**REVISITING THE CONCEPT OF LATE ACCRETION.** R. J. Walker<sup>1</sup> & K. R. Bermingham<sup>1</sup>, <sup>1</sup>Department of Geology, University of Maryland, College Park, MD 20742; rjwalker@umd.edu.

**Introduction:** Late accretion, also known as "the late veneer", is typically defined as the addition of materials with generally chondritic bulk compositions to planetary mantles after core formation has largely ceased [e.g., 1]. It is a concept generated in the 1970's to explain the apparent overabundance of highly siderophile elements (HSE), such as Ir, in Earth's mantle relative to what would be expected from metal-silicate partitioning known at the time. In the case of Earth, the total mass of late accreted materials would need to equal or exceed ~0.5 wt.% of Earth's mass to account for the HSE present in the bulk silicate Earth (BSE) [2]. By contrast, late accretion would have added, on average, only ~10% of the moderately siderophile elements (MSE), such as W and Mo, because of their presumed higher abundances remaining in the BSE following core formation.

In the intervening years between the origin of the late accretion concept and today, arguments and observations have been made that both strengthen and challenge the concept of late accretion. As with any long-standing paradigm, it is wise to periodically review the chief tenets and assess whether or not prior conclusions remain valid.

Evidence supporting Late Accretion: Osmium isotopes are the strongest evidence for late accretion. They leave little wiggle room with respect to the precisely chondritic relative abundances of the long-term Re/Pt/Os in the BSE, as revealed by estimates of <sup>187</sup>Os/<sup>188</sup>Os and <sup>186</sup>Os/<sup>188</sup>Os in the BSE. For example, the <sup>187</sup>Os/<sup>188</sup>Os estimated for BSE of ~0.129 is a good match to ordinary and enstatite chondrites [3-4]. In addition, the relative abundances of HSE projected for the BSE are also within the range of chondritic meteorites, albeit with some possible exceptions [5-6].

Recent lines of evidence have also led to some strengthening of the late accretion concept. Dynamical modelling of late-stage planetary accretion indicates that some form of substantial late accretion to rocky planets is unavoidable 30-100 Myr into Solar System history, although the quantity of material delivered is not well constrained [7]. Further, comparative Earth-Moon mantle abundances of HSE, together with the ~25 ppm difference in <sup>182</sup>W/<sup>184</sup>W between the two bodies provides permissive evidence for disproportional late accretion, whereby late accretion to Earth was dominated by a small number of Pluto mass bodies [8]. This conclusion, coupled with recent dynamical modelling of the fates of objects of that size following impact suggest that if late accretion occurred,

the late accreted materials may have been forcefully injected into the mantle with mantle and cores separating, and should not be thought of as having formed a "veneer" [9].

Evidence refuting Late Accretion: A number of experimental studies have shown that most HSE become considerably less siderophile under conditions of high temperature and pressure. Such conditions would ensue at the bases of deep magma oceans as the Earth grew during the giant impact stage of accretion, as is commonly envisioned to have established the MSE. Thus, it has been argued that late accretion may not be necessary to explain the comparatively high abundances of the HSE in the BSE [e.g., 10-11].

Further, not all HSE concentration data necessarily support the late accretion concept. Most notably, Ru/Ir and to a lesser extent Pd/Ir ratios estimated for the BSE are somewhat higher than is observed in bulk chondritic meteorites [e.g., 5]. This may indicate that an explanation for their abundances relying solely upon late accretion is not optimal.

Finally, recent studies reporting <sup>182</sup>W depletion in modern ocean island basalts suggest that there may be domains in the deep mantle that have isotopically equilibrated with the core [12]. If so, this type of W exchange between the core and mantle could provide a mechanism for lowering the <sup>182</sup>W/<sup>184</sup>W of the mantle over time. This in turn could mean the BSE had a higher initial ratio (more like that of the Moon), consistent with isotopic data for early Earth rocks. If this is true, the W isotopic difference between the Earth and Moon could argue *against* substantial late accretion.

Ambiguous Evidence: Some observations regarding HSE abundances in other planetary bodies provide both support for and against late accretion. Most notably, the mantle of Mars appears to have broadly similar HSE and Os isotopic compositions to the BSE [13]. Although this (and the much lower abundances of HSE projected for the lunar mantle) can potentially be accounted for via stochastic late accretion [8], it remains puzzling why two such different bodies ended up with apparently similar HSE in their silicate shells. Core segregation on Mars likely happened under greatly different conditions and timescales than for Earth, making metal-silicate partitioning an unlikely process to explain HSE mantle abundances. On the other hand, late accretion can only fortuitously re-populate a planetary mantle with a similar proportion of HSE as present in the BSE.

