In Search of Late-Stage Planetary Building Blocks

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Abstract

Genetic contributions to the final stages of planetary growth, including materials associated with the giant Moon-forming impact, late accretion, and late heavy bombardment are examined using siderophile elements. Isotopic similarities between the Earth, Moon and enstatite chondrites for both lithophile and siderophile elements collectively lead to the suggestion that the genetics of the building blocks for Earth and the impactor involved in the Moon-forming event were broadly similar. The bulk genetic fingerprint of materials added to Earth by late accretion, defined as the addition of ~0.5 wt. % of mass to the silicate Earth following cessation of core formation, is characterized by $^{187}Os/^{188}Os$ and Pd/Ir that are similar to those in some enstatite chondrites. However, the integrated fingerprint of late accretion differs from enstatite chondrites in terms of the relative abundances of certain other HSE, most notably Ru/Ir. A minor, final ~0.05% addition of material to the Earth and Moon, believed by some to be part of a late heavy bombardment, included a genetically distinct component with much more fractionated relative HSE abundances than evidenced in the average late accretionary component.

Heterogeneous ^{182}W isotopic data for ancient terrestrial rocks suggest that some very early-formed terrestrial mantle domains remained chemically distinct for long periods of time following primary planetary accretion. This evidence for sluggish mixing of the early mantle suggests that if late accretionary contributions to the mantle were genetically diverse, it may be possible to identify the disparate primordial components in the terrestrial rock record using siderophile element isotopic tracers, such as Ru and Mo.

Keywords: building blocks, giant impact, late accretion, late heavy bombardment, siderophile elements

1. Introduction

The origins of the rocky planets, especially with regard to assembly processes and the chemical nature of their building blocks, have been the topic of intense interest and debate for decades. It is now generally agreed that the terrestrial planets were dominantly built through a series of energetic collisions of bodies of increasingly greater mass, termed *oligarchic growth* (e.g., Kokuba and Ida, 1998; Raymond et al., 2006). In the case of Earth, this process may have culminated in a final giant impact, involving an impactor comprising 5% or more of the mass of the present Earth, and leading to the formation of the Moon (Hartmann and Davis, 1975; Canup and Asphaug, 2001; Cuk and Stewart, 2012; Canup, 2012).

In addition to constraining the dynamical processes involved in the construction of the rocky planets, it is equally important to assess the origins and nature of the materials from which they were built. Comparisons of the general compositions of the terrestrial planets have commonly been made on the basis of chemical models developed for these planetary bodies, most notably the Earth, Moon, and Mars; that is, bodies from which we are reasonably confident we have samples. Such models often require the assumption that the bodies were constructed from a combination of materials that were compositionally similar to primitive meteorites present in our collections (Wänke and Dreibus, 1988; 1994; McDonough and Sun, 1995; Wänke, 2001; Taylor et al., 2006). The bulk planetary concentrations of a number of poorly-constrained elements are then estimated by applying bootstrapping methods that assume that the ratios of these elements to relatively well-constrained, geochemically-comparable major elements, are similar to the ratios observed in primitive meteorites (e.g., McDonough and Sun, 1995). Models of the chemical composition of inaccessible planetary reservoirs, such as Earth's core, necessarily require these types of general assumptions (McDonough, 2003).

The chemical and genetic makeup of the planets can potentially be further constrained by isotopic comparisons to one another and to primitive meteorites. For example, planetary materials exhibit a large range in mass independent variations in $\Delta^{17}O$ (the *per mil* deviation in $^{17}O/^{16}O$ from the terrestrial fractionation line), which can be used as genetic fingerprints of precursor materials. It has been hypothesized that the heterogeneities in $\Delta^{17}O$ originated as a result of self-shielding effects in the photo-dissociation of CO by exposure to ultraviolet light within the solar nebula (e.g., Thiemens and Heidenreich, 1983; Clayton, 2002; Lyons and Young, 2005). Variations in $\Delta^{17}O$ among differentiated bodies have, therefore, commonly been interpreted to reflect the formation of precursor materials at greater or lesser distances from the Sun, possibly coupled with time of formation (e.g., Yurimoto and Kuramoto, 2004). As an example of the application of O isotopes to issues of genetics, the similarity in the $\Delta^{17}O$ of the Earth and enstatite chondrites has commonly been interpreted to mean that the major building blocks of the Earth formed in a region of the protoplanetary disk similar to where enstatite chondrites formed (Clayton et al., 1984; Javoy et al., 2010). Conversely, differences in the $\Delta^{17}O$ compositions of the Earth and Mars have been cited as evidence that the building blocks of these two bodies differed substantially (Franchi et al., 1999). Although there is no perfect fit of all physical parameters between any types (or likely any combination of types) of primitive meteorites and the Earth, Moon or Mars, constraining the general categories of accretionary materials, nevertheless, remains an important objective of cosmochemistry.

Here, we focus mainly on the final ~10 to ~0.05% of Earth's accretion. Late stages of major terrestrial planetary accretion may have included the participation of materials that formed in different portions of the protoplanetary disk, including water- and organic-rich materials (Weidenschilling et al., 1997; Chambers, 2001). Thus, although limited in mass, late stage planetary growth may have had a disproportionate effect on the volatile contents of the rocky planets (e.g., Albarede et al., 2013). Further, late stage additions may have carried genetically distinct elemental and isotopic fingerprints. Because of the comparatively limited mass contributed by these processes, elemental and isotopic tracers comprising major elements, such as O, are of limited value in constraining the nature of these final building blocks. Thus, we will instead explore the possibility of tracing the late-stages of planetary growth using insights gained from elemental and isotopic variability of so-called *siderophile*, or Fe-loving, elements.

In this overview, the elemental and isotopic fingerprints of late stage building blocks that may be recorded in mantle rocks from the Earth, as well as mantle-derived and impact generated rocks from Mars and the Moon, respectively, will be examined. In addition to considering the average elemental and isotopic characteristics of siderophile elements contained in the silicate portions of these bodies, we will also explore the possibility that the signals of individual building blocks might be identified through small differences in the isotopic compositions of the siderophile elements Ru and Mo, which varied among early solar system materials as a result of their incorporating differing proportions of diverse nucleosynthetic components. The basis for this optimism is the discovery that primordial mantle heterogeneities, recorded by lithophile, atmophile and siderophile short-lived radiogenic isotope systems, survived long enough to be preserved in the terrestrial rock record (Caro et al., 2003; Willbold et al., 2011; Mukhopadhyay et al., 2012; Touboul et al., 2012; 2014). If the interpretations of long-lived chemical/isotopic heterogeneity in the mantle presented by these studies are correct, isotopically distinct domains within the mantle, imparted during late stage accretion of genetically distinct materials, might also be preserved in the rock record.

2. Overview of Siderophile Elements

Siderophile elements are those elements that strongly partition into metallic Fe relative to silicate melt, and are consequently concentrated, to greater or lesser extents, in the cores of the rocky planets (Goldschmidt, 1937). Because of this, their concentrations in silicate mantles and crusts are low compared to primitive meteorites, the compositions of which are presumed to be representative of the majority of the planetesimals involved in the final stages of rocky planet accretion (Anders and Grevesse, 1989). Siderophile trace elements are commonly divided into sub-groups based on the intensity of their siderophilic tendencies under the typical 1 atmosphere experimental conditions initially employed to characterize the nature of metal-silicate partitioning of these elements (e.g., Kimura et al., 1974; Borisov et al., 1994). The moderately siderophile elements (MSE), including Co, W, Ni, Ge, and Mo, are characterized by metal-silicate D values (concentration ratio of an element in liquid metal to liquid silicate) ranging from about 10 to 1000. The highly siderophile elements (HSE), including Re, Os, Ir, Ru, Pt, Rh, Pd, and Au, are characterized by D values of greater than 10,000.

One important characteristic of siderophile elements is that the intensity of their siderophilic behavior can shift considerably at increasingly higher temperatures and pressures (e.g., Ringwood, 1966; Murthy, 1991; Li and Agee, 1996; Holzheid et al., 2000). The general tendency of most, but not all, siderophile elements is towards lower D values, as pressure and temperature conditions increase (Righter and Drake, 1997; Mann et al., 2012). Their partitioning characteristics are also affected by other intensive parameters of a given planetary body, such as oxygen fugacity (Cottrell and Walker, 2006; Wade and Wood, 2005). These shifts in partitioning behavior are important to recognize when considering issues of planetary growth and core formation. Depending upon the conditions where metal last equilibrated with silicates during progressive core formation in a growing body, appropriate D values likely changed considerably during growth of sizable planetary bodies, thus, affecting the final absolute and relative concentrations of the siderophile elements in these mantles (Wade and Wood, 2005).

For the purposes of genetic tracing of late stage building blocks, it is also important to recognize that the processes leading to the present abundances of the MSE contained within the silicate portions of the rocky planets may not have been the same as for the HSE. The chondrite-normalized abundances of the MSE estimated for the bulk silicate Earth (BSE) vary considerably (**Fig. 1**). Experimental studies have shown that the abundances of the MSE can be accounted for if metal-silicate equilibration occurred at elevated temperatures and pressures (e.g., Hillgren et al., 1994; Righter et al., 1997; Li and Agee, 2001). Thus, numerous studies have concluded that the abundances of these elements are consistent with metal-silicate equilibration at an average depth equivalent to pressures of 20-60 GPa. A major shift in the O fugacity of the terrestrial mantle, resulting from the disproportionation of ferrous iron into ferric iron plus metal, as occurs in Bridgmanite at high pressure (Frost and McCammon, 2008), has also been proposed as having had a significant influence on the final concentrations of the MSE in the Earth's mantle (e.g., Wade and Wood, 2005).

By contrast, the BSE is characterized by relative abundances of HSE that are in approximately chondritic proportions (**Fig. 1**) (Chou, 1978; Morgan, 1986; Meisel et al, 2001; Becker et al., 2006; Fischer-Gödde et al., 2011), and absolute abundances that are only ~200 times lower than bulk CI chondrite abundances (Morgan, 1986). Further, the ^{187}Os/^{188}Os and ^{186}Os/^{188}Os estimated for BSE, reflecting the long-term decay of ^{187}Re and ^{190}Pt (where $t_{½}$ for ^{187}Re and ^{190}Pt are ~42 and 450 Gyr, respectively), are also within the range of chondritic meteorites, and provide a robust record for long-term, chondritic Re/Os and Pt/Os (Morgan, 1985; Walker et al., 1997; Meisel et al., 2001; Brandon et al., 2006). These characteristics of the HSE in the BSE do not appear to be the consequence of the high pressure and temperature metal-silicate equilibration. Experimental studies have shown that large differences in the metal-silicate distribution coefficients of siderophile elements at relevant temperatures and pressures, would have led to non-chondritic relative abundances in the mantle (Holzheid et al., 2000; Brenan and McDonough, 2009; Mann et al., 2012). This is observed for MSE but not for HSE (**Fig. 1**). Instead, the HSE may owe their presence in the BSE to continued accretion of planetesimals with bulk chondritic compositions, following cessation of core formation (Kimura et al., 1974; Chou, 1978). This process has been termed the *late meteorite influx* by some, and *late accretion* by others (henceforth, we will use the term late accretion).

The addition of bodies with chondritic bulk compositions to silicate mantles would lead to the establishment of comparatively high absolute, and chondritic relative abundances of HSE in the affected mantles. In the case of Earth, mass balance constraints suggest that it would be necessary to add 0.3 to 0.8 wt. % of the mass of the total Earth (~2 x 10^{22} kg) to the mantle by late accretion in order to account for present mantle HSE abundances (Walker, 2009). Implicit in such models are the assumptions that abundances of all HSE in the mantle were very low prior to late accretion, and that metal present in late stage impactors was ultimately oxidized so that the siderophile elements added to the mantle after core formation remained in the mantle (Kimura et al., 1974). Although there are some problems associated with the late accretion hypothesis it currently is the only viable process to explain the HSE characteristics of the BSE (Walker, 2009).

The two mechanisms for the establishment of siderophile elements into the terrestrial mantle are not necessarily in conflict. Models such as those proposed by Wade and Wood (2005) and Rubie et al. (2011; 2015) lead to the establishment of typically >90% of the MSE abundances in the mantle by high pressure and temperature metal-silicate partitioning. Repeated processing of metal through the mantle, as a result of oligarchic growth and the resulting multiple stages of magma ocean formation and evolution, would lead to a biasing of the MSE present in the mantle today towards the mass added by the later major stages of accretion (Azbel et al., 1993; Kramers, 1998; Rubie et al., 2011, 2015). Subsequent late accretion of ~0.5 wt.% mass addition would add >95% of the HSE, but a maximum of only about 10% of an MSE, such as W, to the mantle total. Thus, as noted by Dauphas et al. (2004), the genetics of the MSE present in the mantle are not required to have been the same as the genetics of the HSE.

