence between the chemical and stable isotope composition of the silicate Moon. We then use existing measurements of the isotopic composition of the silicate Moon to place constraints on the bulk chemical composition of the Moon that are consistent with the origin scenario.

#### **4.4. Rainout Model**

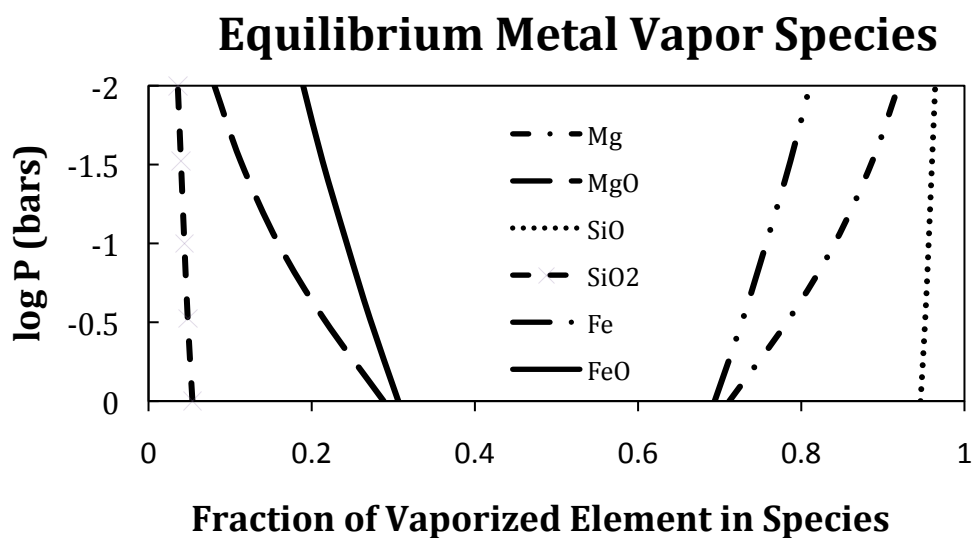
As with chemical fractionation, calculations of isotopic fractionation require two steps: a closed-system step whereby the liquid and vapor equilibrate at a new pressure and temperature, and an open-system step, whereby the newly-equilibrated liquid partially rains out, shifting the isotopic composition of the parcel toward that of the vapor. And as with chemical fractionation calculations, we assume that a fraction,  $f_L$ , of the liquid is removed at each altitude via rainout. In Chapter 3, we used the constraints on the chemical composition of the silicate Moon to limit the fraction of liquid rainout to be in the range 0–40 percent every threefold decrease in pressure. Here, we explore the consequences of this amount of liquid-vapor fractionation in the partially vaporized region of the convective silicate Earth (i.e., the atmosphere) on the stable isotope composition of the silicate Moon.

## 4.5. Isotopic Fractionation

At sufficiently high temperature, equilibrium isotopic differences between co-existing phases approach zero. However, small but significant isotopic fractionation is still possible at high ( $\sim 10^3$  K) temperatures if there is a change in bonding partners, valence, and/or coordination between different phases for the element under consideration. Because the vaporization of silicates involves decomposition reactions, metal-oxygen ratios of vapor species can differ from melt species equivalents, making even high temperature isotopic fractionation possible. In the previous chapter, we explored the possibility that fractionation in the terrestrial silicate vapor atmosphere is responsible for any major-element differences between the silicate Earth and Moon. Here, we ask what the corresponding isotopic fractionation for such a scenario would be for the elements that appear in olivine composition,  $(\text{Fe,Mg})_2\text{SiO}_4$ , and whether the isotopic composition of planetary bodies can be determined with sufficient precision to permit mass-dependent isotopic study of the high-temperature processes of lunar formation and/or an isotopic determination of the lunar bulk chemical composition.

### 4.5.1 Silicon

Silicon isotopes are attractive as a diagnostic for liquid-vapor fractionation for several reasons. First, the bonding environment for silicon between the liquid and vapor is vastly different, making significant ( $\sim$  per mil) high temperature fractionation possible. Silicon in the melt exists in silica tetrahedral ( $\text{SiO}_4^{4-}$ ) whereas silicon monoxide ( $\text{SiO}$ ) dominates the speciation of silicon in the atmospheric vapor for the full range of conditions considered here (Figure 4.1).

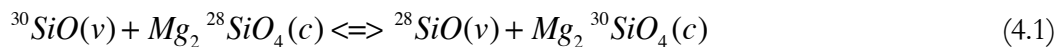


**Figure 4.1.** Equilibrium metal-bearing vapor species in co-existence with silicate liquid in the vapor atmosphere of Earth.  $\text{SiO(v)}$ ,  $\text{Mg(v)}$ , and  $\text{Fe(v)}$  dominate the speciation over  $\text{SiO}_2\text{(v)}$ ,  $\text{MgO(v)}$ , and  $\text{FeO(v)}$ , for the full range of conditions encountered on the post-giant-impact Earth. While lower temperatures in the upper atmosphere favor the formation of molecules, lower pressures favor dissociation into atomic form and overwhelm the temperature effect. Monatomic  $\text{Si(v)}$  is included in the calculations but appears in negligible quantities ( $<3$  ppm).

Second, silicon isotopes have not been observed to display significant fractionation during silicate igneous processes (Fitoussi et al. 2009, Savage et al. 2009) making the isotopic composition of samples potentially diagnostic of the composition of the source reservoirs. Third, high-precision measurements of silicon isotopes in lunar and terrestrial rocks and meteorites have been made (Fitoussi et al. 2008, Fitoussi et al. 2009, Georg et al. 2007) and are ongoing (Armytage et al. 2010, Fitoussi et al. 2010).

The original impetus for these measurements was the fractionation of Si isotopes due to high-pressure terrestrial core-formation. However, because core formation and the evolution of the silicon isotopic composition of the terrestrial mantle was nearly complete by the time of the Moon-forming giant impact, it has become apparent that the silicate Earth-Moon similarity provides evidence for the equilibration hypothesis (Fitoussi et al. 2010, Georg et al. 2007). In the scenario outlined here, in addition to the isotopic homogeneity of the silicate Earth-Moon system due to post-impact turbulent mixing, we are interested in a mass-dependent isotopic offset that may *evolve* depending on the extent to which the liquid separates from the vapor in this earliest period of Earth-Moon history.

We can estimate the magnitude of the isotopic fractionation between the vapor and liquid by considering the corresponding fractionation between vapor 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 uniform silicon isotope compositions (Fitoussi et al. 2009, Savage et al. 2009). To quantify the fractionation, we write the isotope exchange reaction and corresponding equilibrium constant:



$$K_{eq} = \frac{Q(\text{Mg}_2 {}^{30}\text{SiO}_4)}{Q(\text{Mg}_2 {}^{28}\text{SiO}_4)} \bigg/ \frac{Q({}^{30}\text{SiO})}{Q({}^{28}\text{SiO})} \quad (4.2)$$

where  $Q$  is the reduced partition function of the isotopologue in the phase of interest. For the condensate, the **B**-factor (or reduced partition function ratio) of silicon in crystalline forsterite has previously been calculated (Meheut et al. 2009) using density functional theory (DFT) and assuming harmonic vibrations. Here we adopt the results of the DFT calculations. For the vapor, because chemical equilibrium calculations show that the SiO molecule dominates the speciation of silicon (> 94 percent of silicon-bearing molecules) for the full range of conditions here encountered, we simply approximate the silicon in the vapor with the SiO molecule and, in the standard manner (Urey 1947), calculate the partitioning of isotopes by writing down the ratio of partition functions between isotopically substituted and normal populations, assuming purely harmonic vibrations:

