

## PLANETARY SCIENCE

# Volatile element depletion of the Moon—The roles of precursors, post-impact disk dynamics, and core formation

K. Righter

The compositional and isotopic similarity of Earth's primitive upper mantle (PUM) and the Moon supports the derivation of the Moon from proto-Earth, but the Moon's inventory of volatile lithophile elements—Na, K, Rb, and Cs—is lower than Earth's PUM by factors of 4 to 5. The abundances of 14 other volatile elements exhibit siderophile behavior [volatile siderophile elements (VSEs); i.e., P, As, Cu, Ag, Sb, Ga, Ge, Bi, Pb, Zn, Sn, Cd, In, and Tl] that can be used to evaluate whether the Moon was derived from proto-Earth and if core formation or volatility controlled their depletion. At lunar core formation conditions, As, Sb, Ag, Ge, Bi, and Sn are siderophile, whereas P, Cu, Ga, Pb, Zn, Cd, In, and Tl are weakly siderophile or lithophile. VSEs may help to discriminate between physical and chemical processes that formed the Moon such as low- versus high-energy impacts and gas-melt interactions.

## INTRODUCTION

The similarity of Earth and the Moon isotopic composition (O, Ti, Ca, Fe, Mg, etc.), coupled with physical aspects such as angular momentum, lunar mass, and inclination, has led to various impact models for the origin of the Moon. The canonical late impactor (1) model showed that an impactor/proto-Earth mass ratio of 1:9 with a relatively low impact velocity would result in an Earth-Moon system that has many of the observed properties of our own. With relaxation of angular momentum constraints, more energetic collisions such as in highly spun up impactor and proto-Earth (2, 3) or 1:1 impactor/proto-Earth scenarios (3, 4) can also produce an Earth-Moon system as long as they are coupled with an angular momentum loss mechanism. Multiple smaller mass and energy impacts (5) can also produce an Earth-Moon system, with the overall energetics more similar to a canonical model. The latter three models are relatively new and grew out of the last decade of research exploring the details of angular momentum, lunar source material, and preimpact spin state constraints and have led to multiple working hypotheses for the lunar origin (1–5).

The volatile element depletions in the Moon have been recognized for decades (6, 7). Volatile elements can be depleted in the precursor (or building blocks) of the Moon, they can be depleted during the impact and post-impact processes that formed the Moon, and then, some can be partitioned into the Moon's metallic core. Although multiple explanations have been debated, and arguments have become more quantitative, the depletion of many volatile elements remains unexplained in detail. In this study, newly available core-mantle partitioning data for 14 volatile siderophile elements (VSEs) [e.g., (8–12) and references therein] are used to evaluate the roles of precursor volatility, disk dynamics, and core formation in establishing the lunar VSE depletion and to test the hypothesis that the Moon was derived from primitive upper mantle (PUM)-like material. Examination of all 14 elements (P, As, Cu, Ag, Sb, Ga, Ge, Bi, Pb, Zn, Sn, Cd, In, and Tl) at once allows recognition of general trends among the VSEs, without undue focus on one element. The VSE content of the lunar mantle will be updated using published data from lunar samples

(Apollo and Luna basalt and glass samples; see Materials and Methods). The three processes that determine whether PUM-like material could make the Moon (precursor volatile element depletion, protolunar disk dynamics, and lunar core formation) have been modeled to occur in three stages to separately assess their control on the VSE contents (see Materials and Methods).