3. Isotopic Tracers

Two types of isotopic tracers of building blocks are considered here; radiogenic and nucleosynthetic. Long-lived radiogenic tracers have long proved to be useful for constraining the vigor and nature of mixing in the silicate portions of planets. For example, long-lived systems including ^{87}Rb-^{87}Sr, ^{147}Sm-^{143}Nd, ^{176}Lu-^{176}Hf, and ^{238,235}U-^{232}Th-^{206,207,208}Pb have been extensively used to trace mantle mixing over Earth history, particularly with respect to recycled crustal components (Zindler and Hart, 1986; Hofmann, 2003). Of the long-lived systems consisting of HSE, however, only the ^{187}Re-^{187}Os isotopic system, and to a lesser extent the ^{190}Pt-^{186}Os system, have been shown to be useful for characterizing late stages of planetary accretion to Earth, Moon and Mars (e.g., Morgan, 1985; Walker et al., 2002a; Meisel et al., 1996; Day et al., 2007; Brandon et al., 2012).

Short-lived radiogenic isotopic systems have much greater utility for examining the timing of early planetary accretion and differentiation processes with high resolution (e.g., Caro et al., 2003; Foley et al., 2005; Boyet and Carlson, 2005; Debaille et al., 2009; McLeod et al., 2014). Although short-lived isotopic systems, most notably the lithophile-atmophile ^{129}I-^{129}Xe system ($t_{½}$ = 15.7 Myr), the lithophile ^{146}Sm-^{142}Nd system ($t_{½}$ = 103 Myr), and the lithophile-siderophile ^{182}Hf-^{182}W system ($t_{½}$ = 8.9 Myr), were initially pursued primarily to date cosmochemical materials and processes, radiogenic decay of these systems has also led to the production of long-term isotopic heterogeneity in an array of sizable cosmochemical reservoirs, including the lunar and martian mantles (Nyquist et al., 1995; Foley et al., 2005; Debaille et al., 2009). Consequently, variations in the abundances of the daughter isotopes can also serve as tracers of planetary mantle mixing. Because the parent isotopes of these systems were extant for relatively short periods of time, ranging only from about 60 Myr for ^{182}Hf, to as long as 600 Myr for ^{146}Sm, the heterogeneities they record can only have formed early in solar system history. For example, the large differences in ^{182}W/^{184}W and ^{142}Nd/^{144}Nd isotopic ratios between nakhlite and shergottite meteorites, with both groups presumably derived from the martian mantle, can only be explained as a result of a major, possibly global, differentiation event within the first 15 to100 million years of solar system history (Foley et al., 2005; Debaille et al., 2009). Little subsequent mixing between the mantle domains, from which the precursor melts to these rocks originated, has evidently occurred.

Of major significance to the possibility of identifying late-stage building blocks of Earth is the detection of small isotopic anomalies in all three radiogenic isotope systems, present in materials derived from the terrestrial mantle (e.g., Caro et al., 2003, 2006; Willbold et al., 2011; Mukhopadhyay, 2012). Here, the term anomaly refers to an isotopic composition that differs from that of the dominant composition measured for modern terrestrial samples. The existence of these anomalies highlights the long-term survival of isotopically-distinct mantle domains, which likely formed within the first 50 million years of solar system history. With regard to identifying building blocks, the reasoning applied here is that if endogenous radiogenic isotope anomalies that formed very early in Earth history survived hundreds of millions to billions of years, then chemical and potentially nucleosynthetic isotopic heterogeneities, introduced to the mantle through the incorporation of genetically diverse building blocks during the period of late accretion, might also have survived and been incorporated into the rock record.

The application of nucleosynthetic anomalies as tracers of building blocks is based on the observation that the isotopic compositions of numerous elements present in presolar grains reflect diverse formational pathways in high energy, stellar environments. Nucleosynthetic processes include the *slow* accumulation of neutrons, or the *s*-process, such as by He burning in the outer shell of an asymptotic giant branch star; *rapid* accumulation of neutrons, or the *r*-process, such as during a Type II supernovae; and by *proton* enrichment, or the *p*-process, such as by photo-disintegration of heavy elements or neutrino interactions (Burbidge et al., 1957). Evidence for each of these nucleosynthetic processes has been confirmed through the observation of predicted, large-scale isotopic enrichments and depletions in diverse presolar grains extracted from low metamorphic-grade primitive meteorites (e.g., Zinner, 1998; Nittler, 2003). In addition to direct measurement of nucleosynthetic variations in presolar grains, information regarding the identity and origin of presolar materials has also been obtained through chemical leaching of bulk primitive meteorites, followed by separate analysis of leachates and residues (Dauphas et al., 2002a; Hidaka et al., 2003; Schönbächler et al., 2005; Yokoyama et al., 2010).

Although the isotopic variability observed among presolar components was greatly attenuated by nebular mixing processes, some elements continued to remain isotopically heterogeneous during the formation of moderate-sized bodies. For example, Yin et al. (2002) and Dauphas et al. (2002b) reported isotopic variations on the order of several parts per ten thousand for the MSE Mo, in bulk samples of chondrites and iron meteorites. Some of these iron meteorites have been interpreted to sample the cores of diverse asteroidal- to embryonic-size bodies, in certain cases with diameters that may have exceeded 300 km (Yang et al., 2008). More recently, Burkhardt et al. (2011) reported a similar range of mass independent Mo isotopic composition variability among iron meteorites, chondrites and pallasites (**Fig. 2a-b**). Similarly, Chen et al. (2010) reported comparably large ^{100}Ru isotopic heterogeneities among iron meteorite and chondrite groups (**Fig. 3a-b**). The causes for such large-scale isotopic heterogeneity remain debated, but can include the preferential concentration of some types of presolar components into parent bodies, resulting from thermal or physical sorting mechanisms of host phases in the solar nebula (Trinquier et al., 2007; Regelous et al., 2008). Alternately, these large-scale nucleosynthetic anomalies could reflect injections of diverse nucleosynthetic materials from nearby supernovae at different times during the evolution of the nebula (Bizzarro et al., 2007), followed by incomplete homogenization of these materials throughout the nebula (Carlson et al., 2007; Andreasen and Sharma, 2007). Regardless of the true cause, the evidence for isotopic heterogeneity in nucleosynthetic componentry among diverse planetesimals is strong. Like mass independent isotopic differences in O isotopes, the isotopic variations in these elements can potentially serve as fingerprints of their unique origins in the nascent solar system.

4. The Final ~10 wt. % of Accretion

The canonical model for the formation of the Moon involves a giant impact of an impactor comprising approximately 10% of the mass of the Earth (Canup and Asphaug, 2001).

Although recent models for the putative giant impact have expanded the possible range for the mass of the impactor from as little as 5% (Cuk and Stewart, 2012) to as much as 45% of the current mass of the Earth (Canup, 2012), there is little doubt that it was the final major accretionary addition to Earth. The event led to the transit of appreciable metal from the impactor core through the Earth's mantle. As a consequence, it could also have led to a substantial modification of siderophile element abundances and isotopic compositions retained in the silicate portion of the Earth, following the impact (e.g., Rubie et al., 2011). As evidenced by the mass balance constraints discussed above, subsequent late accretion could not have modified the abundances of the MSE in the mantle by more than ~10%. Thus, the giant impact would have been the last major event involved in the establishment of the modern characteristics of MSE in the terrestrial mantle. Consequently, some characteristics of MSE in the mantle today may provide insights to the nature of the final massive impactor involved in the construction of Earth and Moon.

Of all the MSE, the modification of the mantle by giant impact has been most frequently studied using W isotopes, because of the radiogenic tracer capability inherent in the system (Halliday, 2004; Dwyer et al., 2014). Unfortunately, the W isotopic composition of the mantle today can provide only modest constraints regarding the nature of the giant impactor. This is because the outcomes of giant impact models involving the Hf-W isotopic system are strongly dependent on assumptions about the timing of the impact, and of core formation on both the proto-Earth and impactor. Of particular importance is the degree of equilibration that occurred between the core of the impactor and the silicate Earth, as metal from the impactor transited the mantle on its way to merge with the Earth's core (e.g., Halliday, 2004; 2008). In contrast to the W present in metal derived from the core of the impactor, it is assumed that nearly all of the W present in the silicate portion of the impactor ended up mixing into the terrestrial mantle, or being lofted away from Earth to form the silicate portion of the Moon.

With regard to metal-silicate equilibration, one endmember possibility is that the core of the impactor quickly merged with the core of the Earth, with negligible exchange of W between the merging core and the silicate Earth (**Fig. 4a**). In this case, the $^{182}W/^{184}W$ of the Earth's mantle would likely have increased as a result of the addition of W from only the silicate portion of the impactor (Halliday, 2004). The $^{182}W/^{184}W$ of the silicate portion of the impactor was probably more radiogenic that that of the proto-Earth's mantle, because the silicate portion of the embryonic-size impactor is usually presumed to have accreted and differentiated a core more rapidly than Earth, creating a high Hf/W mantle, while ^{182}Hf was still plentiful (Dauphas and Pourmand, 2011). Thus, for this scenario, the ^{182}W isotopic composition of the silicate Earth could have risen 100 ppm or more as a result of the impact.

The other endmember possibility is that the core of the impactor broke into small droplets, resulting from Rayleigh-Taylor instabilities, and the droplets equilibrated with surrounding silicate liquid as they sank through the mantle to merge with the terrestrial core (Dahl and Stevenson, 2010). In this case, the W isotopic composition of the silicate Earth would likely have decreased significantly (**Fig. 4b**), as W with low $^{182}W/^{184}W$ from the impactor core ($\mu^{182}W \leq -200$) equilibrated with the presumably more radiogenic silicate Earth (Halliday, 2008). In this case, the mantle of the Earth just prior to the impact may have been more than 200 ppm more radiogenic than the present mantle.

Because of these uncertainties in the extent of equilibration between metal and silicate, it is currently impossible to estimate the $\mu^{182}W$ value of the impactor mantle, as well as the age of average core formation for either the impactor or Earth. Nevertheless, W isotopes may have some utility in characterizing the differentiation history of this major building block of Earth. One possible explanation for the W isotopic similarity between the Earth and Moon (Touboul et al., in review) is that the impactor and Earth formed from genetically similar materials and had roughly similar average core segregation ages (e.g., Dauphas et al., 2014). Information that is currently being gleaned about the drawdown of mantle HSE abundances at the time of giant impact (e.g., Touboul et al., in review), coupled with an improved understanding of the rate of isotopic versus elemental equilibration between metal and silicate, may one day enable stronger constraints to be placed on the formation and differentiation history of the impactor.

More germane to the current genetic characterization of this stage of terrestrial growth may be the isotopic composition of the MSE Mo. The Mo isotopic composition of the silicate Earth differs from all known chondrite groups and most iron meteorite groups (Dauphas et al., 2002b; Burkhardt et al., 2012)(**Fig. 2a-b**). The only major meteorite group measured to high precision that matches the Mo isotopic composition of the silicate Earth is the group IAB iron meteorites (Burkhardt et al., 2011). It has been proposed that this group of iron meteorites formed as a result of metal pooling at the base of an impact crater following an impact onto a primitive body (Wasson and Kallemyn, 2002). This iron group, however, shares little other elemental or isotopic commonality with the Earth. For example, the $\Delta^{17}O$ composition range of silicates present in IAB irons differs substantially from the Earth (Wasson and Kallemeyn, 2002). Therefore, even if their Mo isotopic compositions overlap, the group is probably not genetically closely related to Earth.

Enstatite chondrites have commonly been touted as good genetic, if not compositional, matches to the Earth (e.g., Javoy et al, 2010). This conclusion has been based on the fact that the isotopic compositions of several lithophile elements in enstatite chondrites, including O, Ti, Cr and Ba, as well as the siderophile element Ni, are excellent (Cr, Ti, Ni, Ba) or near (O) matches to their isotopic compositions in the silicate Earth (Clayton, 2004; Carlson et al., 2007; Trinquier et al., 2007; 2009; Regelous et al., 2008; Herwartz et al., 2014). Not all isotopic compositions match, however. Fitoussi and Bourdon (2012) reported a ~30 ppm difference in the Si isotopic composition between the silicate Earth and enstatite chondrites. They argued that this difference cannot be accounted for by incorporation of Si in the terrestrial core. With the possible exception of the siderophile Ni, however, the previously mentioned elements should provide little constraint on late stages of terrestrial accretion. Instead, their isotopic compositions are fingerprints of the dominant contributors to the bulk planet.

