The origin of volatile elements in the Earth–Moon system

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The origin of volatile species such as water in the Earth–Moon system is a subject of intense debate but is obfuscated by the potential for volatile loss during the Giant Impact that resulted in the formation of these bodies. One way to address these topics and place constraints on the temporal evolution of volatile components in planetary bodies is by using the observed decay of $^{87}\text{Rb}$ to $^{87}\text{Sr}$ because Rb is a moderately volatile element, whereas Sr is much more refractory. Here, we show that lunar highland rocks that crystallized ~4.35 billion years ago exhibit very limited ingrowth of $^{87}\text{Sr}$, indicating that prior to the Moon-forming impact, the impactor commonly referred to as “Theia” and the proto-Earth both must have already been strongly depleted in volatile elements relative to primitive meteorites. These results imply that 1) the volatile element depletion of the Moon did not arise from the Giant Impact, 2) volatile element distributions on the Moon and Earth were principally inherited from their predecessors, 3) both Theia and the proto-Earth probably formed in the inner solar system, and 4) the Giant Impact occurred relatively late in solar system history.

Moon | volatile elements | Giant Impact | Moon-forming impact

Understanding the formation of the Moon has long been a topic of intense interest, although hard constraints on this event only developed after the Apollo program returned lunar samples to Earth. Based on the thousands of lunar rocks that have been studied to date, arguably one of the most stringent of these constraints is that the Moon is strongly depleted in volatile elements relative to the solar photosphere, primitive meteorites, and Earth. Recognition of such a depletion of volatile elements, combined with the orbital mechanics of the Moon and geochemical evidence that it differentiated from a mostly molten state, led to the now widely accepted “Giant Impact” hypothesis, in which the Moon accreted from a volatile element–laden material. The viable alternative, the “Giant Impact from a source that contained essentially no volatile elements relative to the bulk solar system prior to the impact,” is ruled out by the high volatile element abundances in pre-impact meteorites that serve as the building blocks of planetary bodies.

Constraining Volatile Element Distribution through Rb–Sr Isotopic Evolution

Since the late 1960s, research in lunar chronology has widely employed the Rb–Sr isotopic system, which is based on the decay of $^{87}\text{Rb}$ to $^{87}\text{Sr}$ (half-life = 49.4 Ga). The Rb–Sr system not only quantifies the time at which minerals in an igneous sample reached isotopic equilibrium (i.e., crystallized with the same $^{87}\text{Sr}/^{86}\text{Sr}$ ratio) but also it identifies the initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the parental magma at the time of crystallization. In turn, the initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the parental magma can be used to determine the $^{87}\text{Rb}/^{86}\text{Sr}$ ratio of the sources from which the parental magmas were derived. This is a particularly powerful tool for understanding the volatile element history of a planetary body because Rb is a moderately volatile element with a 50% condensation temperature ($T_{50\%}$) of 800 K and is much less refractory than Sr ($T_{50\%}$ = 1455 K). The $^{87}\text{Rb}/^{86}\text{Sr}$ ratio of an igneous system, therefore, acts as a general index for the abundances of volatile elements relative to refractory elements in that system. Thus, $^{87}\text{Rb}/^{86}\text{Sr}$ is an index of the temperature conditions during condensation of the materials that formed that body. Furthermore, the observed relationship between the measured $^{87}\text{Rb}/^{86}\text{Sr}$ and water content measured in primitive meteorites that serve as the building blocks of planetary bodies demonstrates that $^{87}\text{Rb}/^{86}\text{Sr}$ can also serve as a proxy for highly volatile element species in these bodies.

Lunar Samples

To constrain the evolution of volatile elements in the Earth–Moon system using the Rb–Sr isotopic system, lunar rocks that represent the $^{87}\text{Sr}/^{86}\text{Sr}$ of the bulk Moon can be used to determine the initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of any material increases over time, cumulatively recording its volatile element history.

Significance

Understanding the history of volatile species such as water in the Earth–Moon system is a major objective of planetary science. In this work, we use the moderately volatile element Rb, which has a long-lived isotope ($^{87}\text{Rb}$) that decays to $^{87}\text{Sr}$, to show that lunar volatile element depletion was not caused by the Moon-forming impact. The Rb–Sr systematics of lunar rocks mandate that the bodies involved in the impact that formed the Earth–Moon system were depleted in volatile elements relative to the bulk solar system prior to the impact. As such, Earth’s relatively small proportion of water is either primarily indigenous or was added after the Giant Impact from a source that contained essentially no moderately volatile elements.