## RESULTS

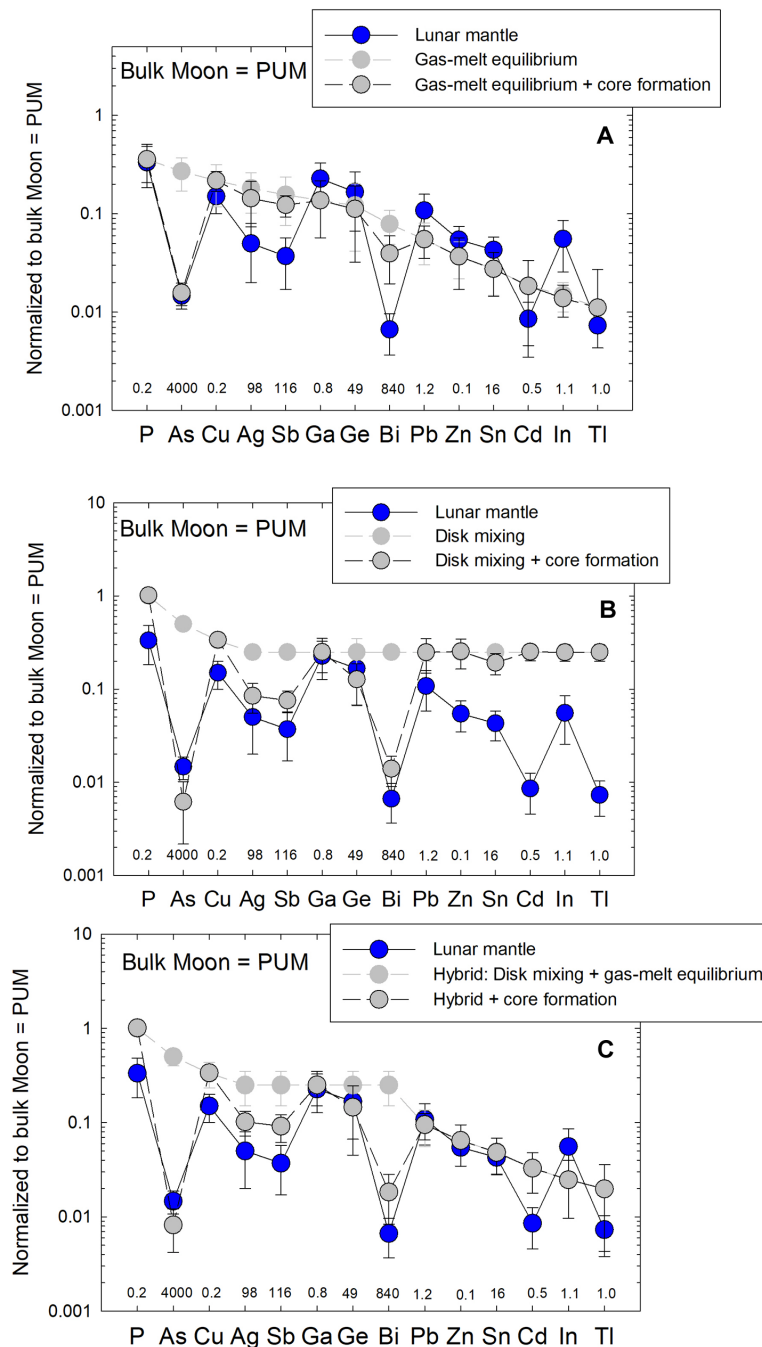
Using Eqs. 1 and 2 and a bulk silicate Earth composition (PUM) for the bulk Moon, we can examine several hypotheses for the origin of lunar volatiles. Discussion in the main text focuses on a PUM-like bulk Moon because this composition provides successful models for lunar mantle VSEs, as will be shown below. The two other Mars-sized impactor mantle bulk compositions do not provide successful models for the lunar mantle VSEs, and they are described in detail in section S4.

First, using a PUM composition, without an Earth-Moon volatility correction, unexpectedly results in lunar mantle VSE concentrations that are too high, indicating the need for depletion mechanisms in addition to stage 1. High-energy lunar formation models produce a gas-rich disk, indicating that the gas-melt fractionation may exert a strong control on volatile elements and can explain the 4× alkali element depletion of the Moon relative to Earth's mantle (3). Assuming that the least volatile element (P) and the most volatile element (Tl) can be explained by gas-melt fractionation with a gas fraction of 0.9 and by varying the  $D(\text{gas-melt})$  from 3 (P) to 100 (Tl) to fit these elements (see table S1) results in a good match to most of the VSEs, but concentrations are still too high for As, Ag, Sb, and Bi—a mismatch of >10 (stage 2; Fig. 1A). It is important to note that all four of these elements are moderately siderophile and thus have a substantial depletion due to core formation. When core formation is accounted for (stage 3), the fit to these four elements is improved, but Ag, Sb, and Bi remain mismatched by ~10 (Fig. 1A). Thus, a scenario of stages 1 to 3 with a gas-rich stage 2 explains many but not all of the VSEs.