The Mo isotopic compositions of enstatite chondrites overlap with the BSE, within the level of analytical precision (Burkhardt et al., 2011) (**Fig. 2b**). Burkhardt et al. (2011), however, concluded that the characteristic w-shaped pattern of isotopic enrichments and depletions for enstatite chondrites, as with ordinary and carbonaceous chondrites, is consistent with minor *s*-process depletion. Even if there is a small difference in the Mo isotopic composition of enstatite chondrites and the BSE, this does not necessarily mean that the Mo isotopic composition of the bulk Earth differs from that of enstatite chondrites. Most of Earth's Mo is sited in the core, and most of that Mo was added to the Earth through initial stages of planetary accretion. It is, therefore, possible that the Mo isotopic composition of the core is characterized by a slight enrichment in *s*-process isotopes compared to enstatite chondrites. In this event, the final ~10% growth of Earth may have involved materials with an average Mo isotopic composition that was slightly depleted in *r*-process isotopes relative to the silicate Earth today, such that the core and silicate Earth combined has a composition that is similar to enstatite chondrites. As with W, the fraction of Mo present in the mantle derived from the impactor is not known, nor is the degree of equilibration between the core of the impactor and the Earth's mantle. Consequently, the true Mo isotopic composition of the impactor cannot be well established at this time. Nevertheless, the present results suggest that the final major addition of Mo to Earth in the form of a giant impact involved an impactor with a Mo isotopic composition broadly similar to enstatite chondrites (see additional discussion below).

Application of the MSE to study the nature of late stage building blocks is not limited to Earth. The Mo isotopic compositions of the two shergottites analyzed by Burkhardt et al. (2011) overlap with the composition of the silicate Earth, so no genetic difference between these two bodies can be detected at the current level of analytical resolution for this element. However, the uncertainties on the measured Mo isotopic composition for these samples are relatively large. Future refinement of the Mo isotopic composition of Mars, and determination of whether or not it has a uniform isotopic composition, will be critical to assessing whether late stage additions to the Earth and Mars came from genetically similar materials, and whether late stage building blocks to Mars were well homogenized before the large-scale differentiation events that led to isotopic heterogeneity in ^{182}W and ^{142}Nd.

5. The Final ~0.5 wt.% of Accretion

5.1. Highly Siderophile Elements in the Bulk Silicate Earth

The absolute and relative abundances of HSE in primitive meteorites vary among the major chondrite groups (Walker et al., 2002a; Horan et al., 2003; Brandon et al., 2005; Tagle and Berlin, 2008; Fischer-Gödde et al., 2010)(**Fig. 5**). For example, Pd/Ir in some enstatite chondrites tend to be higher than for ordinary, carbonaceous, or R-type chondrites. Given that Re/Os also vary among the chondritic groups, the ^{187}Os/^{188}Os of chondrites can serve as an important, complementary parameter to discriminate among chondrite groups. Most notably, carbonaceous chondrites are characterized by generally lower $^{187}Os/^{188}Os$, and therefore lower long-term Re/Os, than ordinary and enstatite chondrites (**Fig. 6**). Modest, long-term differences in Pt/Os have also resulted in small differences in $^{186}Os/^{188}Os$ among some chondrite groups (Brandon et al., 2006).

Although variations in the relative abundances of HSE are becoming increasingly better constrained for chondritic components (e.g., Horan et al., 2009; Archer et al., 2014), except for calcium-aluminum rich inclusions, there has been only limited success in determining the causes of the variations among the HSE characteristics of bulk chondrites (Mason and Taylor, 1982; Sylvester et al., 1990; Fischer-Gödde et al., 2010). Thus, no nebular or parent body processes can currently be firmly linked to the HSE characteristics observed in bulk chondrites. This means the process that led to lower, long-term Re/Os in carbonaceous chondrites, compared to other chondrite groups, may not be related to the accompanying, generally more volatile-rich nature of carbonaceous chondrites. Despite these current limitations to fingerprinting late accretionary additions, if most of the mass of HSE present in the BSE today was added as a result of late accretion, the relative abundances of these elements in the BSE should provide an averaged compositional snapshot of the final ~0.5% of mass addition to Earth.

Establishing HSE abundances in the BSE with sufficient precision to make comparisons to possible cosmochemical precursors is problematic. Because of the sensitivity of $^{187}Os/^{188}Os$ ratios to discriminate among small, long-term differences in Re/Os, Os isotopes have been especially heavily used among the HSE to characterize the nature of late accretion to Earth (Hirt et al., 1963; Morgan, 1985; Meisel et al., 1996; 2001). However, the application is not so straightforward. Although Os is highly compatible within the mantle, the Os isotopic composition of the BSE cannot be measured directly via analysis of the dominant silicate reservoir in Earth, the oceanic mantle. This is because Re behaves incompatibly during mantle melting (Barnes et al., 1985; Rehkämper et al, 1999; Pearson et al., 2004). Consequently, oceanic and continental crustal extraction has modified the Re/Os of the residual oceanic mantle over Earth history. Abundances of Re estimated for the continental crust are relatively low (Peucker-Ehrenbrink and Jahn, 2001), and given its limited mass, its formation is unlikely to have led to significant modification of the Re/Os of the residual mantle. By contrast, the formation of oceanic crust, with its comparatively high Re concentrations, may have significantly modified the Re/Os of the residual mantle. The magnitude of this modification is open for debate, as some of the Re extracted into oceanic and continental crust has been recycled back into the mantle. How much of the recycled Re and Pt has been re-mixed back into the oceanic mantle is problematic to assess (Walker et al., 2002b).

To circumvent this problem, Meisel et al. (1996; 2001) applied a projection method utilizing the compositions of variably melt depleted mantle peridotite xenoliths to estimate the $^{187}Os/^{188}Os$ of the BSE. They plotted $^{187}Os/^{188}Os$ (record of long-term Re/Os) versus Al_2O_3 or Lu, indicators of mantle melt depletion that are not as easily modified by secondary processes as Re, and projected the resulting linear trends to points of intersection with an assumed Al_2O_3 or Lu composition for the BSE. Using this method, Meisel et al. (2001) reported a ratio of 0.1296 ± 0.0008 (2σ). This ratio must be considered a *minimum* because the projections were made mainly from samples derived from sub-continental lithospheric mantle. Such peridotites must have been physically separated from the oceanic mantle at some time prior to isolation as sub-continental lithospheric mantle. The oceanic mantle itself was most likely variably depleted in Re prior to these reservoirs transitioning from oceanic to sub-continental lithospheric mantle, so the melt depletion events recorded in these rocks likely include at least one stage of prior melt depletion. The $^{187}Os/^{188}Os$ estimated for the BSE is at the upper end of the range of compositions recorded in bulk ordinary and enstatite chondrites (**Fig. 6**). Given this, the $^{187}Os/^{188}Os$ of the BSE appears to be most similar to ordinary and enstatite chondrites, or even slightly more radiogenic, and this likely means that carbonaceous chondrites, or similar materials, were not major players in late accretion (Walker et al., 2002a). Given the volatile-rich nature of some carbonaceous chondrite groups, this observation in turn has been taken as evidence that late accretion provided little water to Earth (Drake and Righter, 2002), although as noted, there is currently no known process that relates the incorporation of volatiles and low Re/Os into the parent bodies of carbonaceous chondrites.

Absolute and relative abundances of other HSE have been estimated for the BSE using a similar approach as for $^{187}Os/^{188}Os$ (Becker et al., 2006; Fischer-Gödde et al., 2011). When collectively considering the HSE characteristics estimated for the BSE as compared with chondrites (**Fig. 7**), it appears to be most similar to enstatite chondrites for Re/Os, Os/Ir, Pt/Ir and Pd/Ir (Becker et al., 2006). However, the BSE appears to be modestly suprachondritic with respect to Ru/Ir and possibly Pd/Ir (Becker et al., 2006). Thus, although the current estimate of the HSE composition of the BSE is most like enstatite chondrites, it is not a perfect match to any known chondrite group, or individual chondrites present in our collections. This could mean that late accretion to Earth was dominated by one or more components that were somehow processed in the nebula, or on a parent body, such that HSE were fractionated relative to presently sampled chondrites. This in turn could occur as a result of the location of formation within a chemically heterogeneous protoplanetary disk, or formation at a different time in a chemically evolving nebula. Given that there are bulk chondrites with individual HSE ratios that extend beyond those estimated for the BSE (although no one chondrite has all of the HSE characteristics of the BSE), nebular or parent body processes can evidently cause such fractionations. It is also possible that the fractionated HSE abundances present in the dominant late accretionary component, could result from another process, such as crystal-liquid fractionation of a metal component (e.g., Fischer-Gödde et al., 2011).

It is important to recognize that there are some limitations to the projection approach towards characterizing the BSE and fingerprinting late accretionary additions, using HSE. Of greatest concern is the precision and accuracy of HSE estimates for the BSE. The absolute and relative concentration estimates in the BSE are based on measurements of mantle peridotites that may represent the end stage of multiple processes, including mantle melting, metasomatism and crustal recycling (Alard et al., 2000; le Roux et al., 2007). Thus, although the broadly chondritic nature of the BSE is of little doubt, the relatively small differences in elemental ratios that are key to discriminating among chondritic groups, or fingerprinting a heretofore unidentified chondrite-like contributor to the mantle, have been called into question (e.g., Lorand et al., 2009). The primary question is whether any mantle peridotites can provide sufficient fidelity in recording the BSE composition. The typically strongly compatible natures of Os, Ir and Ru, make them less susceptible to modification by partial melting and metasomatic processes, compared to Pt, and especially the incompatible Pd, Au and Re. Consequently, they provide the strongest constraints on the HSE composition of the BSE, and the suprachondritic nature of Ru/Ir in the BSE appears in little doubt. Further, the similarity of HSE characteristics of large numbers of variably "fertile" mantle peridotites, ranging from abyssal peridotites, to peridotites from the mantle sections of ophiolites, to oceanic mantle xenoliths, supports the contention that the BSE is characterized by suprachondritic Ru/Ir and possibly Pd/Ir (Becker et al., 2006; Fischer-Gödde et al., 2011). However, compilation of an even larger number of data from all types of mantle lithologies, combined with an improved understanding of how HSE from oceanic crust have been recycled back into the oceanic mantle, may ultimately be required to assemble a high-confidence understanding of HSE in the BSE.

5.2. Constraining the Physical Nature of Late Accretion

One key aspect of utilizing siderophile elements as genetic tracers of planetary building blocks requires knowledge of the specific physical processes involved in their incorporation into planetary mantles. This is especially true for the HSE. For example, late accretion of HSE to Earth's mantle may have occurred as a consequence of a relatively gentle rain of smaller bodies onto the surface of the planet, as envisioned by some workers to form a *late veneer* (Anders, 1968; Turekian and Clark, 1969). In this case, a dog's breakfast of HSE-rich materials of diverse genetics may have been slowly mixed downward into the mantle as a result of crustal recycling, coupled with mantle convection. Maier et al. (2009) noted that such a process can potentially account for the low abundances of HSE in some early Archean komatiites. Komatiites are high MgO lavas, which are generally presumed to be derived from high degrees of partial melting in deep mantle upwellings, or mantle plumes (Campbell et al., 1989). Possible identification of a deep mantle source that was initially depleted in HSE, for komatiites >2.9 Ga, is consistent with the slow downward mixing of a late veneer into the deep mantle. Maier et al. (2009) argued that the "normal" HSE abundances found in komatiites formed later than ~2.9 Ga indicates that the putative veneer had become well-mixed into the deep mantle sources of komatiites by that time. The mantle source abundances of HSE have also been estimated for komatiites for which ^{187}Re-^{187}Os isotopic systematics confirm post-crystallization, closed-system behavior of the rocks with respect to HSE abundances (**Fig. 8**). The isotopic evidence for closed system behavior provides some additional confidence that the projected mantles source abundances are accurate. These komatiites systems show significant variations in the absolute HSE abundances between the sources of late Archean komatiite systems, which are generally similar to those in the sources of early Archean komatiite systems, although there are notable exceptions, with the oldest early Archean komatiite system (3.55 Ga Schapenburg) having substantially lower HSE abundances compared to all other komatiite systems studied to-date.

