

RE-EVALUATION OF HSE DATA IN LIGHT OF HIGH P-T PARTITIONING DATA: LATE CHONDRITIC ADDITION TO INNER SOLAR SYSTEM BODIES NOT ALWAYS REQUIRED FOR HSE.

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Introduction: Studies of terrestrial peridotite and martian and achondritic meteorites have led to the conclusion that addition of chondritic material to growing planets or planetesimals, after core formation, occurred on Earth, Moon, Mars, asteroid 4 Vesta, and the parent body of the angritic meteorites [1-4]. One study even proposed that this was a common process in the final stages of growth [5]. These conclusions are based almost entirely on the 8 highly siderophile elements (HSE; Re, Au, Pt, Pd, Rh, Ru, Ir, Os), which have been used to argue for late accretion of chondritic material to the Earth after core formation was complete (e.g., [6]). This idea was originally proposed because the D(metal/silicate) values for the HSE are very high (>10,000), yet their concentration in the terrestrial mantle is too high to be consistent with such high Ds. The HSE in the terrestrial mantle also are present in chondritic relative abundances and hence require similar Ds if this was the result of core-mantle equilibration. The conclusion that late chondritic additions are required for all five of these bodies is based on the chondritic relative abundances of the HSE, as well as their elevated concentrations in the samples. An easy solution is to call upon addition of chondritic material to the mantle of each body, just after core formation; however, in practice this means similar additions of chondritic materials to each body just after core formation which ranges from ~ 4-5 Ma after T_0 for 4 Vesta and the angrites, to 10-25 Ma for Mars, to 35 to 60 Ma for Moon and perhaps the Earth [7].

Since the work of [6] there has been a realization that high PT conditions can lower the partition coefficients of many siderophile elements, indicating that high PT conditions (magma ocean stage) can potentially explain elevated siderophile element abundances [8,9]. However, detailed high PT partitioning data have been lacking for many of the HSE to evaluate whether such ideas are viable for all four bodies. Recent partitioning studies have covered P, T, fO_2 , and compositional ranges that allow values to be predicted at conditions relevant to these five inner solar system bodies. Because the D(HSE) metal/silicate are lowered substantially at higher PT conditions and natural compositions (FeNi metallic liquids and peridotites) it is natural to re-examine the role of core formation on the HSE patterns in a variety of inner solar system bodies. Here I will discuss other processes (including high PT core formation for Mars, Moon and Earth) that can

produce the observed HSE patterns, and demonstrate that there are viable hypotheses other than the “one size fits all” hypothesis of late chondritic additions.

Mars – Compilation of HSE partitioning data for metal/silicate Ds, as well as martian samples led Righter et al. (2014) [10] to conclude that the HSE concentrations in the martian mantle could have been established by an early magma ocean stage for Mars. Such conditions would have been established near the end of growth of Mars during accretion, where metal and silicate equilibrated at 14 GPa, 2400 K, $\Delta IW = -1.5$ and peridotite mantle and S- and C-bearing metallic core. These conditions also satisfy the concentrations of moderately siderophile elements (MSE; Ni, Co, Mo, W), and a number of other siderophile elements (Mn, V, Cr, Ga, Ge, etc.; [11-12]). These results indicate that a late chondritic addition is not required to explain the HSE concentrations in the martian mantle as proposed by a number of investigators, some of whom (e.g., [3]) deferred on evaluating the possibility of high PT core-mantle equilibrium due to lack of appropriate data.