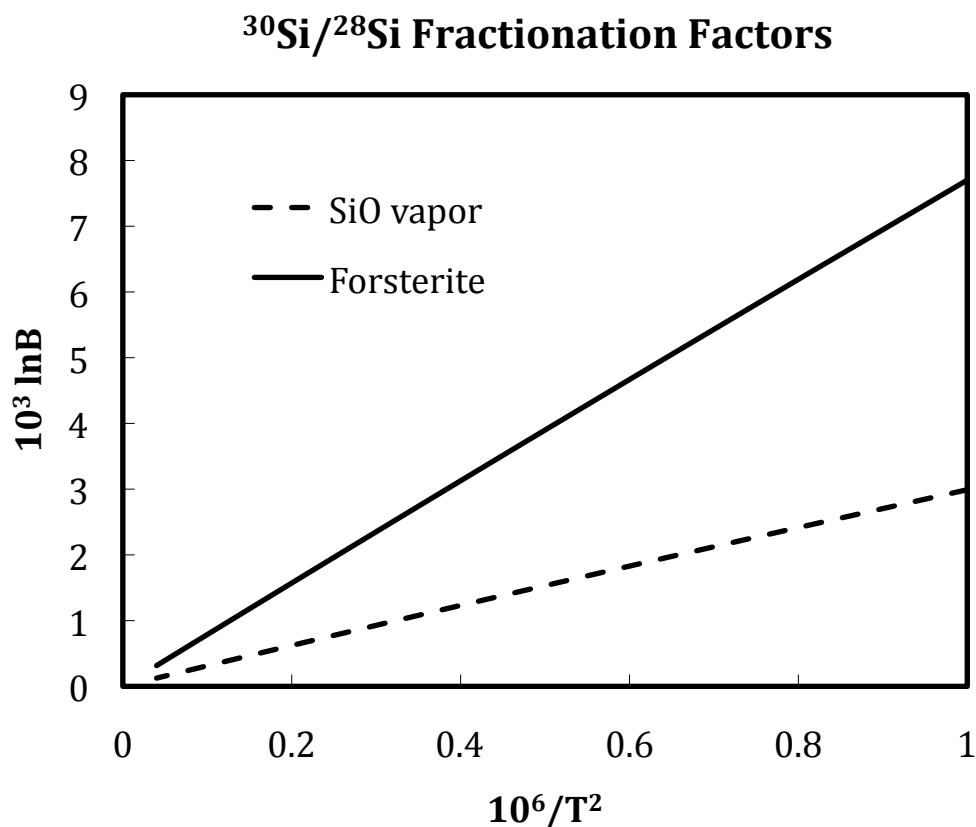
$$\frac{Q'}{Q} = \prod_i \frac{\nu_i'}{\nu_i} \frac{e^{-U_i'/2}}{e^{-U_i/2}} \frac{1 - e^{-U_i}}{1 - e^{-U_i'}} \quad (4.3)$$

where  $\nu$  represents the vibrational frequency of the normal isotopologue and is determined via spectroscopy and adopted from standard sources (Chase et al. 1985),  $\nu'$  represents the vibrational frequency of the substituted isotopologue calculated from  $\nu$  and the known dependence of the vibrational frequency on the reduced mass, and  $U$  is the dimensionless mode energy ( $=h\nu/kT$ ). Vibrational frequencies of the molecules used in these calculations are tabulated in Table 4.1.

**Table 4.1** Vibrational frequencies of vapor molecules. From (Chase et al. 1985)

Molecule	Mode (Degeneracy)	Frequency (cm <sup>-1</sup> )	Reduced mass, m
FeO	Stretch (1)	880	$m_{\text{O}}m_{\text{Fe}}/(m_{\text{O}} + m_{\text{Fe}})$
MgO	Stretch (1)	785	$m_{\text{O}}m_{\text{Mg}}/(m_{\text{O}} + m_{\text{Mg}})$
SiO	Stretch (1)	1241	$m_{\text{O}}m_{\text{Si}}/(m_{\text{O}} + m_{\text{Si}})$
SiO <sub>2</sub>	Symmetric Stretch (1)	980	$m_{\text{O}}$
	Asymmetric Stretch (1)	1430	$m_{\text{O}}m_{\text{Si}}/(2m_{\text{O}} + m_{\text{Si}})$
	Bending Mode (2)	370	$m_{\text{O}}m_{\text{Si}}/(2m_{\text{O}} + m_{\text{Si}})$
O <sub>2</sub>	Symmetric Stretch (1)	1580	$m_{\text{O}}/2$

With this approach, we can calculate the B factor for silicon in the SiO molecule, which quantifies the preference of heavy isotopes to concentrate in this vapor molecule (and, for an isotope exchange reaction involving the exchange of a single atom between species, is simply equal to  $Q'/Q$ ). B-factors for <sup>30</sup>Si/<sup>28</sup>Si as a function of temperature in liquid and vapor are plotted in Figure 4.2.



**Figure 4.2.** The  $^{30}\text{Si}/^{28}\text{Si}$  fractionation factors in forsterite, a proxy for silicon in the liquid, and  $\text{SiO}(\text{v})$ , the dominant Si-bearing vapor molecule. As expected for the high-temperature limit, the fractionation factors decrease as  $1/T^2$ . At a given temperature, the vertical displacement between the two lines gives the difference in  $\delta^{30}\text{Si}$  values between the phases. Hence, at  $10^3$  K, the isotopic fractionation  $\Delta$  ( $=\delta_{\text{L}} - \delta_{\text{V}}$ ) between crystalline forsterite and co-existing vapor is  $\sim 5$  per mil. This is a large fractionation.

Two points are worth noting. First, this result shows that in equilibrium, the isotopic composition of the vapor 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 is nearly equal to unity [ $\Delta = (K_{eq}-1) \times 10^3$ ], and the fact that the vapor speciation does not appreciably change throughout the column, we can write the fractionation of  $^{30}\text{Si}/^{28}\text{Si}$  between forsterite and co-existing vapor:

$$\Delta_{L-v}^{Si} = 5 \times \left(10^3/T\right)^2 \text{ per mil} \quad (4.4)$$

This expression is accurate in the temperature range encountered here ( $T=2,500\text{--}3,500$  K) to better than ten percent. A 5 per mil difference in the  $^{30}\text{Si}/^{28}\text{Si}$  of liquid and vapor at  $10^3$  K is quite significant in the world of stable isotope geochemistry. For comparison, the isotopic fractionation between forsterite and quartz at the same temperature ( $10^3$  K) is about 0.2 per mil. This calculation suggests that, in conditions where silicon undergoes partial vaporization, its isotopes are very sensitive tracers of phase separation.

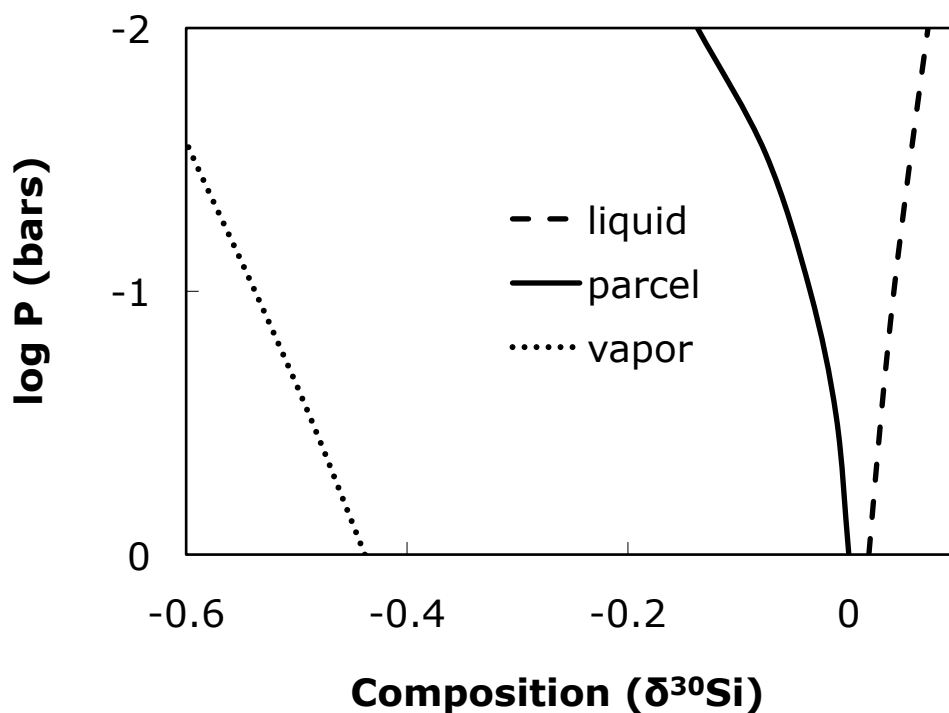
To translate these calculations into a prediction for bulk silicate Earth-Moon differences, we must fold the isotopic fractionation into a scenario for liquid-vapor separation. We have inferred (Chapter 3) the temperatures and degree of liquid-vapor separation needed to derive one postulated aspect of the lunar bulk composition via fractionation in the Earth's silicate vapor atmosphere. We now ask what the isotopic fractionation in such a scenario would be. Since the isotopes are passive tracers, we merely adopt the results of the chemical fractionation calculations. As with chemical