Another way to advance understanding of the physical nature of late accretion is by combining observations of the chemical characteristics of planetary materials with dynamical models for the first ~500 million years of solar system history. Here, comparing the characteristics of the HSE present in the terrestrial mantle with abundances present in the lunar and martian mantles may be particularly important. The abundances and isotopic compositions of the HSE in at least the upper portion of the terrestrial mantle are generally well defined and limited in variation. As noted, the ^{187}Os/^{188}Os and ^{186}Os/^{188}Os estimated for the BSE are within the range of chondritic meteorites (Meisel et al., 2001; Walker et al., 1997; Brandon et al., 2006). Further, oceanic and subcontinental lithospheric mantle peridotites the world over typically have relatively uniform abundances of Os and Ir, two HSE that are highly compatible during partial melting of the mantle (e.g., Rehkämper et al, 1999; Morgan et al., 2001). While there has long been a question as to whether the upper mantle is more enriched in HSE than the lower mantle, seismic tomography over the past 20 years has documented the exchange of matter between upper and lower mantle, providing evidence for mantle plumes rising from the lower mantle into the upper mantle and subducting slabs transiting from the upper mantle into the lower mantle (e.g., Goes et al., 1999; Nolet et al., 2006). It is, therefore, likely that there are no global-scale

HSE concentration variations within the mantle. Consequently, uncertainty in the mass of late accreted materials to the mantle, necessary to account for the observed abundances of HSE, primarily reflects the factor of two variation in HSE abundances between different types of chondritic meteorites (e.g., Horan et al., 2003), rather than uncertainties in the HSE content of the mantle.

The concentrations of HSE in the lunar and martian mantles are much more difficult to constrain than for the terrestrial mantle. No mantle samples have, as yet, been collected from either body. Hence, mantle abundances of the HSE must be deduced from mantle-derived volcanic rocks. Based on HSE abundances present in leached samples of picritic glass spherules and lunar basalts, Walker et al. (2004) and Day et al. (2007), respectively, estimated that HSE concentrations in the lunar mantle are a factor of 20 or more lower than in the terrestrial mantle (**Fig. 9a**). Such a large difference in concentration, if correct, cannot be explained by gravitational focusing or inefficiency of impactor retention. The lower concentrations may instead reflect proportionally much less mass added to the lunar mantle by late accretion, compared to the Earth. This in turn could result from a longer period of late accretion for Earth, compared to the Moon, i.e., one that began well before formation of the Moon. However, recent W isotopic data for the Moon suggest that the Moon-forming giant impact efficiently removed HSE from the mantle to Earth's core and reset the late accretionary clock for the two bodies (Touboul et al., in review). If so, this means that the dominant late accretionary periods of the Earth and Moon began after formation of the Moon, and that they were contemporaneous. Unless substantial quantities of late accreted materials to the Moon are sequestered from our view in its lower crust (Schlichting et al., 2012), an interpretation for which there is currently no physical evidence, there remains a sizable mismatch in the proportions of late accreted materials added to the mantles of the Earth and Moon.

In contrast to the lunar mantle, the martian mantle appears to have HSE abundances that are surprisingly similar to those present in the terrestrial mantle. Basaltic and ultramafic shergottite meteorites, commonly believed to come from Mars, are characterized by HSE abundances that scale with the MgO content of the rocks in a way that is similar to terrestrial volcanic rocks (Brandon et al., 2012)(**Fig. 9b**). In addition, shergottites exhibit a range of initial $^{187}Os/^{188}Os$ that is very similar to the range of compositions present in terrestrial mantle-derived volcanic rocks (Brandon et al., 2012). Given the fact that Mars is commonly presumed to have formed prior to the Earth (Dauphas and Pourmand, 2011), it might be expected to have a larger proportion of late accreted material mixed throughout its mantle. Instead, all existing data suggest that the HSE concentrations in the martian mantle are similar to those in the terrestrial mantle, indicating that a roughly similar proportion of late accreted materials was added to the mantle of Mars (Brandon et al., 2012).

Bottke et al. (2009) reported that one way to account for the similarity of HSE abundances in the terrestrial and martian mantles, but much lower HSE abundances in the lunar mantle is by a process they termed *stochastic late accretion*. The principle of stochastic late accretion is that most late accretionary mass was added to the Earth and Mars by a very limited number of impacts of approximately Pluto mass bodies ($\sim 1 \times 10^{22}$ kg). By chance, the Moon was not struck by any bodies of this size, and so retained relatively low abundances of HSE. Subsequent dynamical models have highlighted the probability that bodies of similar mass may have survived beyond the formation age of the Moon, and thus been available to drive late accretion (Marchi et al., 2014).

If stochastic late accretion correctly accounts for the apparent disparity in HSE abundances between the lunar and terrestrial mantles, it has a major implication for tracing late stage building blocks of the Earth, and possibly Mars. It requires that mass was added to the Earth by a limited number of impact events that likely would have generated discrete magma seas or lakes, rather than as a chemically and isotopically well-mixed veneer of small bodies. Consequently, if late stage impactors were added to the mantle in such a way that global melting did not occur, then the impactors may have imparted isotopically distinct HSE signatures to different portions of the mantle, assuming the impactors were genetically different from the average BSE, and from one another.

But what is the likelihood that moderately-sized, early-formed mantle heterogeneities remained isotopically distinct for hundreds of millions of years, until they melt to produce rocks that become incorporated into the rock record? This is where it is important to consider data for the short-lived radiogenic isotope systems. Perhaps of greatest importance for consideration here are ^{182}W isotopic data for rocks that were ultimately derived from the terrestrial mantle. Anomalous ^{182}W/^{184}W ratios have been identified in a number of ancient rocks, including ≥3.8 Ga supracrustal rocks from Nuvvuagittuq, Quebec (Touboul et al., 2014), ~3.7 Ga supracrustal rocks from Isua, Greenland (Willbold et al., 2011), and 2.8 Ga komatiites from Kostomuksha, Fennoscandia (Touboul et al., 2012). All ^{182}W anomalies for terrestrial rocks, reported to date, range between +5 and +15 ppm (**Fig. 10**).

Terrestrial enrichments in ^{182}W have been interpreted in two different ways. Willbold et al. (2011) reported ^{182}W enrichments averaging ~13 ppm for 3.7 Ga supracrustal rocks from Isua, Greenland. These authors proposed that the enriched compositions reflect derivation of precursor rocks from a mantle domain that formed prior to a final major stage of late accretion, and that this mantle domain remained mostly free of late accreted materials until it melted to form the Isua rocks. Thus, the mantle precursor materials to the Isua rocks formed by normal planetary accretion, were stripped of HSE by metal segregation during core formation, but remained isolated from HSE and W added by subsequent late accretion. This is a process that could lead to isotopic heterogeneity in the mantle long after ^{182}Hf became extinct. It can be viewed as an *exogenous* process because it would have been controlled by the growth of ^{182}W on bodies other than Earth. More importantly, this mantle domain was not contaminated with late accreted HSE as a result of mantle mixing until after the early Archean melting event that produced the Isua precursor rocks, presumably well after completion of the dominant phase of late accretion. This suggests inefficient mixing of the mantle during the Hadean through early Archean. If this interpretation is correct for the Isua rocks, then the mantle domain sampled by them should have been relatively devoid of HSE. Willbold et al. (2011), however, did not report complementary HSE for these rocks, although it should be recognized that constraining the concentrations of HSE in the mantle source(s) of such highly altered supracrustal rocks is challenging.

A second means to account for anomalous ^{182}W in mantle-derived rocks is by solid-liquid fractionation processes that may have occurred in the mantle while ^{182}Hf was still extant. Because the absolute HSE abundances estimated for the mantle source of the Kostomuksha komatiites are identical, within uncertainties (Puchtel and Humayun, 2005), to those in the BSE estimates of Becker et al. (2006), Touboul et al. (2012) excluded the exogenous model of Willbold et al. (2011) for these rocks. They instead concluded that either metal-silicate fractionation in a basal magma ocean, or silicate crystal-liquid fractionation in a more conventional, whole mantle magma ocean led to the creation of a mantle domain characterized by high Hf/W. This in turn led to the formation of a high ^{182}W/^{184}W domain, as ^{182}Hf decayed.

Because of the short lifetime of ^{182}Hf, it was concluded that the fractionation events occurred within the first 30 Myr of solar system history. This process is considered *endogenous* because all of the necessary steps occurred within the Earth. Similar processes may also have led to the creation of some ^{142}Nd anomalies (e.g., Brown et al., 2015).

Regardless of the true mechanisms involved in the generation of terrestrial ^{182}W anomalies, it is clear that their presence in the rock record requires the long term survival of chemical heterogeneity in the terrestrial mantle despite major melting events, such as the Moon-forming giant impact. Much larger ^{182}W and ^{142}Nd isotopic anomalies have been determined for some, but not all martian meteorites, so the martian mantle also likely escaped a final large-scale mixing event during the final stages of its growth. Thus, if these bodies experienced late stages of accretion from genetically diverse materials, it might be expected that attenuated signals from the various materials might be summoned from the rock record.

The most promising element to examine for recording nucleosynthetic heterogeneities created by genetically diverse late accretion to Earth is Ru. As a HSE, Ru was strongly concentrated into metal by core formation processes. As noted above, the large range of nucleosynthetic isotopic compositions recorded in meteorites (e.g., Chen et al., 2010) provides this element with the utility for discriminating among diverse, late accretionary contributions to the mantle. Limited high precision analyses of terrestrial materials have, as yet, not identified any isotopic heterogeneity within the mantle (Bermingham et al., 2015), but the search has just begun.

5.3. The Mo-Ru Connection

In the discussion above, it is noted that the Mo and Ru present in the mantle today were most likely emplaced by different late-stage accretionary processes. The Mo abundance of the mantle was dominantly established by the final stages of oligarchic growth, including the Moon-forming giant impact. It probably represents a mixture of Mo from the silicate portion of the proto-Earth, as well as Mo from both the core and mantle of the giant impactor. By contrast, most Ru was likely added to the mantle by late accretion. Dauphas et al. (2004; 2014) made the important observation that, when plotting the range of nucleosynthetic heterogeneities for Mo and Ru in bulk planetary materials, most of these materials plot along a generally linear trend with the Earth, IAB irons, and enstatite chondrites plotting at one end, and some carbonaceous chondrites plotting at the other end of the trend (**Fig. 11**). Based on this correlation, these authors surmised that because each element recorded the genetics of different, late-stage accretionary events, it is logical to conclude that the materials involved in both stages of late accretion were genetically related and may have been derived from roughly the same portion of the protoplanetary disk. Thus, there may have been no major change in the genetic make-up of materials involved in the Moon-forming giant impact as compared to the final ~0.5% of late accreted materials (Dauphas et al., 2004; 2014). Differing genetics of these additions would otherwise have led to Earth plotting off of this correlation.

However, Mo and Ru isotope data underpinning this important observation remain somewhat limited. The correlation is presently constructed using group averages determined for a limited number of meteorites from which the Mo and Ru isotope compositions are not obtained from the same pieces of meteorite. Consequently, the precise relationship between Mo-Ru in different meteorites needs to be clarified using high precision Mo and Ru isotope composition data obtained from the same meteorite pieces.

6. Late Heavy Bombardment: The final ~0.05% of Late Accretion?

It has long been hypothesized that the Earth-Moon system, and likely the entire inner solar system, underwent a phase of late accretion, termed *late heavy bombardment* (LHB), within the interval from ~4.1 to ~3.8 Ga. The evidence for this putative event primarily comes from geochronologic information obtained from a variety of shocked and/or melted lunar rocks (e.g., Turner et al., 1973; Tera et al., 1974; Kring and Cohen, 2002). For example, Tera et al. (1974) recognized that most rocks collected by the Apollo missions formed a linear trend on a plot of ^{207}Pb/^{206}Pb versus ^{238}U/^{204}Pb that intersects concordia at about 3.9 Ga. Because of the ubiquity of this age, they inferred that the Moon underwent what they referred to as a *terminal cataclysm*. They envisioned the cataclysm to have been a relatively brief period of heavy bombardment (<300 million years) during which the surface of the Moon, and presumably the Earth, was peppered with impactors as large as ~200 km in diameter (e.g., Hurwitz and Kring, 2014), leading to the creation of at least some of the lunar basins. Subsequent studies of lunar impact melt rocks have provided strong support for a major disturbance in ages at about 3.9 Ga (e.g. Dalrymple and Ryder, 1993; Cohen et al., 2000), as few impact-modified lunar rocks yield ages older than ~3.9 Ga. Although the LHB had a major effect on shaping the surface of the Moon, it likely involved much less mass than is envisioned for late accretion as a whole. Even generous estimates for the mass of the LHB place the mass of materials involved as no more than about 10% of estimates for the overall mass of late accretionary additions (Morgan et al., 2001).

