

**LATE CHONDRITIC ADDITIONS AND PLANET AND PLANETESIMAL GROWTH: EVALUATION OF PHYSICAL AND CHEMICAL MECHANISMS.** K. Righter<sup>1</sup>, <sup>1</sup> NASA Johnson Space Center, 2101 NASA Parkway, Houston, TX 77058; kevin.righter-1@nasa.gov.

**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, 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 highly siderophile elements (HSE; Re, Au, Pt, Pd, Rh, Ru, Ir, Os). The HSE are a group of eight elements that 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 so high, yet their concentration in the mantle is too high to be consistent with such high Ds. The HSE also are present in chondritic relative abundances and hence require similar Ds if this is the result of core-mantle equilibration. Since the work of [6] there has been a realization that core formation at high PT conditions can explain the abundances of many siderophile elements in the mantle (e.g., [7]), but such detailed high PT partitioning data are lacking for many of the HSE to evaluate whether such ideas are viable for all four bodies. Consideration of other chemical parameters reveals larger problems that are difficult to overcome, but must be addressed in any scenario which calls on the addition of chondritic material to a reduced mantle. Yet these problems are rarely discussed or emphasized, making the late chondritic (or late veneer) addition hypothesis suspect.

**Problems:** A serious problem with late accretion models is that the Earth and other bodies appear to have gone through a reducing (IW-2) magma ocean phase [8]. Addition of late accreting primitive material (<1 mass %) to a reduced post core-formation mantle will result in the reduction of those materials to a mixture of metal and silicate, with the metal mobilizing into the core by rainfall of small metallic droplets that quickly re-equilibrate with the silicate [9]. The HSE will be partitioned into the metal and then proceed to the core, and will not be mixed efficiently into the mantle because the mantle is too reduced. Homogenization and mixing of chondritic material into a magma ocean is not possible in such an environment. This re-equilibration would not allow the metal to dissolve into the silicate melt as is required in late veneer scenarios. Instead what is missing is an oxidation mechanism that oxidizes the HSE-bearing material and allows it to stay in the mantle. If the young Earth allowed metallic

liquid to pass through its mantle to the core, yet the upper mantle is not reduced enough for iron metal stability, how did Earth's mantle become oxidized?

**Oxidation mechanisms:** Several ideas to oxidize either the mantle or the HSE have been proposed but they all have drawbacks and some are only viable for one or two bodies – no single mechanism is viable for all four bodies (Table 1). A satisfying explanation for this conundrum has remained elusive:

1) Earth's upper mantle has become oxidized over time due to the effects of recycling and plate tectonics. However, no studies have yet revealed a secular trend of oxygen fugacity (e.g., [10]). This mechanism does not apply to other bodies that have not experienced global scale recycling of material from the surface into the interior like Earth.

2) Another idea is that the systematic breakdown of Mg-perovskite into Fe metal and Fe<sup>3+</sup>-bearing silicates has led to natural oxidation of the upper mantle ([11,12]). Although this is an intriguing idea, and one that would occur early enough in Earth history to meet the requirements of current models, it is not without problems or questions. For example, the mantle of Mars is just as oxidized as the Earth's (near FMQ-2) but there is not an Mg-perovskite reservoir in Mars that can produce the oxidation. Such a deep reservoir is not relevant to the small low pressure bodies that are represented by the HED and angrite meteorites. In addition, it is not clear if Fe<sub>2</sub>O<sub>3</sub> added to the upper mantle by Mg-perovskite dissolution is long-lasting - it may simply dissociate into FeO and Fe<sub>2</sub>O<sub>3</sub> in response to the low ambient fO<sub>2</sub> set by core formation.

3) A third possibility is that the mantle was oxidized somewhat by the partitioning of H and C between the core, mantle, magma ocean, and atmosphere [13]. These authors show that C prefers the core while most H prefers the silicate melt, and estimate that the amount of H<sub>2</sub>O partitioned to silicate melt is large enough to explain the amount of H<sub>2</sub>O in the hydrosphere and mantle, provides enough oxygen to partially oxidize ferrous iron to ferric iron in the mantle, and perhaps even be the oxidant for metals which may fail to segregate to the core such as late-accreted highly siderophile elements. This mechanism is relevant for both Earth and Mars, but cannot provide significant H<sub>2</sub>O in small relatively dry bodies like Vesta. The more oxidized angrite meteorites may have had C-H-O fluids associated with them [14], but the low pressure conditions on the angrite parent body would have limited the amount of water that could be soluble in a magma ocean.

