CORE-MANTLE PARTITIONING OF VOLATILE ELEMENTS AND THE ORIGIN OF VOLATILE ELEMENTS IN EARTH AND MOON.

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Introduction: Depletions of siderophile elements in mantles have placed constraints on the conditions on core segregation and differentiation in bodies such as Earth, Earth's Moon, Mars, and asteroid 4 Vesta (e.g., [1]). Among the siderophile elements there are a sub-set that are also volatile (volatile siderophile elements or VSE; Ga, Ge, In, As, Sb, Sn, Bi, Zn, Cu, Cd), and thus can help to constrain the origin of volatile elements in these bodies, and in particular the Earth and Moon. One of the fundamental observations of the geochemistry of the Moon is the overall depletion of volatile elements relative to the Earth [2-4], but a satisfactory explanation has remained elusive. Hypotheses for Earth include addition during accretion and core formation and mobilized into the metallic core (e.g., [1]), multiple stage origin [5], or addition after the core formed (e.g., [6-8]). Any explanation for volatile elements in the Earth's mantle must also be linked to an explanation of these elements in the lunar mantle [9]. New metal-silicate partitioning data will be applied to the origin of volatile elements in both the Earth and Moon, and will evaluate theories for exogenous versus endogenous origin of volatile elements.

Concentrations of VSE in Earth and Moon mantles: Terrestrial primitive upper mantle (PUM) values of VSE can be estimated from measurements made on mantle peridotite and basalts, and by looking at trends with refractory lithophile elements (RLE) that have a similar degree of incompatibility during mantle melting (e.g., Ge-Si, In-Yb, As-Ce, and Sb-Pr; [1,10,11]). For Moon we do not have samples of the mantle, but we can reconstruct lunar mantle values (PLM) by looking at concentrations in lunar basalts and comparing these to the melting trends derived from the terrestrial mantle. This approach has been explained in more detail by [1] and [12] for some of the refractory siderophile elements such as Mo, W, Ni and Co. For the volatile chalcophile elements, magmatic volatility and sulfide retention during melting must be considered as well. The resulting trends of VSE and RLE element pairs can be used to estimate the terrestrial and lunar mantle concentrations (Fig. 1).

Regressions: An approach for predicting metal-silicate partition coefficients as a function of pressure, temperature, oxygen fugacity, and metal and silicate compositions, has been to derive regression coefficients a to h
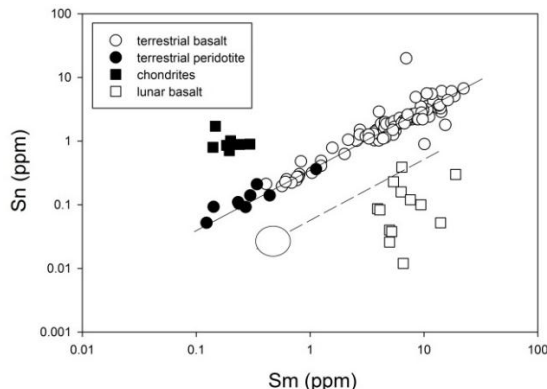

Fig. 1: Sn-Sm correlation diagram illustrating trends for Earth and Moon, and the calculated lunar mantle Sn content (open circle). Peridotite, terrestrial basalt, lunar basalt and chondrite data is compiled from [24].

from published metal-silicate experiments:

$$\ln D(met/sil) = a\ln fO_2 + b/T + cP/T + d\ln(1-Xs) + e\ln(1-Xc) + f\ln(1-X_{Si}) + g(nbo/t) + h$$

Regressions for As, Cu, Sb, Ge, Ga, Zn, Sn, and In were carried out using available experimental results that cover a range of intensive parameters (from references compiled in [24]).

Application to Earth: Recent modeling indicates moderately siderophile element depletions in Earth's primitive upper mantle can be explained by metal-silicate equilibrium between metallic and silicate liquid at high PT conditions during Earth's accretion (~40 GPa, ~3400 K; e.g., [1,13]). Using the regression derived for the volatile siderophile elements above, we can examine the evolution of the composition of the Earth's PUM during accretion scenarios with constant fO_2 (IW-1.5), increasing fO_2 (IW -4 to IW-2.4), or decreasing fO_2 (IW-2 to IW-3.8) (e.g., [14-16]). Calculations have been carried out along the PT conditions of the liquidus for peridotite [17]. Many elements can be fit in each of the scenarios. However, the calculations assuming a constant fO_2 result in the most matches to the Earth's PUM concentrations (e.g., Sn in Fig. 2), and suggest that the VSE can be explained by a rather simple scenario of continuous accretion leading to a high PT metal-silicate scenario that establishes the siderophile element content of Earth's PUM near the end of accretion. This scenario does not require multiple stages of accretion (reduced or oxidized; low pressure