Dynamical models for the evolution of the solar system have suggested some possible causes for a period of LHB (Morbidelli et al., 2001; Strom et al., 2005; Gomes et al., 2005). For example, Gomes et al. (2005) suggested that migration of Uranus and Neptune, resulting from Jupiter and Saturn entering a 2 to 1 orbital resonance, may have led to the perturbation in the orbits of small bodies from both the asteroid belt and the Kuiper belt. Despite these observations and models, it is also possible that the ~3.9 Ga age represents a re-set age for the samples from a limited areal extent on the near-side of the Moon, from which all Apollo samples were collected, or a sampling of ejecta from only the youngest of the major basins (Spudis et al., 2011).

In addition to seeking to understand the timing of the LHB, it is also imperative to constrain the chemical characteristics of the materials involved because of the possibility that they delivered substantial water, and other volatile species, such as water, to the Earth and Moon. The primary means to examine the chemical characteristics of materials from the putative LHB has been to analyze lunar impact melt rocks that were created as a result of the basin-forming impacts. Such studies have been pursued since the Apollo missions, with chemical characterizations focused upon siderophile elements (e.g., Morgan et al., 1972; 1974; Korotev, 1994). Siderophile element data for nearly all studies prior to ca. 2000 were obtained by neutron activation analysis, so elements such as Ir, Au, Ni and Ge, that can be well-measured by this method, were most commonly considered. For example, Morgan et al. (1974) concluded that rocks from the Apollo 17 site included meteoritic components from at least six impactors, none of which had siderophile element characteristics that perfectly matched known meteorites.

Such studies as Morgan et al. (1974) assumed that endogenous lunar highlands or basaltic rocks formed with very low siderophile element abundances, so that the siderophile elements present in the impact melt rocks were nearly entirely derived from one or more large impactors.

A substantial number of studies reporting siderophile element data for so-called pristine lunar rocks have generally borne out this assumption (e.g., Warren and Wasson, 1977; Ryder et al., 1980; Warren et al., 1991; Day et al., 2007; 2010).

Although the early studies provided highly valuable insights into the chemical nature of impactors, some of the chief elements used to discriminate among possible impactors, such as Au and Ge, are somewhat volatile and could potentially have been modified by high temperature impact processes. To circumvent this problem, Norman et al. (2002) first applied the isotope dilution technique, teamed with inductively-coupled plasma mass spectrometry, to measure a larger suite of HSE in Apollo 17 impact melt rocks. That study measured and reported data for Re, Ir, Ru, Pt, and Pd, and identified at least three sources of HSE to the Apollo 17 suite. One source had HSE ratios similar to ordinary chondrites. A second component was characterized by HSE similar to EH chondrites. In order to account for supra-chondritic Re/Ir, Ru/Ir, and Pd/Ir in most of the rocks, Norman et al. (2002) appealed to the possibility of a third component, either an endogenous component enriched in Re, Ru and Pd, or an older component in the target crust that was incorporated into the crust by an earlier impactor with non-chondritic relative abundances of HSE.

Four subsequent studies have utilized similar isotope dilution techniques to measure the abundances of Re, Os, Ir, Ru, Pt, and Pd in lunar impact melt rocks, as well as measure ^{187}Os/^{188}Os, which serves as a sensitive proxy for long-term Re/Os (Puchtel et al., 2008; Fischer-Gödde and Becker, 2012; Sharp et al., 2014; Liu et al., in press). A major difference between these studies and the study of Norman et al. (2002) is that they examined multiple pieces of each rock studied. In approximately half of the rocks examined, the resulting plots of Ir versus each of the other HSE measured yielded linear trends with intercepts indistinguishable from 0, within regression uncertainties (**Fig 12**). In such cases, the trends can be assumed to represent mixing between the exogenous impactor and the HSE poor lunar target rocks, similar to interpretations for terrestrial impact melt rocks (e.g., McDonald et al., 2001). The slopes of the linear trends can, therefore, be assumed to record the HSE ratios of the basin forming impactors.

Puchtel et al. (2008) and Sharp et al. (2014) reported and interpreted data mainly for Apollo 17 impact melt rocks. Both studies reported a "dominant" component for the site, most notably characterized by suprachondritic Re/Os (as measured by ^{187}Os/^{188}Os), as well as Ru/Ir and Pd/Ir comparable to the results from Norman et al. (2002). They interpreted the results to suggest that the dominant source of HSE to the site, most likely the spatially associated Serenitatis basin impactor, shared broad similarities to some chondritic meteorites (enstatite chondrites), but sampling a composition not presently found in our meteorite collections. By contrast, a feldspar rich, or *granulitic* component present as clasts in some of these rocks, was determined to be characterized by relative abundances of HSE more similar to known chondrites.

Fischer-Gödde and Becker (2012) focused mainly on impact melt rocks from the Apollo 16 site. Here, they found Re/Os, Ru/Ir, Pt/Ir, and Pd/Ir ratios extending much higher than in known chondrites, and even well beyond the range of Apollo 17 rocks. They also analyzed some granulitic rocks and reported that, like prior studies, this component is most like ordinary chondrites. Of note, this study recognized that virtually all of the HSE data for Apollo samples plot along linear trends of HSE/Ir versus ^{187}Os/^{188}Os. They interpreted this to mean that all of the Apollo impact melt rocks incorporated at least two HSE-rich components at the time of their formation. One was very similar to carbonaceous chondrites and is the major component in granulitic rocks. The other component resembles a chemically evolved group IVA iron meteorite. Consequently, they proposed that both components became variably mixed during basin-forming impacts, but were not substantially modified by the inclusion of HSE derived from the basin-forming impactors.

Most recently, data from Liu et al. (in press) for Apollo 15 and 16 melt rocks filled in the gaps in the apparent linear trend recognized by Fischer-Gödde and Becker (2012), thus, strengthening their observation. In the compilation of data reported by Liu et al. (in press), nearly all data for lunar impact melt rocks plot along a continuous linear trend ranging from a HSE composition that is broadly chondritic, to an endmember with ^{187}Os/^{188}Os, Ru/Ir and Pd/Ir ratios far above those of known chondrites (**Fig. 13**). Two possible scenarios to explain the observed trends are: 1) Variable mixing between an earlier granulitic contaminant and a series of later-stage impactors that happened to form co-linear, suprachondritic Re/Os, Ru/Ir, Pt/Ir and Pd/Ir. 2) Variable mixing between two components present in the lunar crust prior to the late-stage basin forming impacts. For this scenario, one component was chondritic in composition and the other component had fractionated HSE, and could have been a core fragment, as suggested by Fischer-Gödde and Becker (2012). Although the latter scenario requires the involvement of a portion of an evolved core, it currently appears to be the most simplistic explanation for the trend. It also requires that the later-stage basin forming impacts (e.g., Imbrium) added only very limited HSE to the sampled impact melt rocks from multiple sites. These models await genetic testing using the nucleosynthetic anomalies characteristic of siderophile elements Mo and Ru.

7. Putting It All Together

At the present time, combined lithophile and siderophile element data suggest that the primary building blocks of Earth were broadly isotopically similar to enstatite chondrites, and that there was not a major change in the provenance of building blocks when comparing the pregiant impact Earth, to the Moon-forming giant impactor, and to the materials involved in the subsequent late accretion of ~0.5 wt. % of mass to the silicate Earth. This conclusion is based on the reasoning that the isotopic similarities between the Earth and enstatite chondrites, for lithophile elements such as O and Cr indicate genetic similarity to enstatite chondrites prior to the giant impact. Yet, the siderophile Mo isotopic composition of Earth's mantle is also very similar to that of enstatite chondrites. The isotopic composition of Mo present in the mantle was likely strongly affected by additions from the Moon-forming giant impactor, whereas the isotopic compositions of lithophile elements such as O and Cr were not. Thus, the collective enstatite chondrite-like isotopic compositions of lithophile and siderophile elements suggest that both the Earth and the giant impactor formed in the same region of the protoplanetary disk as enstatite chondrites (e.g., Dauphas et al., 2014).

The genetic heritage of late accreted materials during the final 0.5 wt. % of terrestrial accretion is best monitored via Ru isotopes, combined with the relative abundances of the HSE in the BSE. The Ru isotopic composition of the mantle, as for Mo isotopes, is similar to enstatite chondrites, meaning that the Earth plots near enstatite chondrites at the end of the cosmic Ru-Mo correlation trend. Some aspects of the projected relative abundances of the HSE in the BSE also match certain enstatite chondrites (Pd/Ir and ^{187}Os/^{188}Os). However, other aspects of the HSE signature of the BSE, such as Ru/Ir, do not to match any known chondrite groups. Thus, the late accreted materials must include at least one component with more fractionated HSE than is known to occur in chondrites. The origin of this chemical signature remains poorly constrained, but is suggestive of a not yet sampled primitive meteorite component. Very limited Os isotopic data for Mars suggest a similar late accretionary component was added to its mantle.

Finally, the Earth and Moon were bombarded by an additional flux of planetesimals hundreds of millions of years after primary accretion. The accretionary additions associated with this period could have totaled as much as 0.05 wt. % of the mass of the Earth. The materials involved in this final, minor accretionary period also involved the addition of HSE with some fractionated ratios. The chemical and isotopic natures of these materials are best monitored through the analysis of lunar impact melt rocks that were created by the late-stage basin-forming events. The fingerprints of these impactors are complex and encompass a range of HSE compositions. Some components evident in this bombardment cohort appear to be similar in HSE characteristics to carbonaceous and ordinary chondrites. An additional component was characterized by substantially higher Re/Os, Ru/Ir and Pd/Ir, compared to any known chondrites, including enstatite chondrites. The dominant signature of at least some materials involved in the LHB, therefore, appear distinct from the prior late-stage building blocks. The Ru and Mo isotopic compositions of lunar impact melt rocks have not yet been determined, so it remains unknown whether or not the LHB can be genetically linked to a type of primitive meteorite.

Although the siderophile element data for the Earth suggest that there was no major change in the provenance of its building blocks through to the end of late accretion (but before LHB), it remains unknown whether or not the building blocks consisted of a genetically homogeneous flux, or included diverse materials that ultimately mixed to form what now appears to be a uniform fingerprint for the BSE. As outlined above, the likelihood of isotopic variability of Ru and Mo among possible building blocks, combined with the apparent sluggishness of early mantle mixing of primordial ^{182}W isotopic heterogeneities, suggests that isotopic evidence for diverse late stage impactors might be found in Earth's early rock record, and possibly in younger rocks. Conversely, given the high level of precision that is now available to search for such isotopic heterogeneities, the future lack of discovery of isotopic anomalies may signal either that the materials involved in the final stages of terrestrial accretion were genetically similar, or that early mixing processes attenuated early Earth heterogeneities before evidence for them could be incorporated in the surviving rock record.

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Figure Captions

Figure 1. CI chondrite normalized abundances of moderately and highly siderophile elements estimated for the bulk silicate Earth. Estimates, together with uncertainties are taken from McDonough and Sun (1995) for the moderately siderophile elements, and from Becker et al. (2006) and Fischer-Gödde et al. (2011) for the highly siderophile elements.

Figure 2a-b. a. Molybdenum isotopic variations in iron meteorites relative to terrestrial standards, and **b.** in chondrites and shergottites. The gray fields represent the 2σ analytical uncertainties for measurements of each isotope in terrestrial standards. Error bars associated with symbols reflect the $2\sigma_M$ of data for each group. The figure is modified from Burkhardt et al. (2011).

Figure 3a-b. ^{100}Ru isotopic variations relative to terrestrial standards for **a.** iron meteorites and **b.** chondrites. The gray fields represent the 2σ analytical uncertainty for the measurements. Error bars associated with symbols reflect the $2\sigma_M$ of data for each group. The figure is modified from Chen et al. (2010).