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time must be identified. Relatively young basaltic magmas are not ideal samples due to the fact that they experienced 0.5 to 1.5 Ga of Rb–Sr isotopic evolution in the interval between solidification of their lunar magma ocean (LMO) source regions and basalt crystallization on the lunar surface. Instead, ancient highland rocks, which formed at or very near the time of LMO solidification, are preferred because they did not experience significant Rb–Sr isotopic evolution after the Moon solidified. These rocks therefore preserve a record of the $^8\text{Sr}/^6\text{Sr}$ ratio of the bulk Moon at the time they crystallized, essentially providing a fiducial marker for the Rb content of lunar precursors. However, not all ancient highland samples are well suited for this purpose, as many of these samples have experienced post-crystallization metamorphism associated with impacts on the lunar surface, where Rb is mobilized and removed (4, 5). Consequently, the most reliable highland samples for this work are those that yield undisturbed Rb–Sr ages and the proto-Earth and Theia after they accreted from the protoplanetary disk as represented by primitive CI-type chondritic meteorites (SI Appendix). The second stage of growth occurred in proto-Earth and Theia after they accreted from the protoplanetary disk as planetary bodies. These reservoirs existed until the Giant Impact, when proto-Earth and Theia were mixed and combined to form the Moon and Earth. The timing of the Giant Impact is estimated to range from 4.42 to 4.52 Ga (8–13); however, the exact age of the impact as well as the $^8\text{Rb}/^6\text{Sr}$ ratios of Theia and the proto-Earth are unknown and hence objectives of this investigation. The third stage of Rb–Sr isotopic evolution occurred after the Giant Impact in the lunar accretion disk and in the accreted, but yet undifferentiated, Moon. Previous studies have determined the average $^8\text{Rb}/^6\text{Sr}$ and Sr isotopic compositions of the Moon (Table 1). The observation that Mg-suite samples have ages and initial Sr isotopic compositions that are nearly identical to the FAS samples supports adopting 60025 to represent the bulk Moon Sr isotopic composition at 4.359 Ma.

**Modeling Rb–Sr Isotopic Evolution**

Combining the lunar sample data with Rb–Sr isotopic evolution places constraints on the volatile element budget of the precursor materials involved in the formation of the Earth–Moon system (i.e., proto-Earth and Theia) and thus on the origin and timing of volatile elements on these bodies. This exercise requires knowing the formation ages of each reservoir involved, the duration each reservoir existed, and their respective $^8\text{Rb}/^6\text{Sr}$ ratios. Specifically, lunar Rb–Sr evolution can be considered to have occurred in four stages: 1) protoplanetary disk stage, 2) precursor bodies stage, 3) undifferentiated Moon stage, and 4) lunar magma ocean cumulates stage (Fig. 2). The first stage occurred in the protoplanetary disk before the formation of planetary bodies.

![Fig. 1. Plot of $^8\text{Rb}/^6\text{Sr}$ versus H$_2$O contents of unprocessed primitive meteorites that serve as building blocks to terrestrial planetary bodies. The dark circle "E" represents Earth, the gray "M" represents the Moon and the red symbol represents Mars. The correlation demonstrates that $^8\text{Rb}/^6\text{Sr}$ is a good proxy for the abundance of highly volatile elements and volatile species. Data from Braukmüller et al. (3).](https://doi.org/10.1073/pnas.2115726119)

### Table 1. Initial $^8\text{Sr}/^6\text{Sr}$ and ages of highland samples

| Sample | Suite | Age (Ga) | Initial $^8\text{Sr}/^6\text{Sr}$ | Initial $^{143}\text{Nd}$ |
|--------|-------|----------|---------------------------------|-------------------------|
| 67667  | Mg-suite | 4.352 ± 0.028 | 0.699116 ± 0.000010 | 0.04 ± 0.11 |
| 76535  | Mg-suite | 4.306 ± 0.010 | 0.699105 ± 0.000022 | -0.15 ± 0.22 |
| 78236  | Mg-suite | 4.349 ± 0.019 | 0.699116 ± 0.000022 | -0.27 ± 0.74 |
| 60016  | FAS | 4.302 ± 0.028 | 0.699062 ± 0.000011 | -0.28 ± 0.14 |
| 60025  | FAS | 4.359 ± 0.003 | 0.699050 ± 0.000010 | -0.29 ± 0.09 |