fractionation, parcel calculations require statements of mass balance and fractionation between the phases:

$$\delta_P = f_V^{Si} \delta_V + (1 - f_V^{Si}) \delta_L \quad (4.5)$$

$$\Delta_{L-V} = \delta_L - \delta_V \quad (4.6)$$

where  $f_V^{Si}$  is the mole fraction of Si in the vapor, and comes from calculations described in Chapter 3.  $\Delta$  is the isotopic fractionation between the liquid and vapor and is calculated according to the parcel temperature using equation (4.4). The distillation calculations require two steps: a closed-system step whereby the liquid and vapor isotopically equilibrate at a new temperature and pressure, and an open-system step, in which the newly equilibrated liquid is partially removed by rainout, shifting the isotopic composition of the ascending parcel towards that of the vapor. Subsequent episodes of droplet-vapor equilibration at lower pressure — representing adiabatic ascent — and partial liquid removal make it possible to calculate the isotopic structure of the silicate vapor atmosphere undergoing varying degrees of rainout. An example calculation is shown in Figure 4.3.



**Figure 4.3.** Isotopic structure of the post-impact silicate vapor atmosphere of Earth undergoing rainout ( $f_L=0.4$ ). The parcel represents the composition of an atmospheric parcel (liquid and vapor). Removal of isotopically heavy liquid shifts the composition of the upper atmosphere towards lighter isotopic compositions. The phase separation occurs at temperatures of 2600–3300 K. If rainout in the silicate vapor atmosphere is the process responsible for the elevated lunar FeO/MgO ratio, a  $\sim 0.14$  per mil  $\delta^{30}\text{Si}$  offset should be observed between the silicate Earth-Moon system.

The removal of heavy-Si in the liquid droplets over two orders of magnitude of pressure shifts the isotopic composition of the upper atmosphere relative to terrestrial

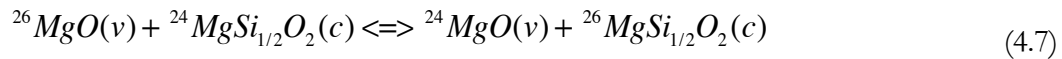
Si. Hence, if the proto-lunar disk acquires a twofold enhancement in the FeO/MgO ratio ( $f_L = 0.4$ ) from an unsettled upper terrestrial atmosphere fractionated by rainout at lower levels, a  $\sim 0.14$  per mil silicon isotope offset should arise between terrestrial and lunar silicates. This is not observed.

Rainout of silicate droplets generates both chemical and isotopic fractionation. However, since the degree of liquid rainout is not well constrained, a range of outcome for the chemical and isotopic composition of the resulting Moon is possible. While inferring the bulk chemical composition of the Moon remains difficult and fraught with uncertainty, it has become possible to determine the isotopic composition of lunar matter to a precision that permits predictive scenarios of lunar bulk composition to be tested. In the absence of rainout, liquid droplets remain fully suspended up to high levels in the Earth's silicate vapor atmosphere and the silicate Moon that results is isochemical with Earth's mantle. In this case, no isotopic offset is expected. However, *to the extent that the lunar composition is distinct from the bulk silicate Earth*, an isotopic offset in the silicate Earth-Moon system should be observed. Conversely, because no offset in silicon isotopes in the silicate Earth-Moon system has yet been observed (Armytage et al. 2010, Fitoussi et al. 2010), the major-element lunar bulk composition isochemical with the Earth mantle, at present a minority viewpoint, is the chemical composition consistent with the lunar isotopic composition. In Section 4.6, we discuss an alternative interpretation for the silicon isotope data that can be evaluated with better thermodynamic models of high temperature magmas ( $\Gamma =$

2,500–3,500 K). This scenario can also be further tested and developed through exposure to other isotopic systems.

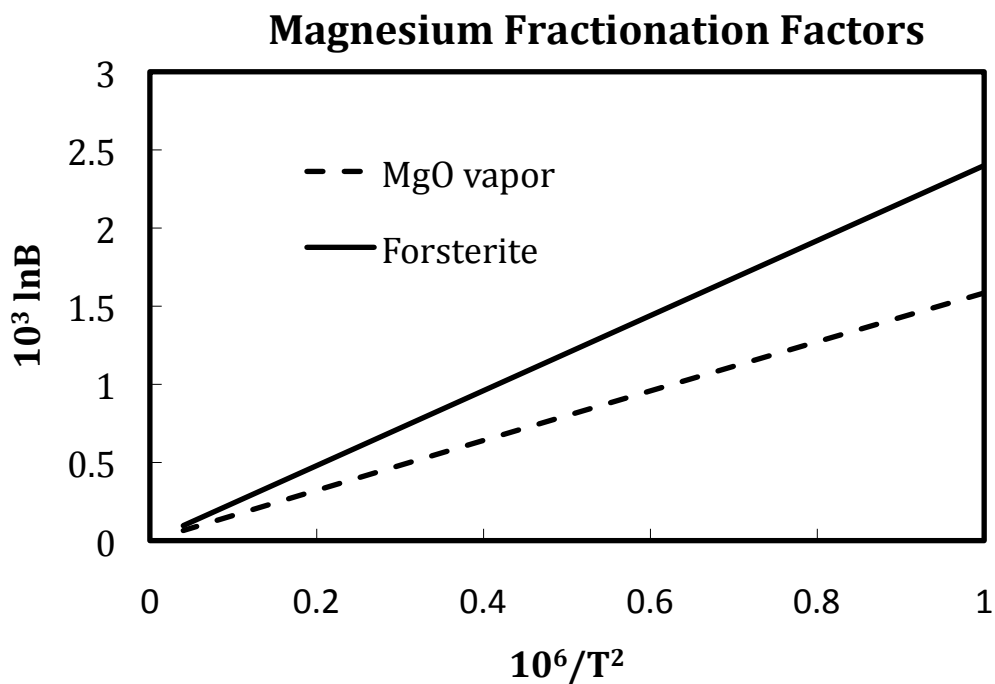
#### 4.5.2 Magnesium

Magnesium isotopes provide an interesting case study because they highlight some of the additional features of fractionation via liquid-vapor separation. The isotopic composition of magnesium in mantle rocks can be determined to a fraction of a per mil (Handler et al. 2009), and fractionation between mantle minerals has been predicted and observed, but is limited in magnitude due to the high temperatures of isotopic equilibration (Young et al. 2009), and the similarity of bonding environments for magnesium between co-existing minerals. On the post-giant-impact Earth, magnesium exists in its dominant natural oxidation state (+2) in the liquid, while magnesium in the vapor appears in mixed valence in the form of the diatomic molecule MgO (+2) and atomic Mg (+0) species, with both species contributing significant partial vapor pressures (Figure 4.1) and isotopic fractionation to magnesium vapor in equilibrium with silicate melts. Hence, we write an isotope exchange reaction between the vapor species and a condensed phase:



$$K_1 = \frac{Q(^{26}\text{MgSi}_{1/2}\text{O}_2)}{Q(^{24}\text{MgSi}_{1/2}\text{O}_2)} \bigg/ \frac{Q(^{26}\text{MgO})}{Q(^{24}\text{MgO})} \quad (4.8)$$

for each Mg-bearing vapor species, where the bonding environment for magnesium in the liquid is approximated by that of crystalline forsterite whose vibrational properties are known from harmonic DFT calculations ( $10^3 \ln B_{\text{Mg-Forsterite}} = 2.4 \times (10^3/T)^2$ , Edwin Schauble, personal communication). The Forsterite-MgO(v) and Forsterite-Mg(v) isotopic equilibria bracket the range of liquid-vapor Mg isotopic fractionation that can be expected, with the actual fractionation dependent on the relative abundances of these two species in the vapor.