Figure 4a-b. a. Model μ^{182}W (parts per million deviation in the ^{182}W/^{184}W of a sample relative to a modern terrestrial standard) evolution of the terrestrial mantle and core as a function of oligarchic growth. In the model the Moon-forming giant impact is assumed to occur 70 million years after solar system formation. It is also assumed that only 5% of the metallic core of the giant Moon-forming impactor equilibrated with the terrestrial mantle as the metal transited the silicate Earth (modified from Halliday, 2004). The increase in μ^{182}W results from the addition of the radiogenic silicate portion of the impactor to the terrestrial mantle. **b.** The same model is used as for **a**, but for this scenario 100% of the core of the giant impactor equilibrates with the silicate Earth (modified from Halliday, 2008). The decrease in μ^{182}W results from the addition of metal with appreciable W and very low μ^{182}W (-200) from the core of the impactor to the terrestrial mantle.

Figure 5. Variance in HSE ratios and ^{187}Os/^{188}Os, which serves as a proxy for long-term Re/Os, in the major primitive meteorite groups. Data for bulk chondrites are from Walker et al. (2002a), Horan et al. (2003), Brandon et al. (2005) and Fischer-Gödde et al. (2010). Also shown is the estimate for the BSE from Becker et al. (2006).

Figure 6a-d. Histogram plot of ^{187}Os/^{188}Os data for bulk chondrites compared with the minimum estimate for the BSE. Chondrite data are from Walker et al. (2002a), Brandon et al. (2005) and Fischer-Gödde et al. (2010). BSE ratio is taken from Meisel et al. (2001).

Figure 7. Plot of the concentrations of HSE estimated for the BSE doubly normalized to CI chondrite concentrations and the Ir/CI in BSE. The normalizing CI data are for Orgueil reported

in Horan et al. (2003) and Fisher-Gödde et al. (2010). The ranges of normalized concentrations for the three major chondrite groups are also from Horan et al. (2003) and Fisher-Gödde et al. (2010. Data for BSE are from Becker et al. (2006) and Fisher-Gödde et al. (2011).

Figure 8. Calculated total Pt+Pd abundances in the sources of Archean komatiites as compared to the BSE estimate of Becker et al. (2006). For each of these systems, ^{187}Re-^{187}Os isochrons consistent with the known ages of the rocks have been generated, consistent with closed-system behavior for other HSE. The late Archean komatiite systems span a substantial range, from 58±7% in the 2.69 Ga Belingwe system to 85±5% in the 2.72 Ga Abitibi system, of the total Pt and Pd present in the estimates for the modern BSE, with the 2.41 Ga Vetreny system being at the lower end of this range. Within the uncertainties, the total Pt+Pd abundances in some of the late Archean komatiite systems, e.g., Abitibi and Kostomuksha, overlap with those in the estimates for the BSE, whereas in the others (Vetreny, Belingwe, and Volotsk-Kamennoozero) fall slightly (by 20-14% when the full uncertainties on the estimates are considered) short of reaching that level. The total Pt+Pd abundances in the sources of the two out of three early Archean komatiite systems from the Barberton Greenstone Belts, South Africa, are within the range of those in the late Archean komatiite systems, albeit on the lower side, varying from 56±12% for the Komati to 65±10% for the Weltevreden, of the total Pt+Pd present in the estimates for the modern BSE, whereas the third system (Schapenburg) is characterized by much lower Pt+Pd abundances (27±4% of BSE). Data sources: Puchtel et al. (2004a,b; 2005; 2007; 2009a,b; 2014), Puchtel and Humayun (2005).

Figure 9a-b. a. Platinum concentration versus MgO data for lunar volcanic rocks (colored symbols), compared to data for terrestrial basalts, picrites, komatiites and peridotites (gray symbols). Lunar data are from Walker et al. (2004) and Day et al. (2007). **b.** Platinum concentration versus MgO data for martian shergottites (red symbols) compared to terrestrial basalts, picrites, komatiites and peridotites (gray symbols). Shergottite data are from Brandon et al. (2012).

Figure 10. Plot of μ^{182}W values for ancient rocks from the ≥3.8 Ga Nuvvuagittuq, Quebec, supracrustal suite, the ~3.7 Ga supracrustal rocks from Isua, Greenland, the 3.5 Ga Komati komatiites from the Barberton Greenstone Belt, South Africa, and 2.8 Ga komatiites from Kostomuksha, Fennoscandia. Data are from Willbold et al. (2011), Touboul et al. (2012) and Touboul et al. (2014).

Figure 11. Plot of ^{92}Mo versus ^{100}Ru of group averages chondrites and iron meteorites showing the linear trend defining *s*-process enriched and depleted compositions. Note that Earth plots at one end of the trend. Data are from Burkhardt et al. (2011) and Chen et al. (2010).

Figure 12. Plot of Re, Os, Ru, Pt and Pd versus Ir for six pieces of Apollo 14 impact melt rock 14321. The linear trends and zero intercepts are consistent with two component mixing of HSE in these rock fragments. One component is presumed to be pristine lunar crust with very low HSE abundances, and the second component appears to be a chondritic impactor with high HSE

abundances. The slopes of the trends likely define the HSE/Ir ratios of the basin forming impactor associated with this site. Figure is modified from Puchtel et al. (2008).

Figure 13a-d. Plots of **a.** Ru/Ir, **b.** Pt/Ir, **c.** Pd/Ir and **d.** Os/Ir ratios versus ^{187}Os/^{188}Os (proxy for long term Re/Os) for impact melt rocks from Apollo 14, 15, 16 and 17 landing sites, as well as two lunar meteorites. Each datum represents the regression of data for multiple fragments of each rock (e.g., Figure 12 for sample 14321). The error bars on the vertical axes represent the 2σ regression uncertainties for each rock. The error bars on the horizontal axes reflect the range of ^{187}Os/^{188}Os among subsamples of each rock. Data are from: Puchtel et al. (2008); Fischer-Gödde and Becker (2012); Sharp et al. (2014); Liu et al. (in press). Open symbols are data for bulk chondrites as shown in Figure 5. Figure is modified from Liu et al. (in press).

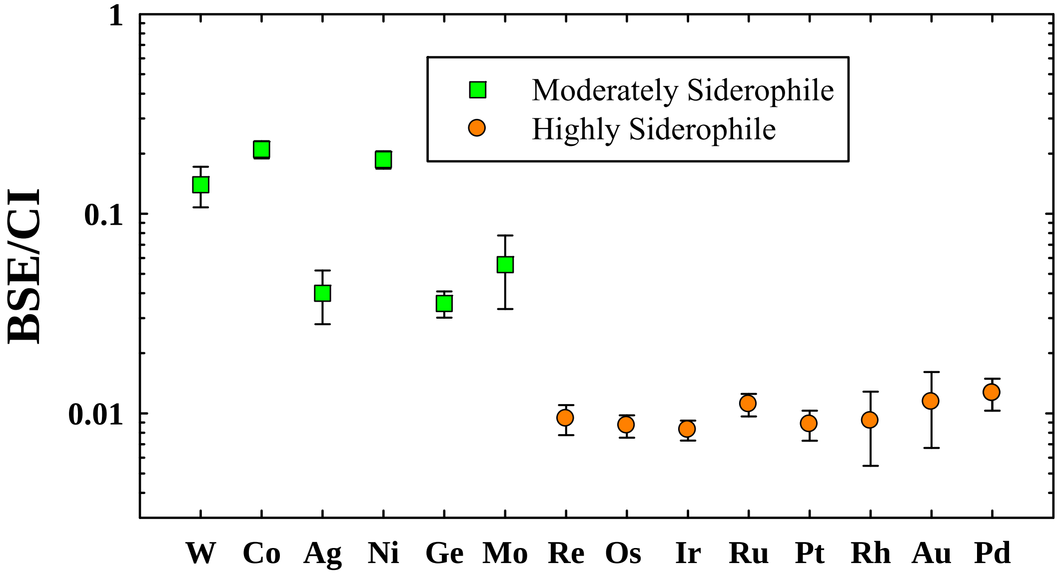

1
0.1
0.01
BSE/CI
🟩 Moderately Siderophile
● Highly Siderophile
W
Co
Ag
Ni
Ge
Mo
Re
Os
Ir
Ru
Pt
Rh
Au
Pd

Figure 1.

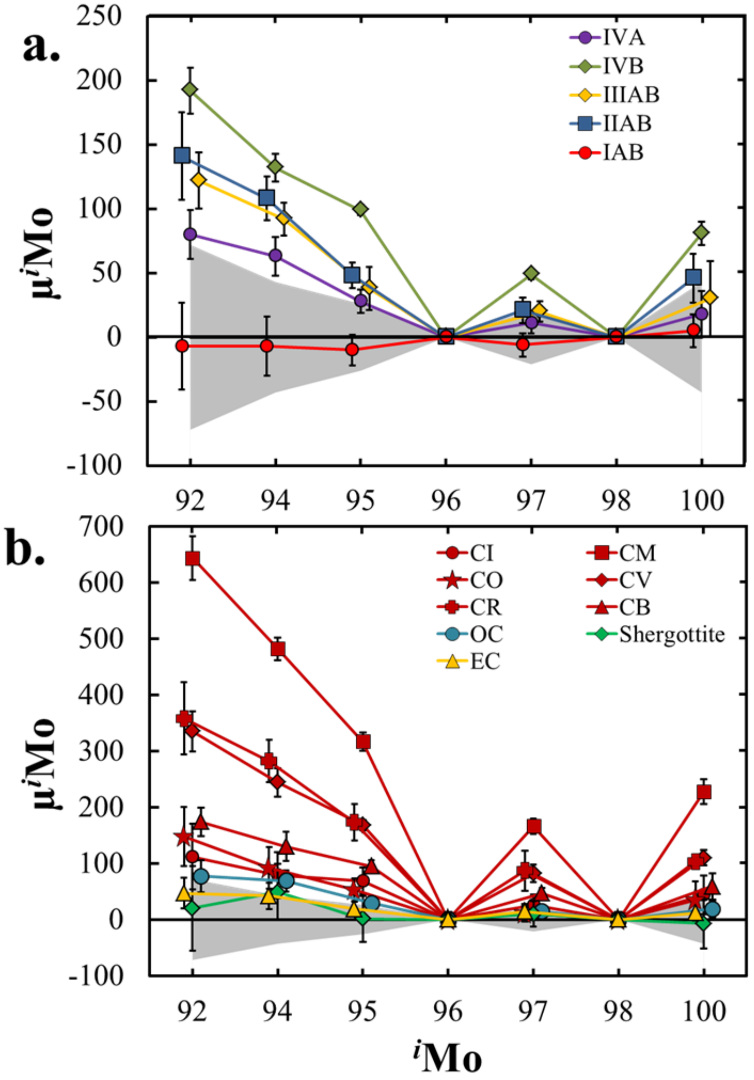

a.
IVA
IVB
IIIAB
IIAB
IAB
250
200
150
100
50
0
-50
-100
μⁱMo
92
94
95
96
97
98
100
b.
CI
CM
CO
CV
CR
CB
OC
Shergottite
EC
700
600
500
400
300
200
100
0
-100
μⁱMo
92
94
95
96
97
98
100
ⁱMo

Figure 2a-b.