Second, lower-energy lunar formation scenarios [such as canonical (1) or multiple impact (5) models] might involve mixing between volatile-depleted hot inner disk and cooler outer disk (volatile bearing) material, which (13) argues can also explain the factor of ~4 depletion of alkali elements in the Moon relative to Earth. If such mixing caused

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Mailcode X12, NASA-JSC, 2101 NASA Parkway, Houston, TX 77058, USA.  
Email: kevin.righter-1@nasa.gov



**Fig. 1. Comparison of sample-based lunar mantle concentrations with those calculated in three stages.** Fourteen VSEs listed in the order of volatility as gauged by their 50% condensation temperature from (14). Blue symbols are lunar mantle estimates from correlations between the VSEs and a refractory lithophile element (RLE; see section S1). Three panels illustrate the three scenarios discussed in the text: gas-melt equilibrium followed by core formation, disk mixing followed by core formation, and a combination of gas-melt and disk mixing followed by core formation. All calculations assume a bulk Moon composition that is Earth's PUM. (A) The calculated lunar mantle if set by gas-melt equilibrium (light gray circles), followed by core formation (heavy gray circles). Gas-melt equilibrium is calculated using Eq. 2 with gas fraction = 0.9 and  $D$  (gas-melt) set for  $P = 3$  (least volatile) and  $TI = 100$  (most volatile) and is varied as a simple linear function for elements of intermediate volatility. For this scenario, Ag, Sb, and Bi are poor fits, while most other elements fit well. (B) The calculated mantle if set by mixing between hot inner disk and cooler volatile-bearing outer disk [as per (13); light gray circles], followed by core formation (heavy gray circles). Most of the moderately VSEs fit well in this scenario, but the higher-volatility Pb, Zn, Sn, Cd, In, and Ti are overabundant compared to the observed mantle concentrations. (C) The calculated lunar mantle for a hybrid model of combined disk mixing and gas-melt segregation (light gray circles), followed by core formation (heavy gray circles). The gas fraction in this model is 0.5, and the gas-melt partition coefficients are the same as for the first scenario (and summarized in table S1). This model fits all 14 elements well, including the Ag, Sb, and Bi contents that did not fit well in the first scenario. Values above the elements on the x axis are the metal-silicate partition coefficients calculated for lunar core formation conditions. Note that the high metal-silicate partition coefficient values for As, Ag, Sb, Ge, Bi, and Sn reflect more siderophile behavior, whereas P, Cu, Ga, Pb, Zn, Cd, In, and Ti are  $\leq 1$ , reflecting their more lithophile behavior.

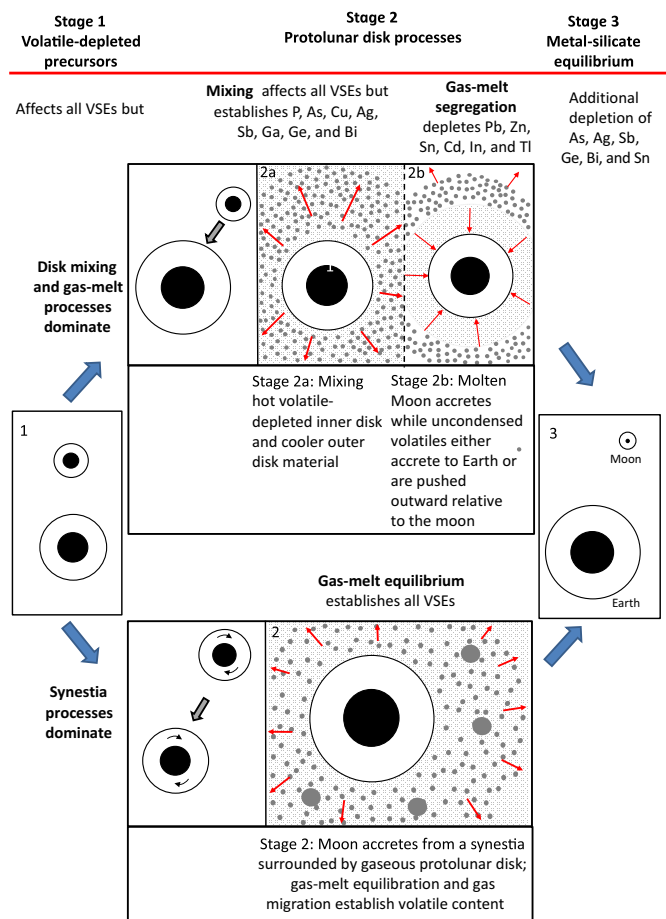
the overall bulk composition of the Moon to be depleted in volatile elements by  $\sim 4\times$ , then many VSEs can be satisfied (Fig. 1B). However, six critical VSEs (Pb, Zn, Cd, Sn, In, and Tl) would remain too high after mixing and require an additional depletion mechanism, since the stage 3 core formation would not significantly affect these six elements (Fig. 1B). Thus, although mixing within the disk can explain many elements, it does not explain the most highly depleted volatiles Pb, Zn, Cd, Sn, In, and Tl, and an additional loss mechanism would be required to explain their abundances.

