THE ORIGIN OF VOLATILE ELEMENT DEPLETION IN THE EARTH-MOON SYSTEM.

L.E. Borg[1], G. A. Brennecka, T. S. Kruijer[1] [1]Lawrence Livermore National Laboratory, Livermore, CA, USA.

Introduction: The first analyses of lunar samples revealed that the Moon is highly depleted in volatile elements [1-2] compared to estimates of the solar photosphere, primitive meteorites, and Earth. Recognition of this 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-depleted debris disk produced by an impact between a Mars-sized body (Theia) and the proto-Earth [3]. The formation of the Moon in such a giant impact scenario raises questions about the composition of the proto-Earth and Theia, their respective contributions to the makeup and subsequent evolution of the Earth-Moon system, and the timing of the giant impact. Of particular interest is how and when the Moon and Earth obtained their present allotments of volatile components, including, and most importantly, water. Below, the Rb-Sr isotopic systematics of lunar samples is used to provide time constraints on the history and distribution of volatile elements in the Earth-Moon system, as well as the characteristics of the giant impact.

Rb-Sr Isotopic Systematics: The ^{87}Rb-^{86}Sr isotopic system is an ideal tool to constrain the history of moderately volatile elements in a geologic system because Rb has a 50% condensation temperature (T_{50}%) of 800 K and is much less refractory than Sr (T_{50}% = 1455 K; [4]). Thus, the ^{87}Rb/^{86}Sr ratio of an igneous system, serves as a general proxy for the relative abundances of volatile elements in that system. Furthermore, the relationship between the measured ^{87}Rb/^{86}Sr and water content measured in primitive meteorites that serve as the building blocks of planetary bodies demonstrates that ^{87}Rb/^{86}Sr may also serve as a proxy for highly volatile element species in these bodies (Fig. 1).

To constrain the evolution of volatile elements in the Earth-Moon system using the Rb-Sr isotopic system, lunar rocks that represent the ^{87}Sr/^{86}Sr of the bulk Moon at a known time must be identified. Young rocks, such as lunar basalts, are inappropriate because in order to use them to calculate the ^{87}Sr/^{86}Sr of the bulk Moon, their measured initial ^{87}Sr/^{86}Sr isotopic compositions must be corrected for growth of ^{87}Sr in their source regions from the time the reservoir formed until the time the basalt was erupted onto the lunar surface requiring a good understanding of the ^{87}Rb/^{86}Sr ratio and age of the basalt reservoir. In contrast, 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. The most reliable highland samples for this work are those that yield undisturbed Rb-Sr ages identified by concordance with ages determined by other chronometers such as ^{147}Sm-^{143}Nd in the same rocks (Fig. 2). The initial ^{87}Sr/^{86}Sr of several Mg-suite rocks, as well as the initial ^{87}Sr/^{86}Sr of ferroan anorthosite suite samples, calculated from the Rb-Sr systematics of plagioclase mineral separates using well defined Sm-Nd ages, are used to estimate the ^{87}Sr/^{86}Sr of the Moon at 4.36 Ga to be 0.69905 (Fig. 2).

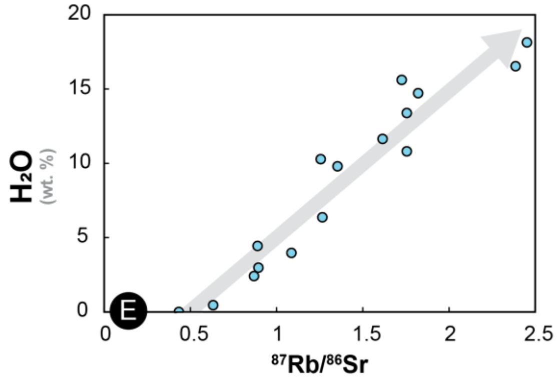

Figure 1. Plot of ^{87}Rb/^{86}Sr versus H_2O contents of unprocessed primitive meteorites that serve as building blocks to terrestrial planetary bodies. Dark circle E represents enstatite chondrites. The correlation demonstrates that ^{87}Rb/^{86}Sr may serve as a good proxy for the abundance of highly volatile elements. Data from [5].

Rb-Sr Evolution of the Moon: The ^{87}Sr/^{86}Sr of the bulk Moon at 4.36 Ga is modeled in 4 stages: (1) protoplanetary disk stage, (2) precursor bodies stage, (3) undifferentiated Moon stage, and (4) lunar magma ocean (LMO) cumulates stage (Fig. 2). The first stage occurred in the protoplanetary disk before the formation of planetary bodies. This reservoir inherited the initial Solar System ^{87}Sr/^{86}Sr value of 0.69898 at 4.567 Ga and evolved for 1-2 million years (Ma) [6-8] with a solar (or chondritic) ^{87}Rb/^{86}Sr ratio represented by primitive CI-type chondritic meteorites. 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 Ga to 4.52 Ga [9-12], however, the exact age of the impact, as well as the ^{87}Rb/^{86}Sr ratios of Theia and the proto-Earth are