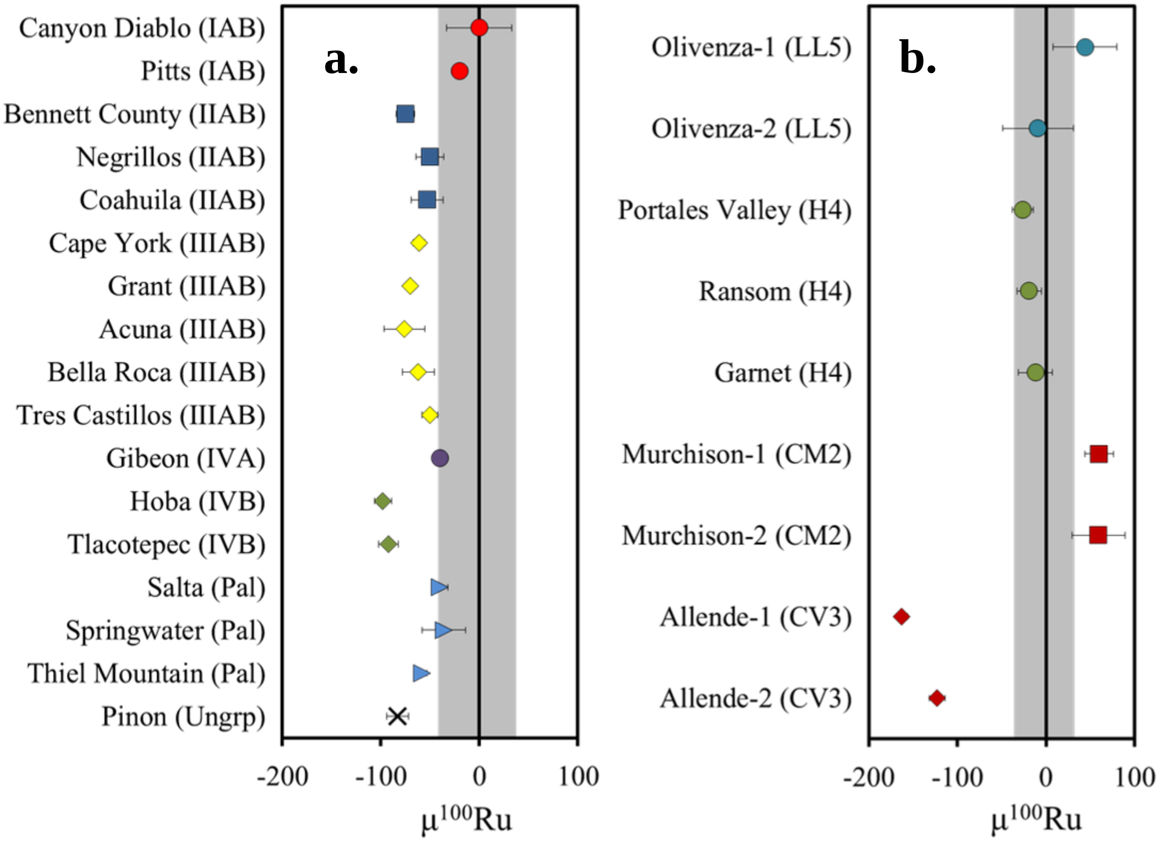
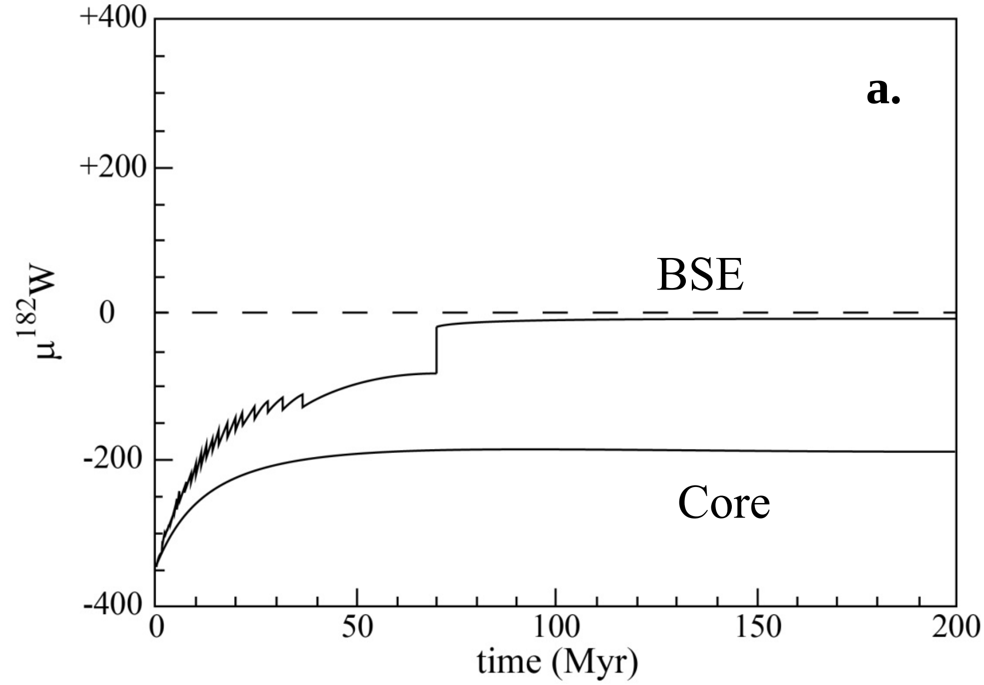

a.
Canyon Diablo (IAB)
Pitts (IAB)
Bennett County (IIAB)
Negrillos (IIAB)
Coahuila (IIAB)
Cape York (IIIAB)
Grant (IIIAB)
Acuna (IIIAB)
Bella Roca (IIIAB)
Tres Castillos (IIIAB)
Gibeon (IVA)
Hoba (IVB)
Tlacotepec (IVB)
Salta (Pal)
Springwater (Pal)
Thiel Mountain (Pal)
Pinon (Ungrp)
-200
-100
0
100
μ^{100}Ru
b.
Olivenza-1 (LL5)
Olivenza-2 (LL5)
Portales Valley (H4)
Ransom (H4)
Garnet (H4)
Murchison-1 (CM2)
Murchison-2 (CM2)
Allende-1 (CV3)
Allende-2 (CV3)
-200
-100
0
100
μ^{100}Ru

Figure 3a-b.


a.
+400
+200
0
-200
-400
μ182W
BSE
Core
0
50
100
150
200
time (Myr)

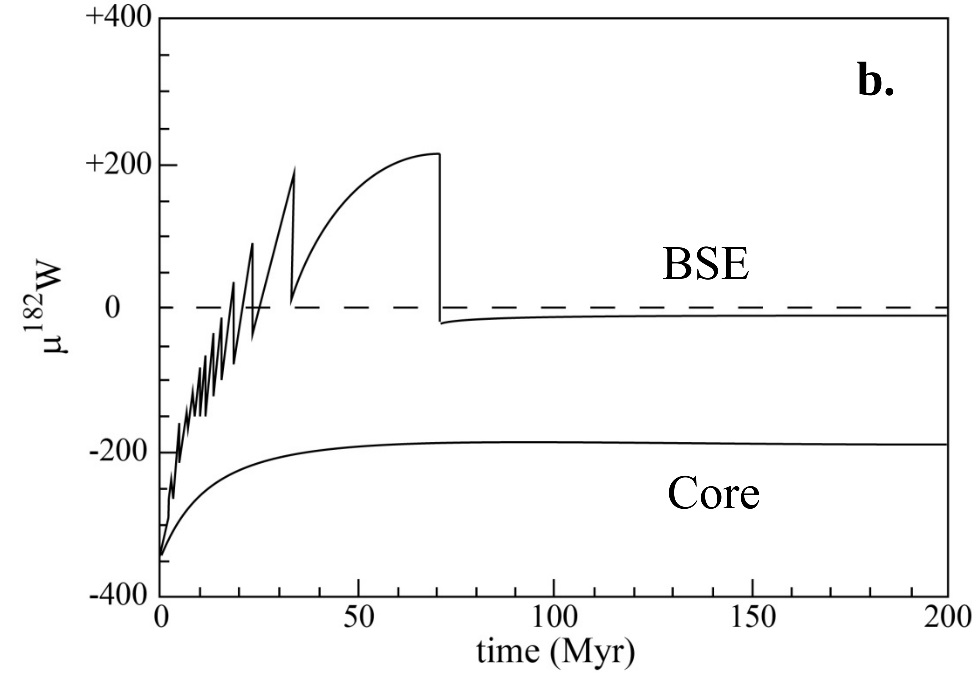

b.
+400
+200
0
-200
-400
μ182W
BSE
Core
0
50
100
150
200
time (Myr)

Figure 4a-b.

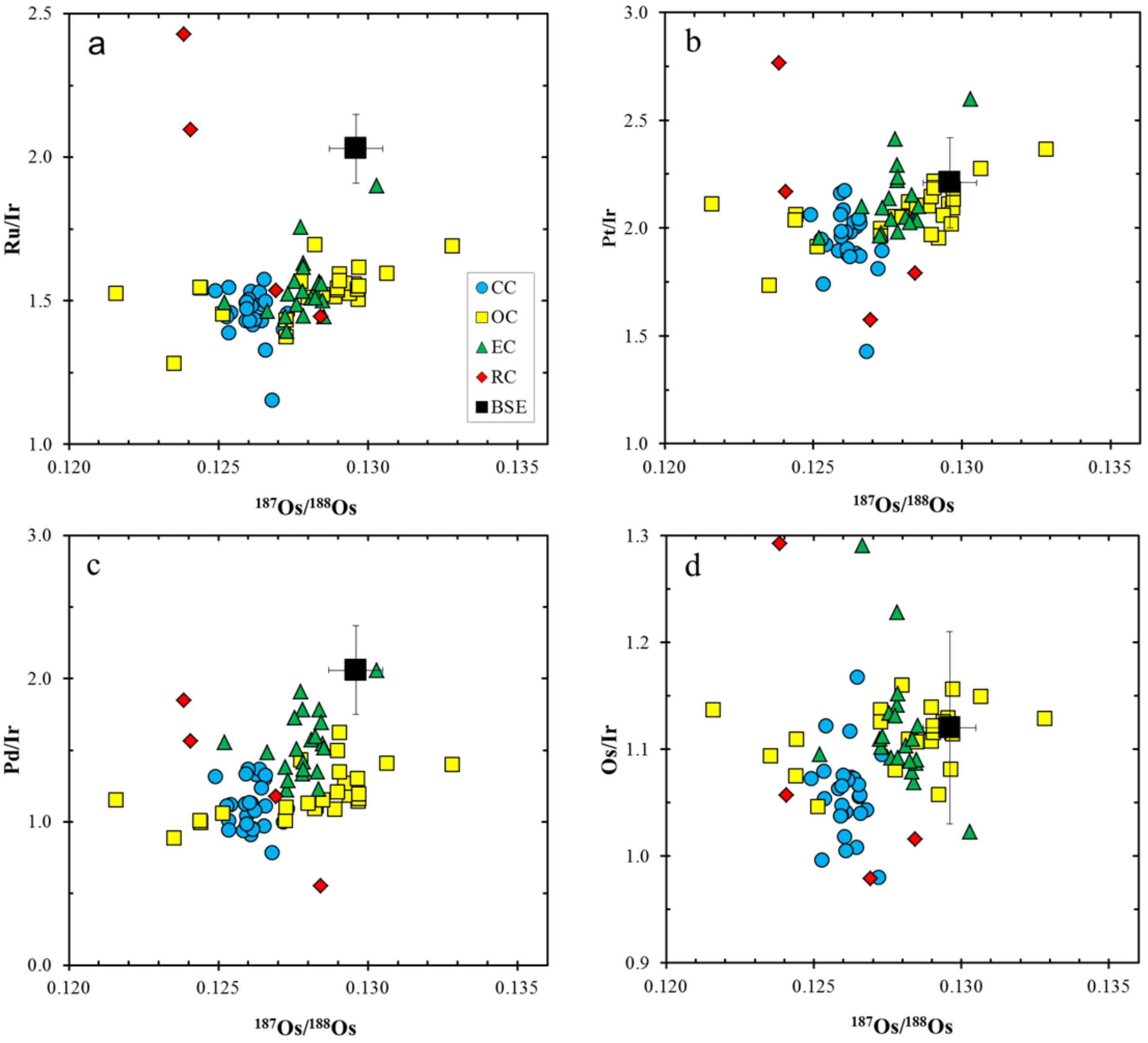

a
Ru/Ir
2.5
2.0
1.5
1.0
0.120
0.125
0.130
0.135
^{187}Os/^{188}Os
● CC
■ OC
▲ EC
◆ RC
■ BSE
b
Pt/Ir
3.0
2.5
2.0
1.5
1.0
c
Pd/Ir
3.0
2.0
1.0
0.0
d
Os/Ir
1.3
1.2
1.1
1.0
0.9

Figure 5a-d.