Data from refs. 40 to 45.
The four stages of Rb–Sr isotopic evolution of the Earth–Moon system. The timing of these stages is defined by ranges of ages from the literature, which are illustrated in blue at the top with the middle of each range selected for display purposes. FAS samples are purple circles, and Mg-suite samples are purple squares. Rb–Sr evolution is discussed in the main text. The total permissible radiogenic growth of $^{87}\text{Sr} / ^{86}\text{Sr}$ from 4.56 to 4.36 Ga is 0.00007 (0.01%) and is represented by two horizontal dashed red lines. The gray diamond represents a modeled composition of the bulk Moon assuming Theia and proto-Earth had an $^{87}\text{Rb} / ^{86}\text{Sr}$ of chondritic meteorites and present-day Earth, respectively, and were evenly mixed by the Giant Impact that occurred at 4.46 Ga (see text). Dark gray, blue, and green lines are $^{87}\text{Sr}$ growth curves starting at 4.57 Ga assuming reservoirs with $^{87}\text{Rb} / ^{86}\text{Sr}$ ratios of chondritic meteorites, bulk Earth, and bulk Moon, respectively.

The initial $^{87}\text{Sr} / ^{86}\text{Sr}$ of the bulk Moon depends on three parameters: 1) the $^{87}\text{Rb} / ^{86}\text{Sr}$ of both Theia and the proto-Earth, 2) the proportions of Theia and the proto-Earth comprising the Moon, and 3) the timing of the Giant Impact as illustrated in Fig. 2. When exemplary calculations using endmember compositions of these estimated parameters are made, important conclusions can be drawn, even when the parameters are poorly known. The details of the calculations are presented in SI Appendix, Table S1. For example, if Theia and the proto-Earth had $^{87}\text{Rb} / ^{86}\text{Sr}$ values similar to chondritic meteorites (0.832 ± 0.028) and the present-day Earth (0.0081 ± 0.009, SI Appendix), respectively, and were mixed in equal proportions in the Moon following the Giant Impact modeled at 4.46 Ga (gray lines on Fig. 2), then the bulk Moon would have an $^{87}\text{Sr} / ^{86}\text{Sr}$ of 0.69975 at 4.36 Ga (gray diamond in Fig. 2 and SI Appendix, Table S1, Model 1). This value is significantly higher than the initial values observed in the ~4.36-Ga highland samples (0.69905 to 0.69912; Table S1, Model 2).

These examples demonstrate that the Moon and proto-Earth must be derived from precursors that were already very strongly depleted in volatile elements shortly after the beginning of the solar system. Furthermore, scenarios in which Theia and the proto-Earth had elevated $^{87}\text{Rb} / ^{86}\text{Sr}$ ratios that were subsequently lowered during volatile element loss after the Giant Impact are not permissible because even a few million years of $^{87}\text{Rb}$ decay in volatile element–enriched reservoirs would have produced enough $^{87}\text{Sr}$ to exceed the observed initial $^{87}\text{Sr} / ^{86}\text{Sr}$ ratios of the highland samples (Fig. 2 and SI Appendix, Table S1, Model 3). This contradicts Rb–Sr isotopic modeling of FAS samples completed by ref. 14 because they used whole-rock Rb–Sr isotopic measurements and mistakenly assumed a crystallization age of these samples of 4.52 Ga (SI Appendix). However, this observation does not require both Theia and the proto-Earth to be equally depleted in volatile elements; it is possible that one precursor body could have been slightly less depleted in volatile elements provided the other body was strongly depleted in volatile elements and contributed the bulk of the material that formed the Moon. Thus, if the Moon simply inherited its low $^{87}\text{Rb} / ^{86}\text{Sr}$ from Theia, the proto-Earth might have a proportionally higher $^{87}\text{Rb} / ^{86}\text{Sr}$ corresponding to more elevated volatile element abundances in Earth relative to the Moon. With the knowledge of the initial $^{87}\text{Sr} / ^{86}\text{Sr}$ of the lunar highland samples derived here, it is possible to constrain the allowable $^{87}\text{Rb} / ^{86}\text{Sr}$ of the proto-Earth and Theia by assuming variable proportions of Theia and the proto-Earth comprising the Moon and the timing of the Giant Impact (Fig. 3).