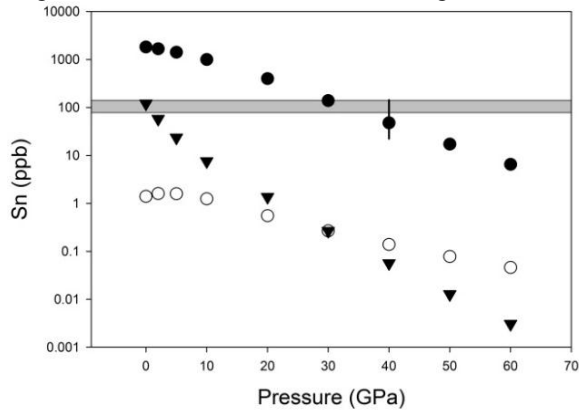then high pressure; e.g., [5]), nor does it require late stage addition of chondritic materials (e.g., [7,18].

Fig. 2: Evolution of Earth's PUM Sn during accretion for 3 fO₂ scenarios; constant (solid circles), decreasing (triangles) and increasing (open circles) (see text). Horizontal bands represent terrestrial PUM [10].

Application to Moon: The giant impact scenario is the generally accepted model for the origin of the Moon, but there is no consensus on whether the Moon formed from material that was part of the proto-Earth or from the impactor (or a mixture of these two). We consider two scenarios: In Scenario A, the Moon may have formed from material from the impactor involved in the Moon-forming impact (e.g., [19]), and in which a pre-impact volatile depletion could have been caused by impact erosion, or by impact of a planetesimal that contains a predominance of volatile element depleted materials that perhaps accreted rapidly in the early solar system. In scenario A, the VSE depletions would have been inherited from both the impactor and the later Moon-forming impact process. In Scenario B, the Moon may have formed from material from the proto-Earth or the primitive upper mantle (e.g., [20-22]). Therefore the bulk composition of the Moon would be modeled as that of the primitive upper mantle [9] and VSE depletions would have been inherited from both the Earth's mantle and the later Moon-forming impact process.

In either of these scenarios, the Moon would have accreted from a circum-terrestrial disk, and then differentiated into a small core and molten mantle. Core formation models for the Moon can explain a broad range of siderophile elements including the refractory (Ni, Co, Mo, W) and slightly (Mn, V, Cr) siderophile elements where metal-silicate equilibrium is at P = 5 GPa, T = 2500 K, and relative fO₂ = IW-2 ([9,23]). Modelling that includes either a small amount of S or C, or no light element at all, results in a good match to the lunar mantle concentrations of most VSE (Fig. 3). However, calculated concentrations of In, Sn, and Zn

(all with T_c < 750 K) are all still too high after core formation, and must therefore require an additional process to explain the depletions in the lunar mantle. We discuss possible processes including magmatic degassing, evaporation, condensation, and vapor-liquid fractionation in the lunar disk.
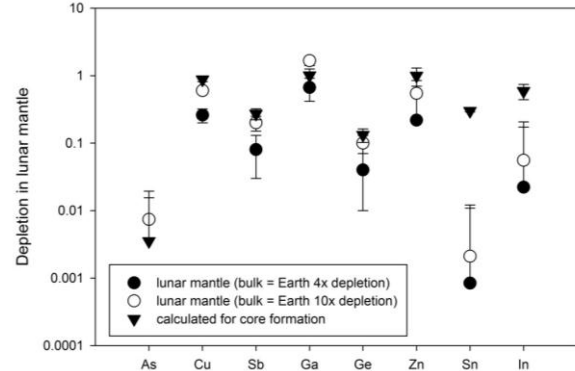

Fig. 3: Lunar mantle VSE deduced from lunar basalt data, calculated for a bulk Moon depleted in volatile elements by a factor of 4 (solid circles), and by a factor of 10 (open circles) compared to the Earth. Inverted triangles show concentrations after segregation of a small core in equilibrium with mantle. The order of presentation of volatile siderophile elements is in order of 50% condensation temperature, with As the highest and In the lowest.

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