**Figure 4.4.** The  $^{26}\text{Mg}/^{24}\text{Mg}$  fractionation factors in Forsterite and the MgO vapor molecule where the fractionation factor for Mg(v) is zero on this scale. The magnitude of the Forsterite-Mg(v) fractionation is much greater than that of Forsterite-MgO(v) fractionation ( $=0.8 \times (10^3/T)^2$  per mil according to this calculation), but both are of the same sign, meaning that the isotopic composition of magnesium in the vapor is lighter

than that in the liquid in equilibrium at all temperatures. Because most of the magnesium vapor is in atomic form (Figure 4.1), appreciable liquid-vapor differences exist ( $\sim 2$  per mil at 1000 K). Despite this significant intrinsic fractionation between liquid and vapor, magnesium isotope fractionation is limited by the strong preference of magnesium to partition into the liquid (see text).

Moreover, the speciation of magnesium in the vapor varies systematically with altitude, with a modest increase in the atomic (versus diatomic) fraction with decreasing pressure due to the shifting of the dissociation equilibrium (Figure 4.1). Therefore, unlike the case for silicon isotopes, where the speciation of SiO dominates throughout the column, magnesium isotope fractionation exhibits sensitivity to the pressure of liquid separation due to the variation of the speciation equilibrium with pressure. The equations of mass balance and isotopic equilibrium between the liquid and vapor read:

$$\delta_p = f_V^{Mg} \delta_V + (1 - f_V^{Mg}) \delta_L \quad (4.9)$$

$$\delta_V = x_{MgO} \delta_{MgO} + (1 - x_{MgO}) \delta_{Mg} \quad (4.10)$$

$$\Delta_1 = \delta_L - \delta_{MgO} \quad (4.11)$$

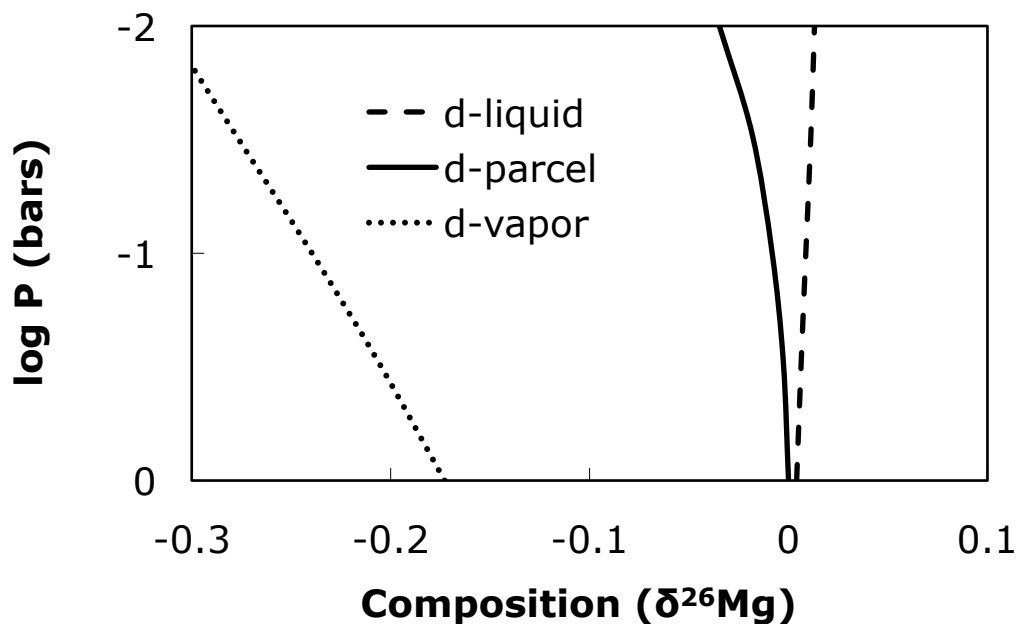
$$\Delta_2 = \delta_L - \delta_{Mg} \quad (4.12)$$

$$\Delta_{L-V} = \delta_L - \delta_V \quad (4.13)$$

where, as before,  $\Delta_i = (K_i - 1) \times 10^3$  for isotope exchange reactions and  $x_{MgO}$  represents the fraction of Mg-bearing vapor species in monoxide form, and magnesium vapor is

assumed to be present only in monoxide and atomic form ( $x_{\text{MgO}} + x_{\text{Mg}} = 1$ ). Using values of the speciation ( $x_{\text{MgO}}$ ) and degree of magnesium vaporization ( $f_V^{\text{Mg}}$ ) from chemical equilibrium calculations (Chapter 3), and isotope fractionation factors ( $\Delta_1, \Delta_2$ ) calculated according to the procedure described above, the magnesium isotopic fractionation ( $\Delta_{\text{L,V}}$ ) between the liquid and vapor is calculated. The fraction of magnesium vaporized ( $f_V^{\text{Mg}}$ ) in equation (4.9) is related to the fraction of silicon (or olivine units) vaporized ( $f_V^{\text{Si}}$ ) via the relation  $f_V^{\text{Mg}} = f_V^{\text{Si}} \times (x_V / x_P)$  where  $x_V$  and  $x_P$  are the composition ( $=\text{Mg}/\text{Mg}+\text{Fe}$ ) of the vapor and parcel, respectively. This is an important distinction. It has the effect of subduing the magnesium isotopic fractionation that results due to rainout because, qualitatively, if little magnesium partitions into the vapor, then the magnesium isotopic composition of the parcel is relatively unchanged by liquid rainout. This behavior will also certainly apply to ultra-refractory elements (i.e., CaO, TiO<sub>2</sub>) that, in this scenario, experience isotopic homogenization with negligible subsequent fractionation. MgO is not classified as an ultra-refractory component. However, its fractionation in the scenario here explored is limited by the fact that fayalite (Fe<sub>2</sub>SiO<sub>4</sub>) is much more volatile than forsterite (Mg<sub>2</sub>SiO<sub>4</sub>) and the vapor fraction in isentropic columns in the vapor atmosphere of Earth is low (4–8 percent for  $S = 10k_B/\text{atom}$ ) and can largely be accommodated with the less abundant fayalite component. This feature of an isentropic post-impact Earth — of low degrees of partial vaporization — limits the magnitude of magnesium isotopic fractionation that can occur in Earth’s silicate vapor atmosphere (Figure 4.5).





**Figure 4.5.** Magnesium isotopic structure of a silicate vapor atmosphere of Earth. The lighter isotopes of magnesium have a preference for the vapor, and liquid rainout therefore generates upper atmospheres with compositions shifted towards lighter isotopes. However, despite the significant difference between the composition of the liquid and vapor ( $\sim 0.2\text{--}0.3$  per mil), the parcel composition evolves only slightly, due to the small degree of magnesium vaporization. This is consistent with no magnesium isotopic offsets observed in the silicate Earth-Moon system at the level of 0.1 per mil.