A third scenario offers a hybrid solution that can explain most, if not all, VSEs. If mixing occurred in the early disk, then the moderately VSE contents of the bulk Moon may have been set by mixing between the hot inner and cool outer disks (Fig. 1C). The greater depletion of the more highly VSEs can be caused by temperature-dependent gas-melt interactions as the Moon accreted: The six highly VSEs may have remained in the gas phase as Moon accretion completed [with a gas fraction of 0.5 and with  $D(\text{gas-melt})$  being the same as for the first scenario; Fig. 1C]. The transition from these eight moderately VSEs to the six more highly VSEs at 50% condensation temperature ( $T_c \sim 725$  K) may correspond to an actual temperature near  $\sim 1700$  K (at 1 bar) (14, 15), perhaps reflecting the temperature for the top of the lunar photosphere [i.e.,  $\sim 2000$  K proposed by (16)]. The condensed lunar material would have to segregate from the gas-rich portion of the disk, which could migrate toward or away from Earth; if inward, then such late terrestrial accretion would have little effect on Earth's more highly VSE budget but would leave the Moon severely depleted in these six more highly VSEs. Last, further depletion of the siderophile As, Ag, Sb, and Bi due to core formation would leave the lunar mantle with a good fit to all 14 VSEs (Fig. 1C). Thus, volatile elements in the lunar mantle can be attributed to a combination of volatile-depleted precursors, mixing, and gas-melt equilibria in the protolunar disk, followed by lunar core formation.

## DISCUSSION

The hybrid scenario, involving both mixing and gas-melt equilibrium, would require a mechanism for gas-melt segregation, and currently, there are a number of viable possibilities. The combined modeling of Lindblad resonances in the inner disk and N-body simulations of the outer disk material has shown that the Moon accretes from a mixture of hot inner disk material and cooler outer disk material and that inner gas-rich disk material will ultimately fall back onto Earth (17). Alternatively, tidal interactions between the disk and the accreting Moon may cause migration of the forming body outward and away from the gas-rich portions of the disk (16, 17). On the other hand, magnetohydrodynamic modeling has suggested that turbulence-driven viscosity can lead to expansion of gas outward independent of the melt (18) and that post-impact disk volatilization can transport gas  $\sim 10$  Earth radii outward within several days of the impact (19). Turbulence at the gas-melt interface of a slightly higher pressure disk could move vapor outward as well (20, 21). Last, the vapor-rich environment of a synestia (3) coupled with disk dynamics offers potential for gas-melt segregation that could represent the more highly VSEs identified here. More work on gas-melt dynamics in the protolunar disk is obviously required.