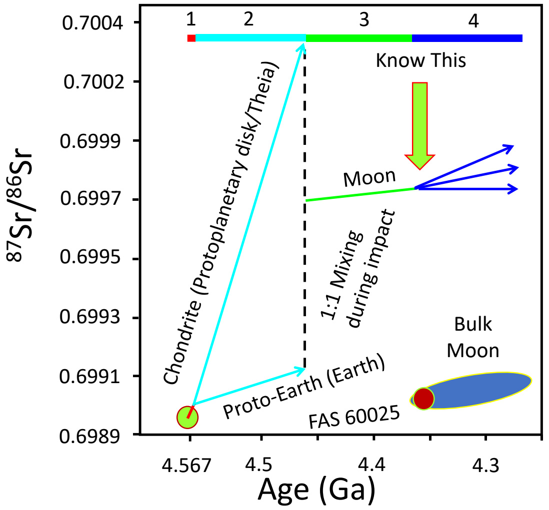

Fig. 2. Figure illustrating 4 stages of ^{87}Sr growth on Moon. Sample 60025 provides best current estimate for bulk ^{87}Sr/^{86}Sr of Moon at 4.36 Ga.

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 ^{87}Rb/^{86}Sr of the bulk Moon to be 0.019 ± 0.006, and this value is used in our calculations [13]. The final stage of evolution occurred within the cumulate rocks of the LMO. This final stage of Rb-Sr evolution did not contribute, or contributed negligibly, to the overall Rb-Sr systematics of the highland samples because the FAS and Mg-suite samples have ages between 4.30 Ga and 4.36 Ga and are approximately the same age as the LMO.

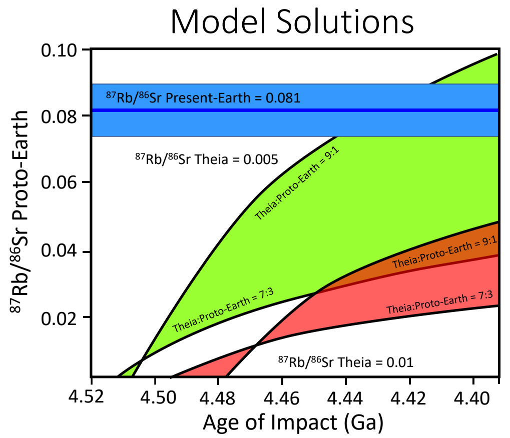

Fig. 3. Set of model solutions for variable ^{87}Rb/^{86}Sr of the proto-Earth and Theia, age in giant impact, and proportions of Theia and proto-Earth that comprise the Moon. Model solutions that do not require a substantial amount of accretion to the Earth after the giant impact are defined when the proto-Earth and Earth have similar ^{87}Rb/^{86}Sr (blue field).

Figure 2 depicts ^{87}Sr/^{86}Sr evolution of the Moon when Theia and proto-Earth are assumed to have solar and terrestrial ^{87}Rb/^{86}Sr ratios respectively, the giant impact occurred at 4.45 Ga, and materials from Theia and proto-Earth are mixed equally to form the Moon. Obviously, these conditions do not reproduce the ^{87}Sr/^{86}Sr of the bulk Moon at 4.36 Ga. In fact, in order to reproduce the estimated ^{87}Sr/^{86}Sr of the bulk Moon, Theia must have ^{87}Rb/^{86}Sr ratios significantly lower than the solar value, the Moon must be derived mostly from Theia, and the giant impact must occur relatively late in Solar System history.

There are numerous solutions to the model calculations because there are several free parameters (Fig. 3). An additional constraint on the models is that unless the Earth accreted significant amounts of material after the giant impact, the proto-Earth probably had about the same ^{87}Rb/^{86}Sr as the present Earth. In this case, successful models must fall in the space on Fig. 3 defined by the modern Earth (blue field). Thus, Theia must have ^{87}Rb/^{86}Sr = ~0.05, the Moon must be derived from ~90% Theia, and the giant impact must have occurred after ~4.45 Ga.

There are several ramifications of these observations and models including: (1) the giant impact was relatively late in solar system history, (2) the Moon was not depleted in volatile elements by the giant impact, (3) both the proto-Earth and Moon were derived from volatile element depleted materials in the inner Solar System. This is consistent with their similar stable isotope compositions [e.g., 14]. Additionally, the correlation between water content and ^{87}Rb/^{86}Sr implies that the Earth and Moon could have formed with roughly their current allotments of water.

References: [1] Keays et al. (1970) *Sci.* **167,** 490–3. [2] Morrison et al. (1970) *Sci.* **167,** 505–7. [3] Hartmann & Davis (1975) *Icarus* **24,** 504–15. [4] Lodders (2003) *Astrophys. J.* **591,** 1220–47. [5] Braukmüller et al. (2018). *GCA* **239,** 17–48. [6] Chambers (2004) *EPSL* **223,** 241–52, [7] Hans et al. (2013) *EPSL* **374,** 204–14, [8] Kruijer et al. (2017) *PNAS* **114,** 6712–16. [9] Connelly & Bizzarro (2012) *EPSL* **452,** 36-43. [10] Bottke et al. (2015) *Sci.* **348,** 321–23, [11] Kruijer & Kleine (2017) *EPSL* **475,** 15–24, [12] Thiemens et al. (2019) *Nat. Geosci.* **12,** 696–700, [13] Newson (1995) AGU Reference Shelf I, 159–89. [14] Dauphas (2017) *Nature* **541,** 521–24.

Work was performed under the auspices of the U.S. DOE by LLNL under Contract DE-AC52-07NA27344. This research was an outgrowth of LDRD project 22-ERD-003, “High Resolution Chronology”.