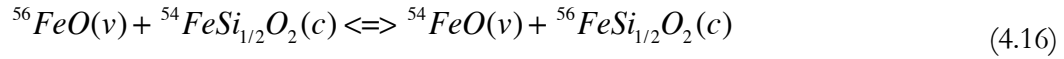
#### 4.5.3 Iron

Iron isotopes provide potentially unique information on the processes of lunar formation. Fe isotopes have been measured in igneous rocks from the inner Solar System, including the Earth and Moon (Poitrasson et al. 2004), and the initial findings

were that terrestrial basalts were enriched by  $\sim 0.1$  per mil in  $^{57}\text{Fe}/^{54}\text{Fe}$  relative to basalts from Mars and Vesta, and that lunar igneous rocks were enriched by a further  $\sim 0.1$  per mil relative to the Earth. As anyone well versed in Leninist ideology knows, sometimes, things must get worse before they get better. The Fe isotope story is a case in point, as the initial observations and interpretation of (Poitrasson et al. 2004) have been supplemented by observations of systematic differences between different lunar lithologies (Weyer et al. 2005), evidence for Fe isotope fractionation during silicate differentiation of the Earth (Williams 2005, Weyer and Ionov, 2007), an argument that high-temperature, high-pressure core formation can significantly fractionate Fe isotopes (Polyakov 2009), and a quantitative model for Fe isotopic fractionation during petrogenesis (Dauphas et al. 2009) that relies on the experimentally calibrated high-temperature fractionation between ferric ( $\text{Fe}^{+3}$ ) and ferrous ( $\text{Fe}^{+2}$ ) iron (Shahar et al. 2008). While progress in defining the Fe isotope composition of the bulk silicate Earth has been made, the Fe isotopic composition of the Moon is still not well known. Here, we merely note that liquid-vapor separation can fractionate Fe isotopes and identify the sign and quantify the magnitude of such fractionation in the silicate vapor atmosphere of Earth.

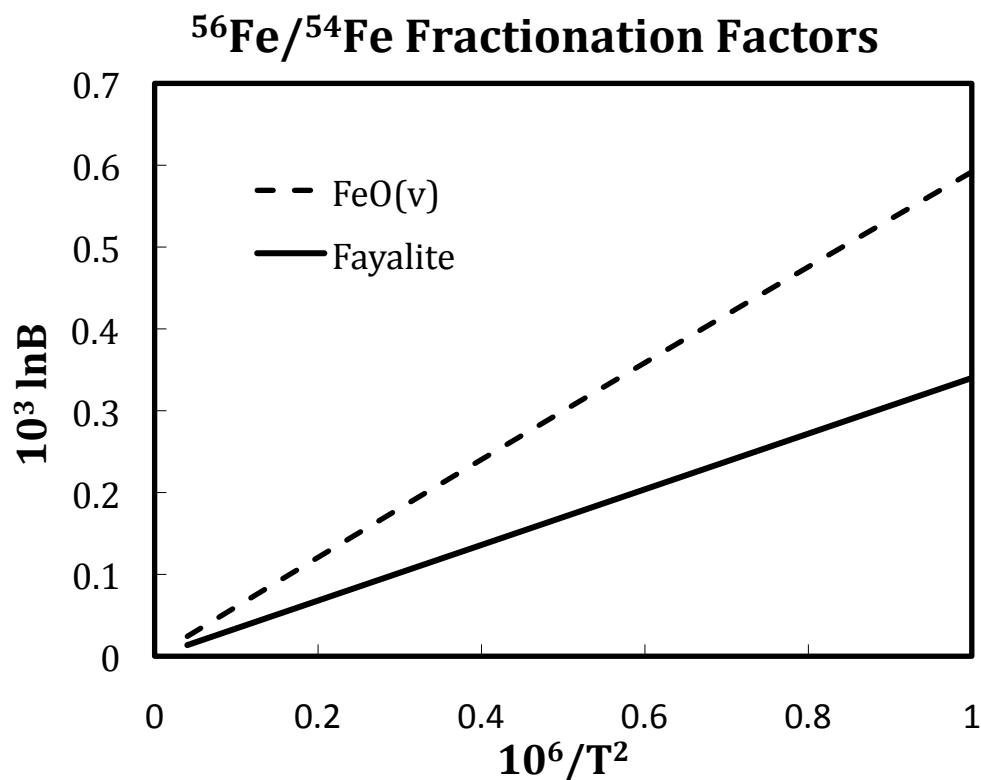
The behavior of Fe on the post-impact silicate Earth is analogous to that of Mg, but it does exhibit some new features. In the liquid,  $\text{Fe}^{+2}$  is expected to dominate the valence, while iron in the vapor appears in mixed valence, with  $\text{FeO}(\text{v})$  and  $\text{Fe}(\text{v})$  both contributing significantly to the total vapor pressure of iron, especially in the lower

atmosphere (Figure 4.1). Hence, two isotope exchange reactions between liquid and vapor — one for each Fe-bearing vapor species — must be written:



$$K_1 = \frac{Q({}^{56}\text{FeSi}_{1/2}\text{O}_2)}{Q({}^{54}\text{FeSi}_{1/2}\text{O}_2)} \bigg/ \frac{Q({}^{56}\text{FeO})}{Q({}^{54}\text{FeO})} \quad (4.17)$$

where the octahedral coordination of Fe in crystalline fayalite is assumed to approximate the bonding environment of iron in the silicate liquid ( $10^3 \ln B_{\text{Fe-Olivine}} = 0.34 \times (10^3/T)^2$ ), and is derived from Mossbauer spectroscopy (Polyakov and Mineev 2000).



**Figure 4.6** The equilibrium constant for the exchange reaction involving  $\text{FeO(v)}$  is less than unity (since  $10^3 \ln B_{\text{FeO(v)}} = 0.6 \times (10^3/T^2)$ ), i.e., heavy isotopes are concentrated in this vapor molecule relative to the liquid. Differences in the bonding environment of  $\text{Fe}^{+2}$  in various crystals are small on this scale, strengthening this conclusion. However, atomic  $\text{Fe(v)}$  is the most abundant Fe-bearing vapor species, and, lacking vibrational degrees of freedom, is isotopically lighter than the liquid. It is zero on this scale, causing the iron-vapor in equilibrium with a silicate liquid to be — on average — enriched in the lighter isotopes. Hence, not only the magnitude, but the sign of the fractionation depends on the speciation. The net effect of having two vapor species with a greater ( $\text{FeO}$ ) and lesser ( $\text{Fe}$ ) preference for the heavy isotopes relative to the liquid is to subdue an already subtle isotopic fractionation.

The equations of mass-balance and isotopic equilibrium between the liquid and vapor-species read:

$$\delta_p = f_V^{Fe} \delta_V + (1 - f_V^{Fe}) \delta_L \quad (4.20)$$

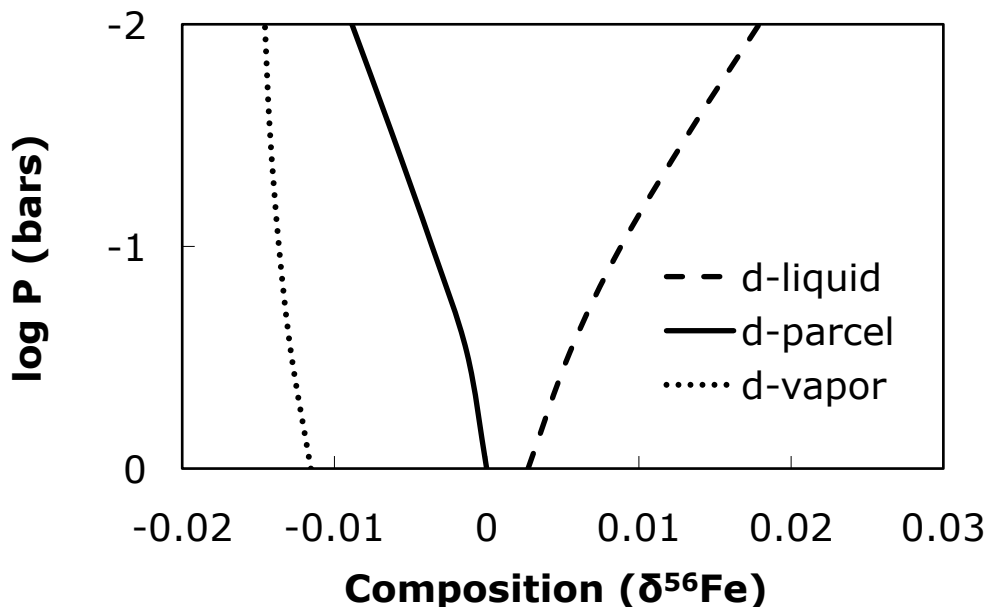
$$\delta_V = x_{FeO} \delta_{FeO} + (1 - x_{FeO}) \delta_{Fe} \quad (4.21)$$