Testing of the various Moon formation models for volatile contents has been incomplete, and the current work provides some guidance. Testing the canonical model has only quantitatively included Zn (13), but inclusion of additional elements, and measuring  $D(\text{VSE})$  gas-melt,



**Fig. 2. Schematic illustration of the stages proposed to explain the volatile element concentrations in the lunar mantle.** Stage 1 is the initial volatile-depleted precursor material. In this study, three different bulk Moon compositions are considered: terrestrial PUM, a Mars-sized impactor mantle that is less volatile depleted than PUM, and a Mars-sized impactor that is more volatile depleted than PUM. Stage 2 has two possible scenarios depicted in the top and bottom panels. **Top:** Stage 2a is caused by mixing of hot volatile-depleted inner disk material with cooler volatile-bearing outer disk material in the post-impact protolunar disk. Stage 2b is the segregation of melt and gas in the protolunar disk, which depleted the Moon of volatile elements with  $T_c$  (50%)  $< \sim 725$  K and may correspond to an actual temperature near  $\sim 1700$  K (at 1 bar) (14, 15), perhaps reflecting the temperature for the top of the lunar photosphere [i.e.,  $\sim 2000$  K proposed by (16)]. The pattern of volatile element depletion may thus reflect the thermal structure of the protolunar disk or a quasi-steady-state temperature at the top of the photosphere (21). Remaining gas might move inward or outward depending on the driving physical mechanism. **Bottom:** Stage 2 is a simple gas-melt equilibrium such as may exist in a terrestrial synestia (3). Last, stage 3 is the formation of the lunar core that further depleted the most siderophile elements As, Ag, Sb, Ge, Bi, and Sn. A multistage model (disk mixing and gas-melt equilibrium) can potentially provide a quantitative explanation for these 14 VSEs and lithophile volatile elements Li, Na, K, Rb, and Cs but needs to be tested for specific lunar formation models (see detailed discussion in the main text).

should reveal whether gas-melt dynamics in the lunar disk established the VSE pattern for the bulk silicate Moon. We show above that a three-stage process could potentially explain the lunar VSEs. More energetic lunar formation models include a collision between a highly spun proto-Earth and impactor that forms a high-temperature protolunar disk (2, 3) or a direct collision that produces a terrestrial synestia out of which the Moon accretes (3, 4). The moderately volatile element

depletions may reflect equilibration between disk melt and vapor during cooling at pressures between 10 and 50 bar as was shown for Cu and Zn (3). Calculations for Ge, however, result in values lower than lunar mantle estimates and do not account for the siderophile nature of Ge ( $D_{\text{metal-silicate}} = 50$ ) that will result in a more severe depletion than previously calculated (3). The ability of the synestia model to account for both the moderately and highly VSEs will require examination of more elements. For example, Lock *et al.* (3) argue that the behavior of some VSEs is pressure dependent but these authors only model Cu, Zn, and Ge, which have similar pressure effects. Including more elements will provide more leverage of the pressure dependence: Increased pressure causes Ga and Zn to switch their degree of volatility, while Pb becomes more volatile (22). In addition, the relative volatility of some of the VSEs changes if nonideality is considered (22, 23): In, Sb, As, and Bi all become less volatile (and Zn and Ge become more volatile).

The close similarity of lunar mantle VSE estimates (from samples) to those calculated assuming that the bulk Moon is similar to the terrestrial PUM is supportive of the idea that the Moon was derived from proto-Earth. Our new calculations and assessments using this large group of elements illustrate the degree of volatile depletion across a wide temperature range for the Moon and establish an important baseline for interpreting and evaluating lunar origin models in the future. The effect of core formation on the moderately siderophile VSEs (As, Sb, Ag, Ge, Bi, and Sn) must be included in any modeling efforts. The origin of volatiles might also be tested by combining the bulk VSE contents with Ga, Zn, Cl, and K isotopic variation in lunar and terrestrial samples (24–27). Future modeling (i) that quantifies precursor materials, disk-melt interactions, and core-mantle partitioning, (ii) that includes pressure and nonideality constraints on gas-melt equilibria for more elements, and (iii) that has the strong effects of core formation is likely to provide an important test of lunar formation models for volatile elements. Specifically, the VSEs may help to understand the chemical (evaporation, condensation) and physical (disk dynamics, core formation) processes, and discriminate between lower-energy [canonical (1) or multiple impact (5)] and higher-energy [synestia (3, 4) and sub-Earth (2, 3)] models for the origin of the Moon.

