

DEVELOPING THE RARE EARTH ELEMENT CONSTRAINT FOR SCENARIOS OF LUNAR ORIGIN.

K. Pahlevan, Dept. of Geology & Geophysics, Yale University, New Haven, CT 06520 (kaveh.pahlevan@yale.edu)

Introduction: In the “standard” giant impact hypothesis, the Moon forms from debris ejected into orbit by the impact of a Mars-sized body onto the proto-Earth towards the very end of planetary accretion [1]. Such an impact is capable of explaining the lunar mass, iron deficit, and the system angular momentum, but does not explain why the impact of two isotopically distinct bodies should result in a high level of isotopic homogeneity between Earth and Moon [2,3], a problem that is exacerbated by simulations of the impact that derive the proto-lunar disk primarily from the impacting planet [4,5]

To reconcile the standard impact scenario with the high level of isotopic homogeneity observed in the silicate Earth-Moon system, it has been suggested that the system undergoes turbulent mixing in the $\sim 10^3$ years after the impact but before lunar accretion while the system exists in a fluid state [6]. This scenario can potentially provide an explanation for a high level of oxygen and tungsten isotopic homogeneity in the Earth-Moon system and predicts a concomitance between chemical and mass-dependent isotopic differences between silicate Earth and Moon (e.g. for Si isotopes [7]), but requires that lunar accretion lasts for a time period of order $\sim 10^2$ years [8].

Recently, impact models have been re-evaluated in order to investigate the role that the mechanics of the impact itself may play in generating the lunar isotopic characteristics. In particular, the evection resonance has been recognized as a mechanism that can transfer angular momentum from the lunar orbit to the system’s heliocentric motion [5,9,10] making possible reduction of the system angular momentum. Although the magnitude of the reduction is not known, potential relaxation of the angular momentum constraint renders a wide range of Moon-forming impacts possible, ranging from a high-velocity 0.05 Earth mass body colliding with a rapidly rotating Earth [10] to nearly symmetric impacts between 0.4-0.6 Earth mass bodies [11], both of which can generate proto-lunar disks that are sourced mostly from Earth even before disk evolution. Interestingly, both sets of new impacts generate proto-lunar disks that are predominantly composed of vapor, rather than liquid, potentially resulting in distinct predictions for lunar observables from the “standard” giant impact and its aftermath.

It would clearly be advantageous to develop new constraints that can discriminate between the proposed models, perhaps by incorporating data that have not been previously included in the models. In this regard, chemical and isotopic constraints, interpreted in the

context of physical scenarios of evolution, may serve an important purpose. Here, I discuss the development of one such chemical signature and what the requirements are for articulating the constraints that this signature poses for scenarios of lunar origin.

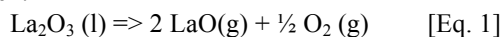
Liquid-Vapor Fractionation: Any scenario of lunar origin that attempts to make a connection between the formation process and the lunar chemical composition must describe the physical conditions under which the proto-lunar liquids and vapors evolve. At present, such modeling has only been done for one major element ratio (FeO/MgO) and in one of the settings potentially relevant to lunar composition: the silicate vapor atmosphere of the post-impact Earth [7]. The fact that the major-element lunar bulk composition is known – within certain limits – to be similar to Earth’s mantle [12] places constraints on the conditions and amount of liquid-vapor separation accompanying lunar origin [7]. Here, the approach is to use the constraints on liquid-vapor fractionation derived from the general major-element similarity of Earth mantle and bulk Moon, and to ask how the rare earth elements (REE) would behave under the range the conditions permitted by this similarity. The question that is addressed is: how sensitive is the development of volatility-related REE anomalies to liquid-vapor separation at the conditions prevailing after the Moon-forming giant impact?

Rare Earth Elements: The abundance patterns observed in lunar samples are the product of two sets of processes: (1) crystal-liquid equilibria, which have operated on the lunar material during its silicate differentiation, and (2) liquid/vapor equilibria, which acted on the lunar material during the processes of origin. Because the silicate Moon has undergone a series of igneous differentiation events, all accessible samples carry the imprint of petrologic processes. For this reason, in order to study liquid-vapor fractionation relevant to lunar formation, it is necessary to select chemical tracers whose behavior during the formation process is distinctly different from that during subsequent igneous differentiation. The relative abundances of the rare earth elements are one such tracer.

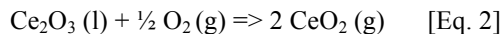
Aside from pervasive Eu anomalies, which are the result of crystal/liquid equilibria [13], there are no REE anomalies reported from measurements of lunar samples. As has been pointed out [14], this observation is potentially surprising for a body whose material was once molten and vaporized because, in contrast to their behavior during crystal-liquid equilibria, the REEs do not display a monotonic behavior with atomic number during condensate-vapor equilibria as observed in, e.g.

the abundance patterns of some CAIs [15,16]. Here, I will explore the conditions under which such anomalies would evolve, and whether their observed absence in lunar samples can be used to rule out any of the proposed scenarios for lunar origin.