4 Vesta – Studies of diogenites have revealed high and somewhat chondritic relative HSE abundances that have been interpreted as due to late chondritic additions to the mantle of 4 Vesta [5]. In addition, recent Si isotopic data for 4 Vesta [13] that are distinct from chondrites were interpreted as due to core formation at reduced conditions (IW-4) followed by addition late chondritic materials to satisfy the HSE. There are several aspects to these interpretations that are problematic, and an alternative explanation is necessary. First, core formation at IW-4 would leave the Vestan mantle nearly FeO-free. Addition of a small mass late chondritic material would not raise the FeO content to values that are consistent with current geochemical or geophysical estimates [14]. Second, most of the diogenites are pieces of the crust that have experienced chondritic contamination and brecciation. It would require only a small amount of chondritic metal in $\ll 1$ modal %, to explain the HSE patterns measured in diogenites. Other non-brecciated diogenites are also from the crust and have experienced post-shock annealing of brecciated diogenitic material [15]. Finally, the HSE patterns for diogenites are variable and fractionated [5], especially compared to the terrestrial primitive upper mantle. A more plausible explanation is that

Vesta experienced a magma ocean at IW-2.5, and diogenites experienced either addition of core metal by impact deformation [16] or simple addition of chondritic materials to the diagenitic breccias, this producing the widely variable but sometime chondritic relative HSE patterns. The latter are post core formation additions, but to the crust not the mantle.

Angrites – Angrites exhibit a wide range of rock types (including breccias, and cumulate or igneous textured rocks), and their HSE patterns also demonstrate high and somewhat chondritic relative abundances. This led [4] to conclude that the angrite parent body also experienced late chondritic additions. Although the angrites are certainly depleted in siderophile elements, and may have experienced core formation [17], their detailed geochemistry (elevated Ge and Ir) and their petrography suggests that they more plausibly formed as impact melts [18]. In this case, there may have been chondritic impactor that provided HSE. This was not the same as late chondritic additions to post-core formation mantle, but instead due to impacts that are quite common in the meteoritic record.

Earth and Moon - HSE studies of lunar materials have demonstrated some elevated concentrations and some chondritic relative patterns that have been attributed to late chondritic additions, or to stochastic late chondritic additions. However, a recent study [19] showed that in both the post core formation mantle and subsequent liquids in equilibrium with anorthosite, the HSE Ru, Pd and Au are fractionated by several orders of magnitude and not chondritic. If there had been post core formation but pre-anorthosite crust genesis addition of chondritic material to the lunar mantle, the HSE patterns would be elevated and chondritic relative, but they are not. Therefore late chondritic additions to the lunar mantle, if they occurred at all, must have been after anorthosite genesis, which means later than 100-200 Ma after T_0 ; this is a young event and more syn-contemporaneous with heavy bombardment history.

Earth remains the only body to have compelling evidence for a late chondritic addition, but the uniqueness of this interpretation is also being challenged. The elevated and chondritic relative HSE patterns in the terrestrial PUM have been explained numerous times by addition of the “late veneer” or late chondritic additions after the core formed. This interpretation is due entirely to the inability of available (low PT) metal/silicate partition coefficients to explain the higher concentrations in the mantle. As new studies have been completed at higher PT conditions and on more Earth-like compositions (peridotite and Fe-bearing metallic liquids that also contain a light element), it is clear that partition coefficients decrease

substantially at the conditions that are more relevant to nature. Recent studies [20] at high PT conditions conclude decrease of D(HSE) metal/silicate, but nonetheless argue the need for late veneer because the Ds are not lowered enough. This however, was for metallic liquid that contained no light element. When calculated for the high PT conditions of core formation for Earth (~40 GPa), metal/silicate partition coefficients for Au, Pd, and Pt are all low enough to allow an equilibrium explanation for the concentrations in the primitive upper mantle (~600±200). The other five HSE elements – Re, Rh, Ru, Ir, and Os – are less well understood at these extreme conditions, but extension to high pressure conditions and to peridotites and FeNi metallic liquids with C, Si, O, and S may reveal possible solutions to the HSE abundances that do not require a late veneer or late chondritic additions. Sulfur alone has a substantial lowering effect that can almost explain several additional HSE [21]. For the Earth, lack of a late veneer would be consistent with recent other geochemical evidence such as water and D/H ratios also not requiring late additions of volatiles, as once had been argued [22].

Each of these five bodies possesses unique and specific aspects of their early history. Only Earth has compelling evidence for late chondritic additions, and this may also require revision in light of high PT metal-silicate partitioning data.

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