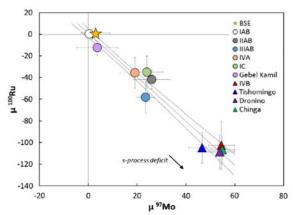
Alternative Models and Fresh Concerns: Hybrid models to account for siderophile element abundances in the BSE and other planetary bodies have also been proposed. For example, the concept of a Hadean matte has been used to argue that high pressure and temperature metal-silicate partitioning of HSE may have left abundances of the HSE in the BSE that were higher than at present [14]. An eventual stage of S saturation and sulphide precipitation from a late-stage magma ocean has been posited, which then stripped most of the HSE from the BSE but left behind higher abundances of Ru and Pd than other HSE as these elements are the least chalcophile of the HSE [15]. A final stage of late accretion could then account for the chondritic relative abundances of other HSE, but with abundance promontories for Ru and Pd.

Incomplete core separation is a mechanism by which it has been proposed that the HSE present in the BSE and other planetary mantles originated from metal added during the primary stage of accretion, and that some amount of residual metal simply never merged with the core [16]. Most metal that was retained in the mantle after a planet-building accretionary event would presumably sink to the core during subsequent accretion events that would lead to partial or complete mantle melting. Thus, retained metals would be expected to be periodically "distilled" into the core. So it is only the later additions that remain late into the accretionary history. Of course the retention of late accreted metal in the silicate Earth is an important aspect of the late accretion concept, so late accretion and incomplete core segregation are two processes that invariably overlap.

It is also important to re-examine the data on which the pro and con arguments for late accretion are based. For example, one possible explanation for the apparent suprachondritic Ru/Ir estimated for the BSE is that our ability to precisely project BSE ratios from upper mantle materials is not as good as we might wish. Estimates for absolute and relative HSE abundances of Ru in the BSE are dominated by data for peridotites from subcontinental lithospheric mantle. It is possible, however, that the mobility (and enrichment) of Ru in some portions of the upper mantle has modified its abundances in such rocks in ways that other HSE have not, providing an incorrect view of the Ru/Ir of the BSE.

Additional Insights? If it is assumed that late accretion played a major role in the establishment of HSE abundances in the BSE, then some other new insights follow from recent developments. For example, Ru is an especially important HSE when considering late accretion. Some studies have argued that late accretion consisted largely of oxidized, carbonaceous chondrite-like materials, potentially delivering sub-

stantial water and organics to Earth [e.g., 1]. Osmium isotopes have long weighed against the involvement of substantial carbonaceous chondrite-like material during late accretion. Recent Ru nucleosynthetic isotope data for the mantle, however, appear to definitively rule out any substantial contributions by carbonaceous chondrite- type (CC) materials, which are most likely to have formed in the wetter, outer portion of the Solar nebula [17]. This is especially apparent in a plot isotopic ratios of Ru and Mo that reflect nucleosynthetic variations that were present in the solar nebula (Fig. 1).



**Fig. 1.**  $\mu^{100}$ Ru versus  $\mu^{97}$ Mo for grouped and ungrouped iron meteorites (where  $\mu$  refers to the deviation from the standards in ppm). All meteorites of the carbonaceous chondrite type (CC) (triangles) plot at the bottom right side of the plot. Non-carbonaceous type (NC) meteorites are shown as circles. If the CC region of the nebula was water rich, then it seems unlikely that the BSE received much water from this region of the nebula. Figure from [17].

**References:** [1] Chou C.-L. (1978) *Proc. LPSC* 9<sup>th</sup>, 219-230. [2] Walker R.J. (2009) Chem. der Erde 69, 101-125. [3] Meisel T. et al. (2001) GCA 65, 1311-1323. [4] Day M.D. et al. (2017) GCA 200, 232-254. [5] Becker H. et al. (2006) GCA 70, 4528-4550. [6] Fischer-Gödde M. et al. (2011) Chem. Geol. 280, 365-383. [7] Marchi S. et al. (2014) Nature 511, 578-582. [8] Bottke W.F. et al. (2010) Science 330, 1527-1530. [9] Marchi S. et al. (2017) Nat. Geosci. 11, 77-81. [10] Cottrell E. & Walker D. (2006) GCA 70, 1565-1580. [11] Righter K. et al. (2008) Nat. Geosci. 1, 321-323. [12] Mundl A. et al. (2017) Science 356, 66-69. [13] Brandon A.D. et al. (2012) GCA 76, 206-235. [14] Rubie D.C. et al. (2016) Science 353, 1141-1144. [15] Laurenz V. et al. (2016) GCA 194, 123-138. [16] Jones J.H. & Drake M.J. (1986) Nature 322, 221-228. [17] Bermingham K.R. et al. (2018) EPSL 487, 221-229.