## MATERIALS AND METHODS

### Lunar mantle concentrations of VSEs—Constraints from samples

Mantle concentrations were defined by correlations between the VSEs and a refractory lithophile element (RLE) of comparable behavior during mantle melting (i.e., compatible or incompatible) in basalt and volcanic glass suites from differentiated bodies (28). Many lunar mantle melts (basalts and volcanic glasses) from the Apollo and lunar meteorite collections were analyzed and were used to reconstruct the mantle source concentrations of the VSEs using a known and comparable behavior of the VSEs and RLEs, which are unfractionated during melting and differentiation [e.g., (29–34)] (see section S1 and figs. S1 and S2 for summary and data file S1 for full sample analyses and details).

### Modeling the VSE content of the lunar mantle

In modeling the VSE content of the lunar mantle, several stages, which reflect known processes that contributed to the formation of the Moon, are considered: Stage 1 represents the degree to which the bulk Moon composition was volatile depleted; stage 2 represents the process(es)

after the Moon-forming impact(s) that controlled the accretion of the Moon from a gas-melt disk; and stage 3 represents the syn- or post-accretion segregation of a metallic core and its equilibration with the mantle. These processes were likely separated in time and represent distinct processes and thus are referred to here as stages (Fig. 2).

### Stage 1: Volatile-depleted building blocks

Most inner solar system bodies have a recognized volatile element depletion relative to chondritic proportions that originated with the building blocks or precursors, and Earth is no exception. Three different lunar bulk compositions that represent possible scenarios for Moon formation were considered: (i) The bulk Moon is from the terrestrial PUM (35–38), as suggested in some formation models for the Moon; (ii) the bulk Moon is from a Mars-sized (but initially more volatile-rich than PUM) impactor mantle for which we will use Mars as a proxy, and the mantle and bulk composition of Mars are relatively well known from meteorite studies and geochemical constraints (39, 40); and (iii) the bulk Moon is from a Mars-sized (but initially more volatile-depleted than PUM) impactor mantle, similar in overall bulk composition to Earth. Bulk compositions are described in more detail and discussed in section S2.

### Stage 2: Protolunar disk dynamics

Most lunar formation models predict that, after an impact, the Moon will accrete from a disk of material that surrounds proto-Earth, as either a gas-melt disk (2) or a synestia (3). This material is likely to be initially hot and largely vapor and then, upon cooling, a mixture of melt and gas, so the volatile content of the Moon may depend on either mixing within the disk (13) or partitioning between melt and gas (3) and on the possibility of subsequent gas-melt segregation in the disk. Elemental fractionation during condensation of the impact-generated vapor is not expected (3), but the remaining gas would later be incorporated into the protolunar disk. Is there a gas-melt segregation mechanism that is consistent with the early lunar disk thermal structure that can also explain the pattern of volatile element depletion in the Moon?

Mixing between the inner volatile-depleted and outer volatile-bearing disks was proposed (13) as a way to explain the volatile depletions in the Moon and is modeled here by modifying the bulk composition of the Moon to match the volatile lithophile element (Li, Na, K, Rb, and Cs) concentrations in the lunar mantle, assuming that they are due to mixing. Depletion of the volatile lithophile elements in the three bulk compositions was guided by comparisons with Earth's PUM, where Moon/Earth ratios are known to be ~1 for Li and ~0.25 for Na, K, Rb, and Cs, and corresponding adjustments to VSE contents must be made (see section S3 and fig. S3).

Disk modeling identified segregation mechanisms for melt and gas in the protolunar disk, but there is currently little agreement and a need for additional work. The details and timing of the early stages of lunar history are uncertain, but there are several physical settings and models that can segregate melt and gas, moving gas either inward or outward relative to the melt, including disk resonances, disk-Moon tidal interactions, or turbulence at the gas-melt interface (see discussion below). Gas-melt partitioning was captured with a simple term in Eq. 2 that quantifies the partitioning of an element between gas and silicate melt, and the gas fraction of the system, understanding that the specific mechanism has not yet been identified, as discussed below. This term is meant to be illustrative of possible gas-melt equilibrium and not demonstrative but is motivated by expected behavior for these elements.