One endmember scenario that maximizes the $^{87}\text{Rb} / ^{86}\text{Sr}$ ratio of the proto-Earth assumes Theia had no volatile elements ($^{87}\text{Rb} / ^{86}\text{Sr} = 0$) and that the Moon contained the largest (90%) proportion of Theia (15, 16). In this case, the $^{87}\text{Rb} / ^{86}\text{Sr}$ of the proto-Earth is calculated to range from 0 (SI Appendix, Table S1, Model 4) to 0.13 (SI Appendix, Table S1, Model 5) depending on whether the Giant Impact occurred at 4.52 or 4.42 Ga, respectively. Even in this unrealistic scenario in which Theia had zero Rb, the calculated $^{87}\text{Rb} / ^{86}\text{Sr}$ value of proto-Earth is well below estimates for chondritic meteorites (0.832), confirming that Theia and the
proto-Earth were both strongly depleted in volatile elements. A more reasonable approach diagrammed in Fig. 3 assumes Theia had an \(^{87}\text{Rb}/^{86}\text{Sr}\) of 0.005, approximately the value of the most volatile element–depleted igneous samples known in the solar system, angrite meteorites. This output shows that, even assuming Theia was equivalent to the most volatile-depleted body known, either the proto-Earth must have had a lower \(^{87}\text{Rb}/^{86}\text{Sr}\) than the Earth does today or that the Giant Impact occurred no earlier than 4.43 Ga (Fig. 3 and SI Appendix, Table S1, Model 6). Note that if the Moon is comprised of a greater proportion proto-Earth, say only 70% (Theia (17–20)), then the proto-Earth must have an even lower \(^{87}\text{Rb}/^{86}\text{Sr}\) of \(\leq 0.04\) (SI Appendix, Table S1, Model 7). For a more volatile element–rich scenario for Theia, we assume an \(^{87}\text{Rb}/^{86}\text{Sr}\) of 0.01, roughly half that observed in the bulk Moon \((^{87}\text{Rb}/^{86}\text{Sr} = 0.019)\). In this case, the proto-Earth must also be strongly depleted in volatile elements and have an \(^{87}\text{Rb}/^{86}\text{Sr}\) that is \(\leq 0.04\) (Fig. 3 and SI Appendix, Table S1, Model 8).

**Ramification of Modeling**

All Giant Impact mixing scenarios outlined in the calculations presented in SI Appendix and shown in Fig. 3 require exceedingly low \(^{87}\text{Rb}/^{86}\text{Sr}\) for both Theia and the proto-Earth, and this places several important constraints on hypotheses for the origin and evolution of the Moon and Earth. Since most model solutions require the proto-Earth to have an \(^{87}\text{Rb}/^{86}\text{Sr}\) that was substantially less than present-day Earth, the first important implication of volatile element–depleted precursors relates to the ultimate source of extant volatile elements on Earth. For example, impurity of volatile element–depleted precursors relates to the was substantially less than present-day Earth, the first important implications for the formation location of these bodies. Proto-

**Methods Summary**

**Rb–Sr Isotopic Data.** The Rb–Sr isotopic data were culled from previous investigations (42–46) and presented in Table 1. The initial \(^{87}\text{Sr}/^{86}\text{Sr}\) for Mg-suite rocks were calculated from Rb–Sr isochron regressions that yielded slopes corresponding to ages that were concordant with ages determined on the same mineral fractions using the Sm–Nd isotopic system. The ages presented in Table 1 are the weighted average of all concordant measured ages. The data for FAS are calculated from Rb–Sr data obtained from plagioclase mineral fractions using the Sm–Nd ages. All data are normalized to the NBS-987 Sr isotopic standard \(^{87}\text{Sr}/^{86}\text{Sr}\) of 0.710250.

**Sm–Nd Isotopic Data.** The initial \(^{143}\text{Nd}/^{144}\text{Nd}\) of the samples are derived from the y-intercept of regressions through mineral fraction data on Sm–Nd isochrons. The \(^{143}\text{Nd}/^{144}\text{Nd}\) illustrates the deviation of the initial \(^{143}\text{Nd}/^{144}\text{Nd}\) from an idealized undifferentiated reservoir with Sm–Nd isotopic systematics of chondritic meteorites measured by ref. 46.
The $^{143}\text{Nd}$ was calculated using the following equation:

$$e^{143}\text{Nd} = \left[ \frac{\text{Nd}_{\text{Chondrite}}}{\text{Nd}_{\text{Chondrite}}} \right]^{143} - 1 \times 10^3.$$

The initial $^{143}\text{Nd}$ calculated from the Sm–Nd isochron of these highland rocks are within uncertainty, or very close to 0, indicating that these they were derived from precursor materials with $^{150}\text{Sm}$/$^{144}\text{Nd}$ that were similar to undifferentiated chondritic meteorites (47). The sources of these samples therefore must either be derived from sources that formed close to the crystallization age of the samples or have experienced only minimal amounts of melting and fractional crystallization. In addition, the ages determined for these samples are very close to $^{150}\text{Sm}$/$^{144}\text{Nd}$ ages determined for the solidification of the LMO of $4.336 \pm 0.030$ and model ages for late-stage crystallization products (urKREEP) of the magma ocean, which range from 4.35 to 4.38 Ga (SI Appendix).

Data Availability. All study data are included in the article and/or SI Appendix.

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