$$\Delta_1 = \delta_L - \delta_{FeO} \quad (4.22)$$

$$\Delta_2 = \delta_L - \delta_{Fe} \quad (4.23)$$

$$\Delta_{L-V} = \delta_L - \delta_V \quad (4.24)$$

where, as before,  $\Delta_i = (K_i - 1) \times 10^3$  for the isotope exchange reactions and  $x_{FeO}$  represents the fraction of Fe-bearing vapor species in monoxide form, and it is assumed that the iron in the vapor only appears as a monoxide or atomic vapor ( $x_{FeO} + x_{Fe} = 1$ ). Using values of the speciation ( $x_{FeO}$ ) and degree of iron vaporization ( $f_V^{Fe}$ ) from chemical equilibrium calculations (Chapter 3), and isotope fractionation factors ( $\Delta_1, \Delta_2$ ) calculated with the procedure described above, the iron isotopic fractionation ( $\Delta_{L-V}$ ) between the liquid and vapor is calculated. The fraction of iron vaporized ( $f_V^{Fe}$ ) is related to the fraction of silicon (or olivine units) vaporized ( $f_V^{Si}$ ) via the relation  $f_V^{Fe} = f_V^{Si} \times (x_V / x_p)$  where  $x_V$  and  $x_p$  are the composition ( $=Fe/Mg+Fe$ ) of the vapor and parcel, respectively. The result of a distillation calculation is plotted in Figure 4.7.



**Figure 4.7.** Even for the maximum amount of rainout consistent with the lunar chemical composition, the Fe isotope fractionation that would evolve is  $\sim 0.01$  per mil. Unlike magnesium, whose isotopic effects are muted mostly due to its near-complete partitioning into the liquid, the smaller intrinsic isotopic fractionation of Fe limits the degree to which the isotopes of this element can shed light on the process of liquid-vapor fractionation. However, even the smaller intrinsic magnitude of liquid-vapor Fe isotope fractionation is comparable to the crystal-melt fractionation of Fe isotopes inferred for partial melting of Earth's mantle, but is muted due to high temperatures encountered in the afterglow of the giant impact.

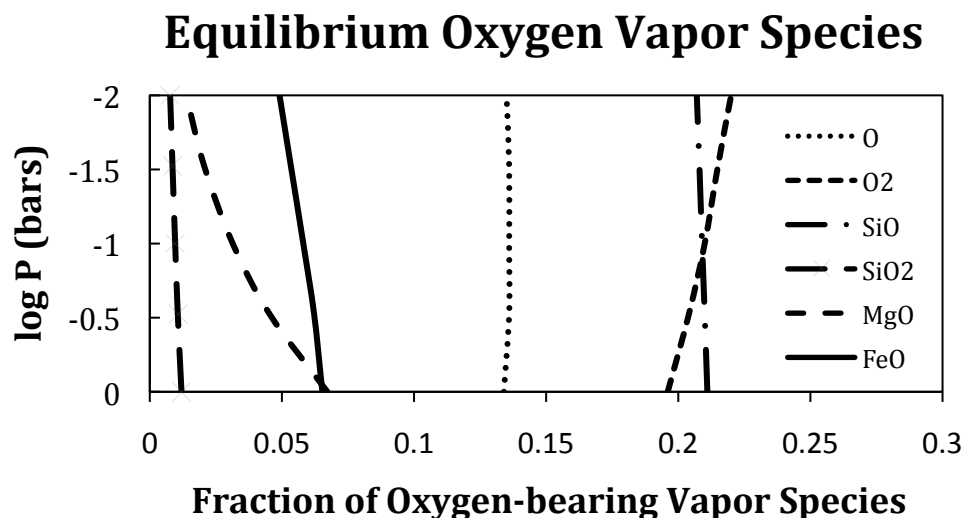
Hence, if the claimed  $\sim 0.1$  per mil silicate Earth-Moon difference in  $^{57}\text{Fe}/^{54}\text{Fe}$  (or equivalently, the  $\sim 0.067$  per mil difference in  $^{56}\text{Fe}/^{54}\text{Fe}$ ) is real, it must be due to

liquid-vapor fractionation in another setting relevant to lunar origin, or to kinetic processes. It cannot be explained through equilibrium liquid-vapor fractionation in the silicate vapor atmosphere of Earth. From an experimental point of view, it is of central importance to determine whether an Fe isotope difference in the silicate Earth-Moon exists, since it would clearly point to a setting beside the one here explored as responsible for the major element isotopic (and hence, elemental) composition of the Moon.

#### 4.5.4 Oxygen

No discussion of stable isotope geochemistry would be complete without a discussion of oxygen isotopes. The oxygen isotope composition of peridotites from the Earth's mantle have been measured and found to be relatively uniform, making the precise determination of the  $^{18}\text{O}/^{16}\text{O}$  ratio of bulk silicate Earth conceivable. The similarity of the oxygen isotopic composition of lunar samples with Earth — even before the discovery of mass-independent effects — was recognized, and this similarity in  $\delta^{18}\text{O}$  between these silicate reservoirs has only gotten stronger since the laser-fluorination revolution rocked the world of oxygen isotope geochemistry some 20 years ago. For this reason, subscribers to the view that the oxygen isotopic composition of the Moon is derived from the Moon-forming impactor without turbulent mixing with the fluid silicate Earth must posit two coincidences in the composition of the impactor, one a near identity with Earth in  $\Delta^{17}\text{O}$ , another in  $\delta^{18}\text{O}$ . Indeed, the fact that isotopic fractionation is small at the high temperatures encountered after the Moon-forming giant impact is an attractive feature of the equilibration hypothesis, as was first pointed

out by Bob Clayton, the father of oxygen isotope cosmochemistry. With improved analytical techniques, differences (of order  $\sim 0.1$  per mil) between the silicate Earth and Moon have tentatively been claimed (Spicuzza et al. 2007). Here, we explore the behavior of oxygen isotopes in an equilibrium liquid-vapor system and show that — at least with an olivine model — such an offset cannot evolve in the silicate vapor atmosphere of Earth. Oxygen is unique among the elements here studied because it appears in several abundant vapor phase species (Figure 4.8).

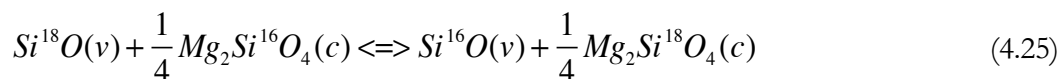


**Figure 4.8.** Oxygen-bearing vapor species in equilibrium with liquid olivine in the silicate vapor atmosphere of Earth. In decreasing order of atomic abundance, oxygen in the vapor resides in  $O_2$ ,  $SiO$ ,  $O$ ,  $FeO$ ,  $MgO$ , and  $SiO_2$  with only subtle variations in the relative abundances of the species with pressure. Note that the crossover (at 100 millibars) of  $SiO$  and  $O_2$  as the most abundant reservoir of oxygen is illusory because twice as many oxygen atoms reside in the  $O_2$  molecule. This abundance spectrum of