Model: The evaporation-condensation equilibrium of REE oxides is intrinsically sensitive to the oxygen partial pressure of the environment because (with a few exceptions) the REEs exist in the +3 valence in silicate liquids but in a different valence in co-existing vapor [17]. I consider two cases for illustration: lanthanum and cerium. If, as in the case of the solar nebula, the dominant La-bearing species in the vapor is the monoxide, LaO [18], the evaporation reaction can be written:



such that increases in the oxygen partial pressure of the environment cause the equilibrium to shift to the left, i.e. for lanthanum to become more refractory. If, by contrast, the dioxide species dominates the gas-phase speciation, as in the case of cerium in the solar nebula, the evaporation reaction reads:



such that increases in the oxygen partial pressure of the environment cause the equilibrium to shift towards the vapor, i.e. for the element to become more volatile. In this way, if the Moon-forming liquid separates from its co-existing vapor while cerium is partially vaporized, Ce anomalies may be expected to arise. In this regard, it is important to note that oxygen fugacity in the post-giant-impact environment is 10-20 orders of magnitude higher than that in the solar nebula (Figure 1).

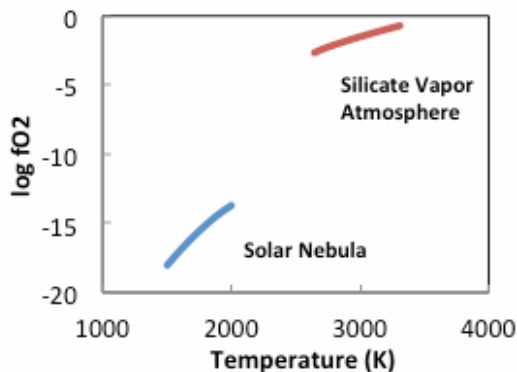


Figure 1 – The oxygen fugacity prevailing in the silicate vapor atmosphere of the Earth (specific entropy = 10 kJ/atom) and the solar nebula ($\text{H}_2\text{O}/\text{H}_2 = 5 \times 10^{-4}$).

As a result, differential redox-sensitivity can change the relative volatilities (and hence relative abundances) of REEs in the post-giant-impact environment. Such a signal is of interest because, like certain isotopic signa-

tures, REE abundances in planetary reservoirs may be derived by analysis of individual samples without the processes of igneous fractionation overprinting signatures of earlier energetic events.

While thermodynamic data exist for rare earth element condensates and vapor species [e.g. 18], the mixing properties (i.e. activity coefficients) of these components in high-temperature silicate liquids are not known, but can be parameterized. I will present calculations for how much liquid-vapor fractionation can be tolerated without generating REE anomalies (e.g. in the Ce abundance) in the lunar material. The activity coefficients of REE oxides in high-temperature silicate liquids may be determined experimentally or computationally. In this way, it may soon become possible to convert this decades-old qualitative observation into a quantitative constraint on scenarios of lunar origin.

Conclusions: We do not yet have a predictive theory of the events that occurred between the giant impact and lunar accretion. Chemical and isotopic signatures are capable of informing us of the processes operating during this earliest period of Earth-Moon history. That there are no volatility-related rare earth element anomalies observed in the lunar material constrains the chemical conditions and degree of liquid-vapor separation accompanying lunar origin in all of the settings potentially relevant to the lunar composition, a list that includes the silicate vapor atmosphere of Earth and the melt-vapor proto-lunar disk. Whether it is possible for REEs to have measurable isotopic fractionation [19] without measurable elemental fractionation will be a topic of future research.

References: [1] Canup R. M. and Asphaug E. (2001) *Nature*, 412, 708-712. [2] Wiechert U. et al. (2001) *Science*, 294, 345-348. [3] Touboul et al. (2007) *Nature*, 450, 1206-1209. [4] Canup, R. M. (2004) *Icarus*, 168, 433-456. [5] Canup, R. M. (2008) *Icarus*, 196, 518-538. [6] Pahlevan, K. and Stevenson, D. (2007) *EPSL*, 262, 438-449. [7] Pahlevan et al. (2011) *EPSL*, 301, 433-443. [8] Salmon and Canup (2012) *Ap.J.*, 760, 83. [9] Touma, J. and Wisdom, J. (1998) *Astron. J.*, 115, 1653-1663. [10] Cuk and Stewart (2012) *Science*, 338, 1047-1052. [11] Canup (2012) *Science*, 338, 1052-1055. [12] Warren, P. H. (2005) *Meteorit. Planet. Sci.* 40, 477-490. [13] Weill, D. F. and Drake, M. J. (1973) *Science*, 180, 1059-60. [14] Taylor, S. R. (1987) *GCA*, 51, 1297-1309. [15] Tanaka, T. and Masuda, A. (1973) *Icarus*, 19, 523-530. [16] Boynton (1975) *GCA*, 39, 569-584. [17] Fegley and Cameron (1987) *EPSL*, 82, 207-222. [18] Lodders and Fegley (1993), *EPSL*, 117, 125-145. [19] Albalat, E. et al. (2012) *EPSL*, 355-356, 39-50.