4) A fourth possibility is that the  $\text{Fe}^{3+}/\text{Fe}^{2+}$  ratio of a magma ocean increases at high pressures [15] such that a deep magma ocean would become oxidized. This might be anticipated for a number of reasons such as melt structure and coordination chemistry, but there are no data to evaluate how large such an effect might be. Furthermore, such a mechanism would be viable only at high pressures relevant to Mars or Earth, because the low pressure  $\text{Fe}^{3+}/\text{Fe}^{2+}$  systematics are well known and can't provide oxidation for the HED or angrite meteorites parent bodies.

5) A fifth possible hybrid solution lies in the oxidizing capacity of a thick atmosphere. Magnesioferrite spinels form during impacts of meteoritic material with the Earth – they form out of the oxidized vapor plume that is created during the impact [16]. Such spinels are also capable of hosting significant amounts of many HSE (Ru, Rh, Re, Ir, Os; [17]). If the early Earth had an oxidized atmosphere (e.g. [18]) and some HSEs were oxidized and condensed in magnesioferrite in an impact event, the HSEs could be delivered to an oxidized mantle in an oxidized form. They would then have to be mixed efficiently into the primitive mantle. Such a mechanism may work for a subset of the HSE and for the Earth and possibly Mars - some argue for a hybrid model where some of the HSE (Au, Pd, Pt) are set by core formation and some (Re, Rh, Ru, Ir, Os) by late accretion ([19,20]. But this mechanism is not viable for the smaller airless bodies represented by the HED and angrite meteorites.

**Discussion:** None of the oxidation mechanisms are viable for all four bodies, but several may be viable for one or more bodies. An additional problem is that addition of such chondritic material, if mixed into the mantle, would affect other elements as well, such as Ni, Co, or Cu. For example, addition of 1% chondritic material to the HED mantle would boost Ni (and other siderophile elements) to levels near 150-200 ppm, much higher than observed in HED materials [5]. Finally, high PT metal-silicate equilibrium remains a viable possibility for HSE signatures. Progress in filling the gap in HSE distribution coefficient data has been difficult due to analytical problems (nugget effect and very low solubilities). Despite these problems, there have been a large number of studies in the last decade. When calculated for the high PT conditions of core formation for Earth and Mars (i.e., 14 to 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 ( $\sim 600 \pm 200$ ) (Figure 1). The other five HSE elements – Re, Rh, Ru, Ir, and Os – are less well understood at these extreme conditions, but conditions at which Ds for these five elements are lowered to equilibrium values (e.g.,  $\sim 600 \pm 200$ ) have not yet been identified; extension to high pressure conditions and to peridotites

and metallic systems with C and S has not been done yet. Much additional work must be done on these HSE before there is a thorough understanding of the behavior of HSE and an assessment of theories for their origin (e.g., late veneer/accretion or high PT metal-silicate equilibrium) is made.

Table 1: Oxidation mechanisms for HSE in mantles

	Earth	Mars	Vesta	Angrite
1	X			
2	X			
3	X	X		X ?
4	X	X		
5	X	X		

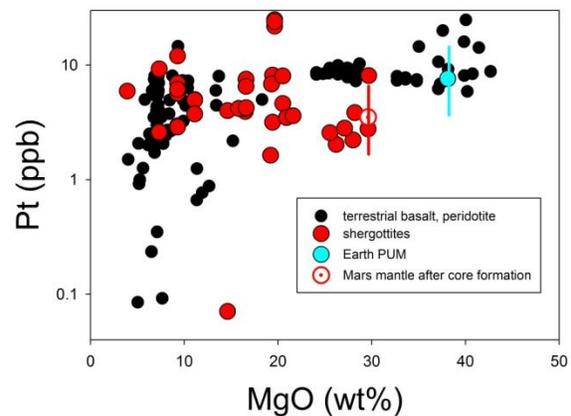


Figure 1: Pt-MgO contents of martian and terrestrial samples, along with calculated mantle concentrations from core-mantle partitioning.

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