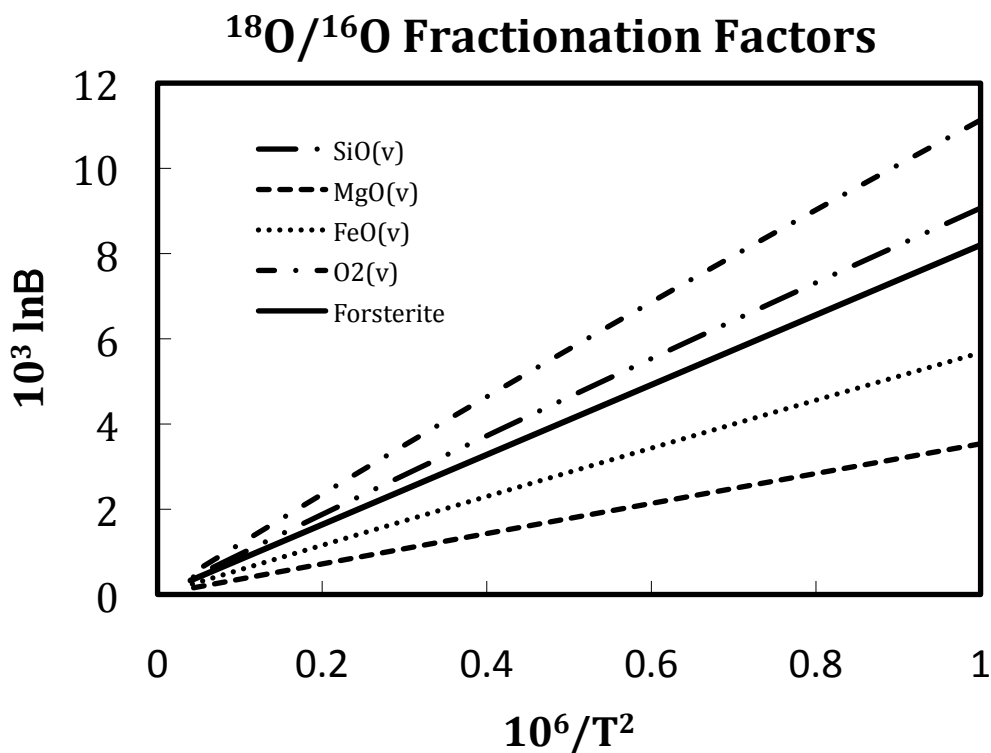
vapor-phase species happens to have nearly the same oxygen isotopic composition as liquid olivine (see text).

The vibrational frequencies of all these molecules, at least in their ground electronic state, are known (Table 4.1), and an exchange reaction between the oxygen in the liquid and vapor is written for each vapor species:



$$K_{eq} = \left[ \frac{Q(Mg_2Si^{18}O_4)}{Q(Mg_2Si^{16}O_4)} \right]^{1/4} / \left[ \frac{Q(Si^{18}O)}{Q(Si^{16}O)} \right] \quad (4.26)$$

where, as before, liquid-vapor equilibria are approximated by the corresponding crystal-vapor equilibria. For oxygen in particular, it has been recognized for some time that the behavior of the isotopes in silicate melts can be approximated by considering their behavior in the minerals that would form upon crystallization of such melt. Although mineral-melt fractionations of oxygen isotopes have been observed, this is primarily due to the distinct chemical composition of melt and co-existing minerals in multi-component silicate systems. Here, we assume that this approach is valid even at the temperatures here encountered that are further removed from the melting point of these minerals. We adopt the fractionation factor for oxygen in olivine from (Clayton and Kieffer, 1991) and note that, as in the case of iron, there are vapor species with isotopic compositions both lighter ( $O$ ) and heavier ( $O_2$ ) than the liquid (Figure 4.9).



**Figure 4.9.** The  $^{18}\text{O}/^{16}\text{O}$  fractionation factors in forsterite and various oxygen carriers in the vapor. As expected in the high-temperature limit, the fractionation factors scale with temperature as  $\sim 1/T^2$ . For forsterite, we adopt  $10^3 \ln B_{\text{O-Olivine}} = 8.2 \times (10^3/T)^2$  and note that there are species with ( $\delta^{18}\text{O}$  at 1,000 K) both heavier  $\text{O}_2$  (+3.2 per mil),  $\text{SiO}_2$  (1.5‰),  $\text{SiO}$  (+1‰) and lighter  $\text{FeO}$  (-2.5‰),  $\text{MgO}$  (-4.6‰),  $\text{O}$  (-8.2‰) isotopic compositions than the liquid. Therefore, not only the magnitude, but the sign of the isotopic fractionation depends on the vapor speciation.  $\text{SiO}_2(\text{v})$  is included in the calculations but only constitutes 2 percent of oxygen in the vapor and is omitted in the plot for clarity.

The equations for calculating the isotopic fractionation between liquid and vapor in a parcel read:

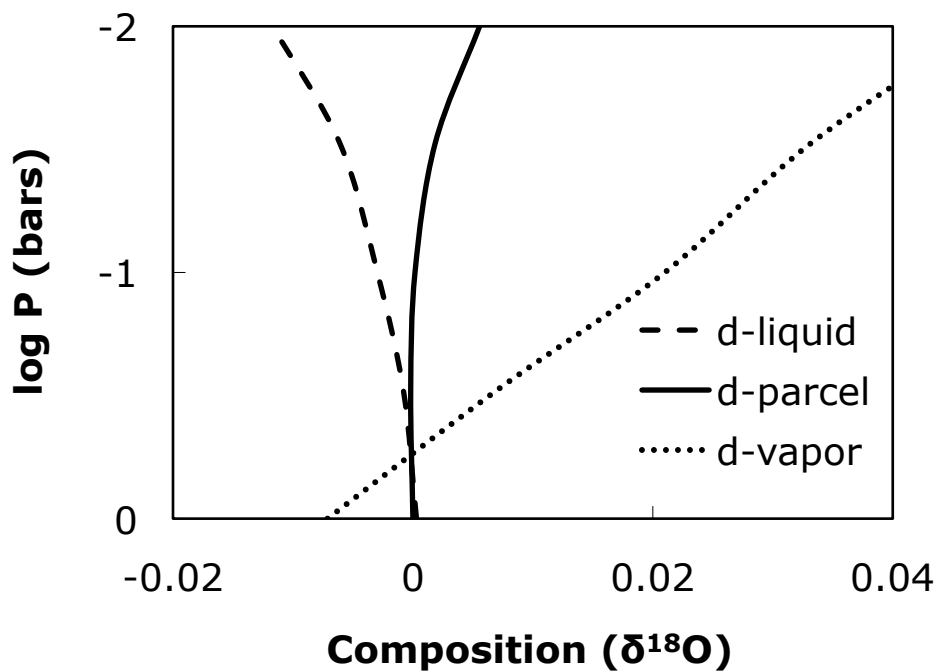
$$\delta_p = f_v^O \delta_v + (1 - f_v^O) \delta_L \quad (27)$$

$$\delta_v = \sum_i x_i \delta_i \quad (28)$$

$$\Delta_i = \delta_L - \delta_i \quad (29)$$

$$\Delta_{L-v} = \delta_L - \delta_v \quad (30)$$

where,  $f_v^O$  is the fraction of oxygen in the parcel that is vaporized, and is simply equal to the fraction of silicon vaporized ( $f_v^{Si}$ ) because olivine is assumed to vaporize congruently, i.e., there are 4 atoms of oxygen for each silicon atom, in the vapor as in the liquid (Chapter 3). An equation like equation (4.29) is written for each of 6 oxygen-bearing vapor species. Folding these equilibrium liquid-vapor fractionation calculations into a rainout scenario yields the vertical oxygen isotope structure of a silicate vapor atmosphere. An example calculation is shown in Figure 4.10.



**Figure 4.10.** Oxygen isotopic structure on a model olivine vapor atmosphere of Earth. An unexpected result of these calculations is that the opposing effects of vapor species both lighter and heavier than the liquid in terms of oxygen isotopes nearly cancel. This is readily seen as the oxygen isotopic composition of the vapor transitions from light-enriched in the lower atmosphere to heavy-enriched at pressures  $< 500$  mbars. The modest change in the oxygen vapor speciation (Figure 4.8) can only result in a change in sign if the opposing effects of light and heavy vapor species nearly cancel.

Oxygen isotope fractionation in an olivine atmosphere is limited to  $< 0.01$  per mil. However, given that such a small liquid-vapor fractionation factor is a fortuitous sum of several large positive and negative fractionations between the liquid and individual

vapor species, perhaps a more important conclusion from these calculations is that liquid-vapor fractionation in the silicate vapor atmosphere of Earth can evolve both heavy and light oxygen isotope compositions. In the case of oxygen, the limitations of the present model should be kept firmly in mind. A more realistic model that does not approximate the silicate Earth with olivine composition will have a different prediction for the vapor composition and vapor speciation, and therefore a different prediction for the lunar oxygen isotope composition. Nevertheless, in an olivine atmosphere, the oxygen isotope fractionation due to liquid rainout is  $< 0.01$  per mil.