### Stage 3: Core formation

Previous work showed that a wide range of mantle siderophile element concentrations (e.g., Ni, Co, Mo, W, V, and Cr) can be explained by the equilibration of a small metallic core with the mantle, at ~4.5 GPa, ~2273 K, and oxygen fugacity near IW-1, where IW-1 refers to the oxygen fugacity 1 logfO<sub>2</sub> unit below the iron-wüstite buffer (41–43). Metal-silicate partitioning was predicted for 13 of the VSEs using an expression derived elsewhere [e.g., (44)]

$$\ln D(i) = a \ln fO_2 + b/T + cP/T + \ln \gamma_i + g[nbo/t] + h \quad (1)$$

where  $\gamma_i$  is the activity of element  $i$  in Fe metallic liquid (table S1),  $nbo/t$  is the ratio of nonbridging oxygens to tetrahedrally coordinated cations and is a gauge of silicate melt compositional variation [a value of 2.8 for the bulk silicate Moon (41)], and the coefficients  $a$ ,  $b$ ,  $c$ ,  $g$ , and  $h$  are derived by multiple linear regression of various datasets. Regression coefficients and  $\gamma_i$  for the VSEs are available from recent experimental and partitioning studies (see table S1 for more information about the partition coefficients). Tl partitioning studies among metal, sulfide, and silicate melt reveal that Tl is compatible in sulfur-rich or sulfide liquids but weakly siderophile to lithophile at the S-poor conditions of lunar core formation, so we have adopted  $D(Tl)_{\text{metal-silicate}} = 1$  for the Moon (Supplementary Materials and table S1). These new constraints were applied to lunar core formation, with the additional assumption that equilibration between the core metal and the lunar mantle is complete, which is the expected outcome in lunar-sized bodies experiencing impacts (45).

### Calculation of lunar mantle VSEs resulting from three processes

Combining these three stages can be done using a simple approach tracking gas, melt, and metallic liquid phases that are relevant to the early Moon environment. One can calculate the concentrations of VSEs resulting in the lunar mantle,  $C_{\text{sil}}^i$ , according to

$$\begin{aligned} C_{\text{bulk}}^i &= x C_{\text{sil}}^i + (0.985 - x) C_{\text{gas}}^i + 0.015 C_{\text{met}}^i \\ C_{\text{bulk}}^i / C_{\text{sil}}^i &= x + (0.985 - x) C_{\text{gas}}^i / C_{\text{sil}}^i + 0.015 C_{\text{met}}^i / C_{\text{sil}}^i \\ C_{\text{sil}}^i &= C_{\text{bulk}}^i / \left[ x + (0.985 - x) D_{\text{gas/sil}}^i + 0.015 D_{\text{met/sil}}^i \right] \quad (2) \end{aligned}$$

where  $x$  is the mass fraction of the Moon that was supplied from a silicate melt phase (so that, in the limiting case where all of the Moon's silicate was derived from the melt,  $x = 0.985$  for a metal core fraction of 0.015),  $C_{\text{bulk}}^i$  is the bulk composition of the VSEs in the Moon (see the "Stage 1: Volatile-depleted building blocks" section), the core fraction is 0.015 from GRAIL (Gravity Recovery and Interior Laboratory) constraints (46), and  $D_{\text{met/sil}}^i$  is calculated according to Eq. 1 (see the "Stage 3: Core formation" section).

### SUPPLEMENTARY MATERIALS

Supplementary material for this article is available at <http://advances.sciencemag.org/cgi/content/full/5/1/eaau7658/DC1>

Section S1. Lunar mantle concentrations of the VSEs

Section S2. Bulk Moon compositions

Section S3. Disk mixing assumptions

Section S4. Alternative models with impactor bulk compositions

Fig. S1. Hypothetical behavior of a siderophile-RLE pair during mantle melting and subsequent processes (trapped metal, residual sulfide, and later degassing).

Fig. S2A. Correlations of 12 VSEs with a refractory lithophile element of similar degree of incompatibility.

Fig. 2B. Pb-Ce correlation.

Fig. S3. Volatile lithophile element corrections for bulk Moon compositions.

Fig. S4. Model calculations for bulk Moon = primitive martian mantle.

Fig. S5. Model calculations for bulk Moon = Mars-sized impactor mantle.

Table S1. Summary of bulk and mantle compositions, volatility corrections, activity coefficients, and core-mantle regression coefficients.

Data file S1. Lunar data (Excel).

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K. Righter

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