Given that no samples escaped the primordial lunar differentiation and systematic differences between the oxygen isotopic composition of lunar anorthosites and low-Ti and high-Ti mare basalts have been observed, modeling of the isotopic evolution of magmas and minerals during the crystallization of the lunar magma ocean is necessary before knowledge of the  $^{18}\text{O}/^{16}\text{O}$  composition of the bulk Moon from measurements of differentiated samples can be claimed, and compared to reconstructions of the bulk isotopic composition of the silicate Earth.

#### **4.6. Discussion**

In Chapter 2, we explored the possibility that the terrestrial isotopic composition of the silicate Moon arose due to turbulent mixing of the melt-vapor proto-lunar disk and the silicate vapor atmosphere of Earth. In Chapter 3, we showed that widely postulated major-element differences between the silicate Earth and Moon may have arisen due to liquid separation in the convective silicate vapor atmosphere. In this

chapter, we have quantified the isotopic fractionation for the elements silicon, magnesium, iron, and oxygen under the assumption that liquid rainout was the process responsible for generating such major-element silicate differences. We have used a model olivine atmosphere to demonstrate that measurable isotopic offsets between the silicate Earth and Moon — at the limit of current analytical precision — could have evolved in the silicate vapor atmosphere of Earth for the stable isotopes of the element silicon. By contrast, the offsets evolved in such a model atmosphere for iron, magnesium, and oxygen isotopes would be negligible. While the bulk isotope composition of iron and oxygen for the silicate Earth and Moon are, at present, not precisely known due to fractionation accompanying geologic processes, measurements on silicon isotopes have not resolved the expected offset. Here, we briefly summarize the results from the previous section and discuss ways to make progress in the interpretation of such data in the future.

Magnesium isotopes are not significantly fractionated in the vapor atmosphere by rainout because — at the entropies relevant to the post-giant-impact silicate Earth — magnesium remains mostly partitioned into the liquid droplets and gets isotopically homogenized without subsequent fractionation. Iron isotopes are not significantly fractionated because of the small intrinsic liquid-vapor differences at the high temperatures encountered in a silicate vapor atmosphere. Silicon isotopes are unique in that they fractionate significantly during liquid-vapor but not crystal-melt separation and can evolve a  $\sim 0.1$  per mil difference in the  $^{30}\text{Si}/^{28}\text{Si}$  ratio between the silicate Earth and Moon during the formation era. However, silicon isotopes may require high

degrees of vaporization to fractionate. Oxygen isotopes experience relatively large fractionations between the liquid and vapor species, but the fractionation factors for diverse vapor species nearly cancel, and oxygen is fractionated negligibly in an olivine atmosphere.

This kind of approach — at the confluence of high-temperature thermodynamics, isotopic fractionation, and physical modeling — by constraining the compositions that can be derived from the partially vaporized terrestrial mantle, has the potential to resolve long-standing questions on the lunar bulk chemical composition. However, at present, none of the isotopic systems studied provides unequivocal evidence for liquid-vapor fractionation in the aftermath of the giant impact. However, each of these isotopic systems highlights an avenue of research that can strengthen the connection between the formation process and the resulting signature in the lunar composition. Here, we discuss two such avenues.

#### 4.6.1 High-Temperature Thermodynamics

The temperatures encountered in the silicate vapor atmosphere ( $T = 2,500\text{--}3,500\text{ K}$ ) are higher than those normally encountered in igneous systems on the modern Earth. For this reason, we have approximated the silicate Earth by a mineral composition, olivine, for which thermodynamic data at the relevant temperatures exist. The fact that olivine is the most abundant mineral in the low-pressure mantle of the Earth lends plausibility to such an approximation, but the primary advantage to such an approach is its simplicity. In reality, the terrestrial mantle has plenty of pyroxene, and

quantitative comparisons of calculations to isotopic data are meaningful only to the extent that the calculations are robust to such refinements in the silicate composition. Silicon isotopes provide a relevant example. Calculations of rainout in an olivine atmosphere sufficient to cause a twofold enrichment in FeO/MgO is accompanied by a  $\sim 0.14$  per mil depletion in the  $^{30}\text{Si}/^{28}\text{Si}$  ratio, but this is only because olivine vaporizes congruently, with every two atoms of Fe in the vapor being accompanied by one atom of Si. However, in vaporization experiments with magmas in the FeO-MgO-SiO<sub>2</sub>-CaO-Al<sub>2</sub>O<sub>3</sub> system present in cosmic proportions, nearly all of the FeO vaporizes before any SiO<sub>2</sub> enters the vapor phase. Although these are kinetic experiments at low temperatures ( $\sim 2,000$  K), they suggest that the behavior of FeO may be decoupled from that of other components in the terrestrial vapor atmosphere, and the low degree of vaporization in the silicate vapor atmosphere may be mostly accommodated by the FeO component. Such a behavior would result in an enhanced FeO/MgO without silicon isotope fractionation. Indeed, the extent to which the silicon isotope data can constrain liquid-vapor fractionation depends on the extent to which silicon partially vaporizes. Hence, the silicon isotope data is one example where the interpretation can be clarified with an improved thermodynamic model of silicate liquids at the relevant temperatures that can quantify the extent to which the volatility of FeO and SiO<sub>2</sub> are coupled. To the extent that they are, the minority viewpoint that the silicate Moon is isochemical with the terrestrial mantle must be taken seriously.



#### 4.6.2 Volatile Element Depletion

Even if the silicate Earth-Moon system is isochemical in terms of major elements, the silicate Moon appears to be depleted in its abundance of volatile elements relative to the terrestrial mantle. Interest in the question of volatiles in the Moon has been renewed by the discovery of water in the lunar interior (Saal et al. 2008). The source of the water is, at present, not clear. One possibility is that the process responsible for the depletion of moderately volatile elements (i.e., Na, K) from the lunar material was incomplete, even for hydrogen. At present, the setting(s) for such elemental separation is not known, but the abundance, distribution, and isotopic composition of lunar volatiles may be diagnostic of the depletion process. Theoretical discussions to date have focused on kinetic processes (Pritchard and Stevenson 2000), but we have shown that equilibrium offsets can evolve for elements removed by partial vaporization, and future work will involve extending calculations for equilibrium isotopic fractionation to trace elements. However, even in the absence of equilibrium effects, new insights may be gleaned by quantifying the magnitude of kinetic processes. In terrestrial meteorology, disequilibrium (for example, > 100 percent saturation in clouds) is commonly observed. Indeed, such departures from equilibrium are necessary to drive the system towards equilibrium. As an example, if the recently discovered water in the lunar interior is primordial, it should be possible to derive the measured lunar D/H from the primordial terrestrial value via kinetic and/or equilibrium processes. As in the case of the hydrologic cycle on the modern Earth, both may be important.

#### 4.7. Conclusions

The primary conclusions of this chapter are as follows. Liquid-vapor separation, even for phases in equilibrium at the temperatures following the giant impact, can generate significant ( $\sim 0.1$  per mil) isotopic differences. The isotopic composition of silicate vapor is lighter than that of co-existing liquid for the elements silicon, magnesium, and iron, and can be lighter or heavier than the liquid for oxygen, depending on the vapor speciation. In one of the settings relevant to the lunar composition, and assuming that olivine approximates the partial vaporization behavior of silicates, magnesium, iron, and oxygen isotopes are fractionated negligibly ( $< 0.05$  per mil) while silicon isotopes can evolve  $\sim 0.1$  per mil differences between the silicate Earth and Moon. However, chemical and isotopic fractionation is concomitant, and such offsets are expected only to the extent that major-element compositions (i.e., FeO/MgO) of the silicate Earth and Moon are different. The observed absence of a silicate Earth-Moon difference in terms of silicon isotopes argues that either an olivine composition mantle does not capture the partial vaporization behavior of the silicate Earth, or that the minority viewpoint that the major-element composition of the silicate Moon is the same as the terrestrial mantle (or nearly so) may be correct. Finally, determining the stable isotope composition of the silicate Earth and Moon to higher precision can yield new insights into the lunar formation process.

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