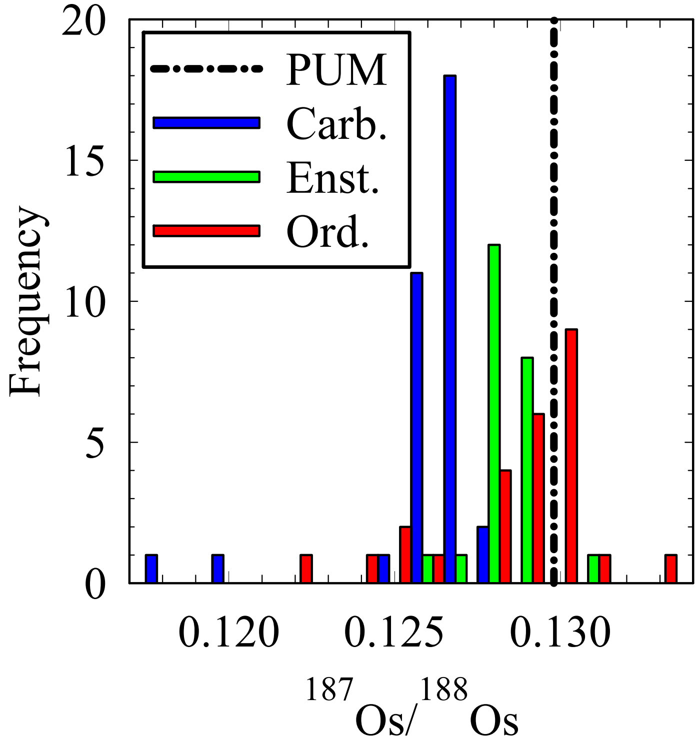

20
15
10
5
0
Frequency
PUM
Carb.
Enst.
Ord.
0.120
0.125
0.130
^{187}Os/^{188}Os

Figure 6.

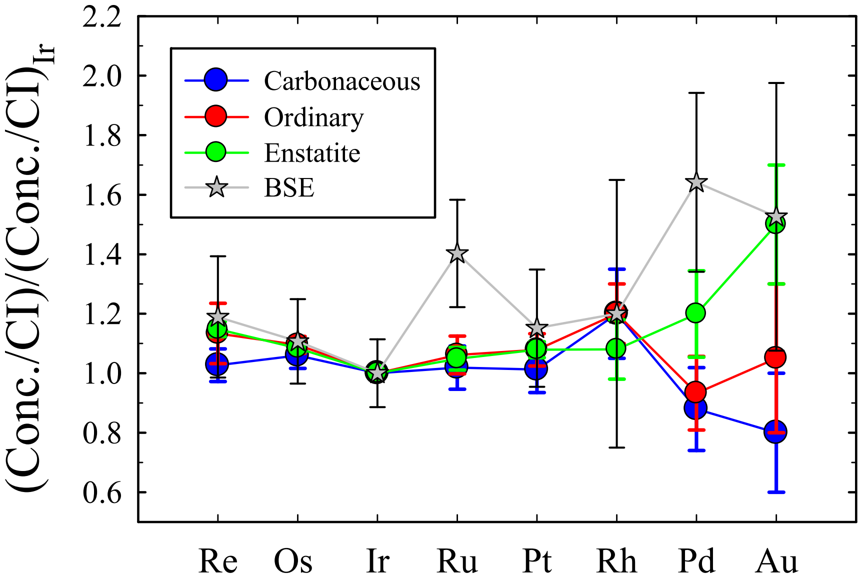
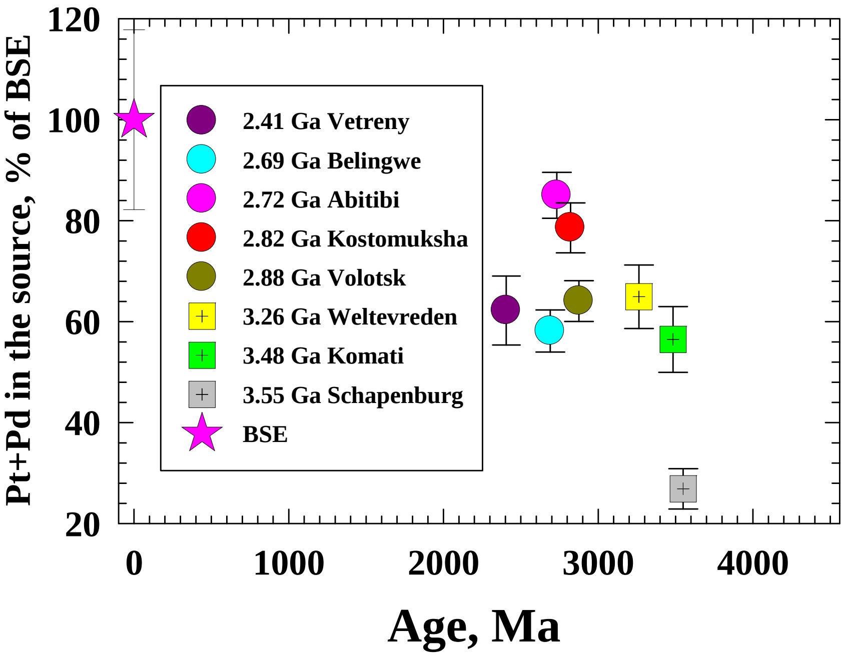

(Conc./CI)/(Conc./CI)$_{Ir}$
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
Carbonaceous
Ordinary
Enstatite
BSE
Re
Os
Ir
Ru
Pt
Rh
Pd
Au

Figure 7.



Pt+Pd in the source, % of BSE
120
100
80
60
40
20
0
1000
2000
3000
4000
Age, Ma
2.41 Ga Vetreny
2.69 Ga Belingwe
2.72 Ga Abitibi
2.82 Ga Kostomuksha
2.88 Ga Volotsk
3.26 Ga Weltevreden
3.48 Ga Komati
3.55 Ga Schapenburg
BSE

Figure 8.

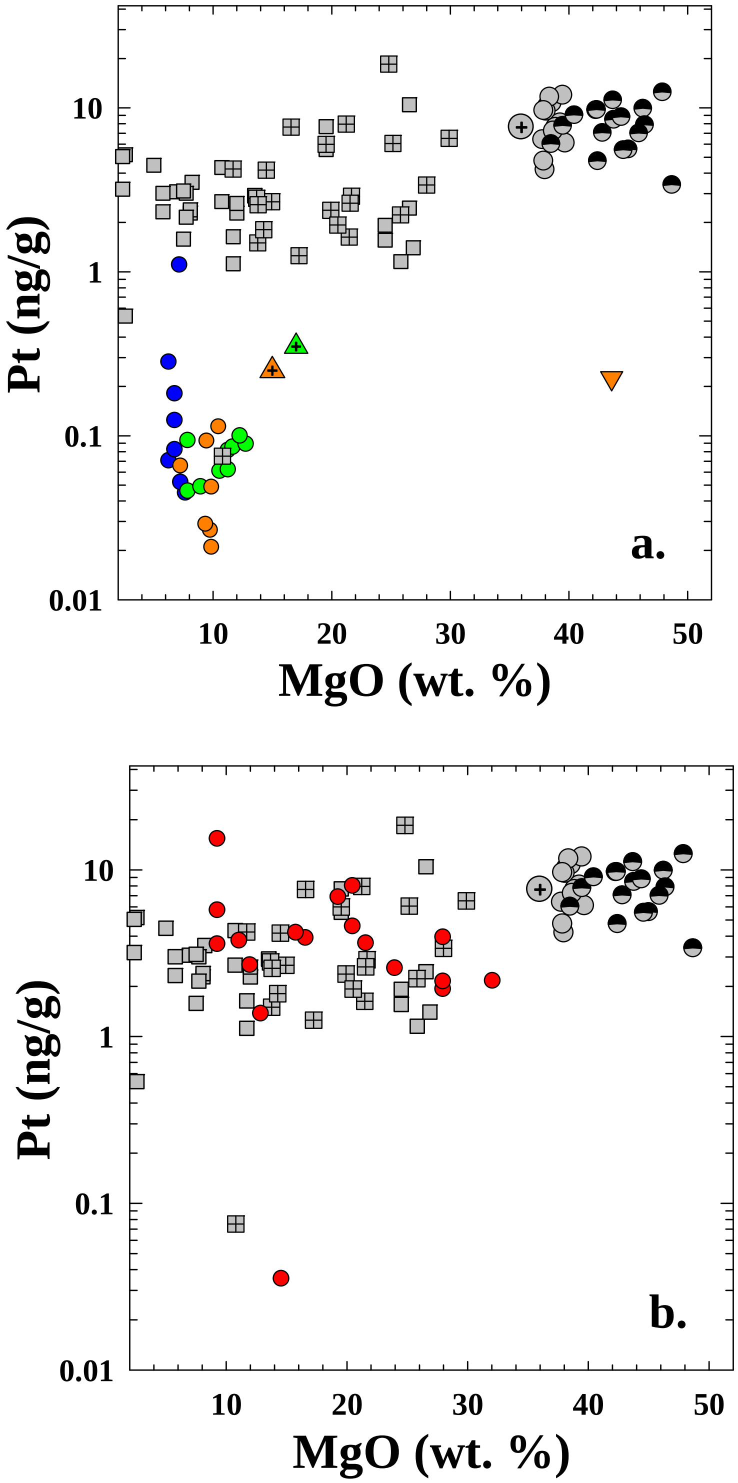

Pt (ng/g)
10
1
0.1
0.01
10
20
30
40
50
MgO (wt. %)
a.
Pt (ng/g)
10
1
0.1
0.01
10
20
30
40
50
MgO (wt. %)
b.

Figure 9a-b.

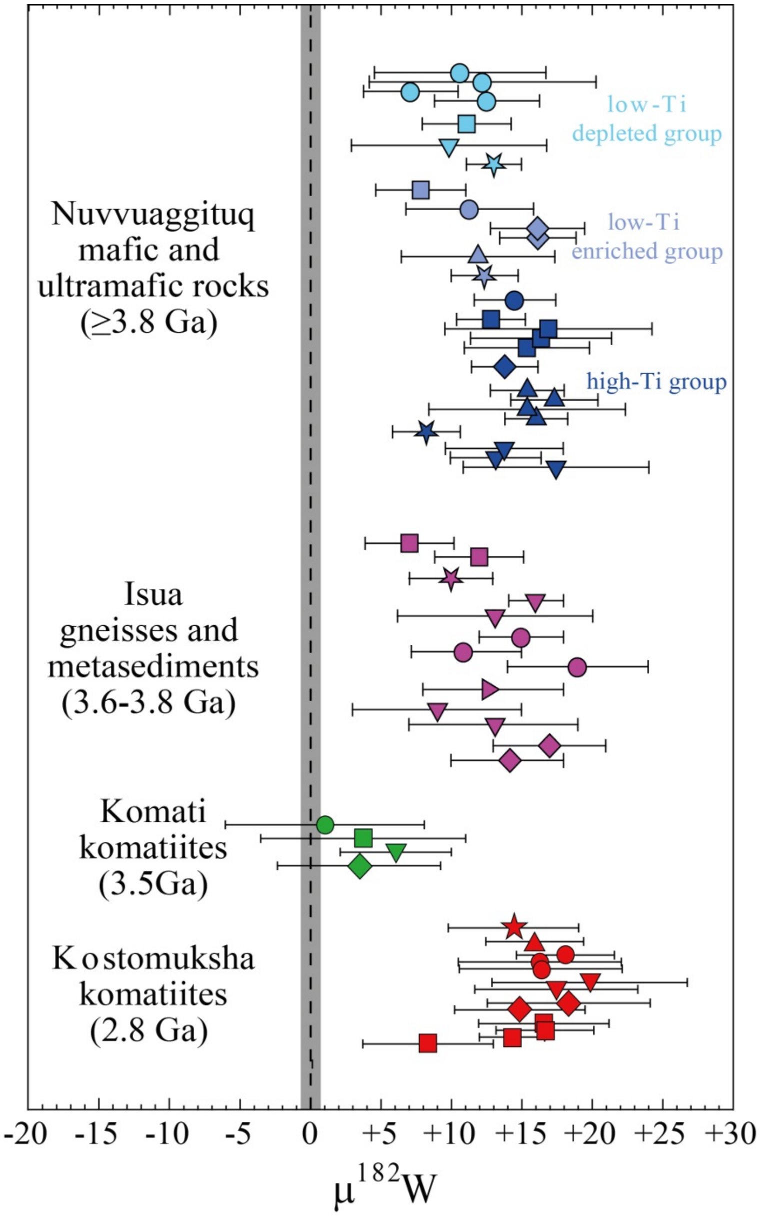

low-Ti
depleted group
low-Ti
enriched group
high-Ti group
Nuvvuaggituq
mafic and
ultramafic rocks
(≥3.8 Ga)
Isua
gneisses and
metasediments
(3.6-3.8 Ga)
Komati
komatiites
(3.5Ga)
Kostomuksha
komatiites
(2.8 Ga)
-20
-15
-10
-5
0
+5
+10
+15
+20
+25
+30
μ182W

Figure 10.

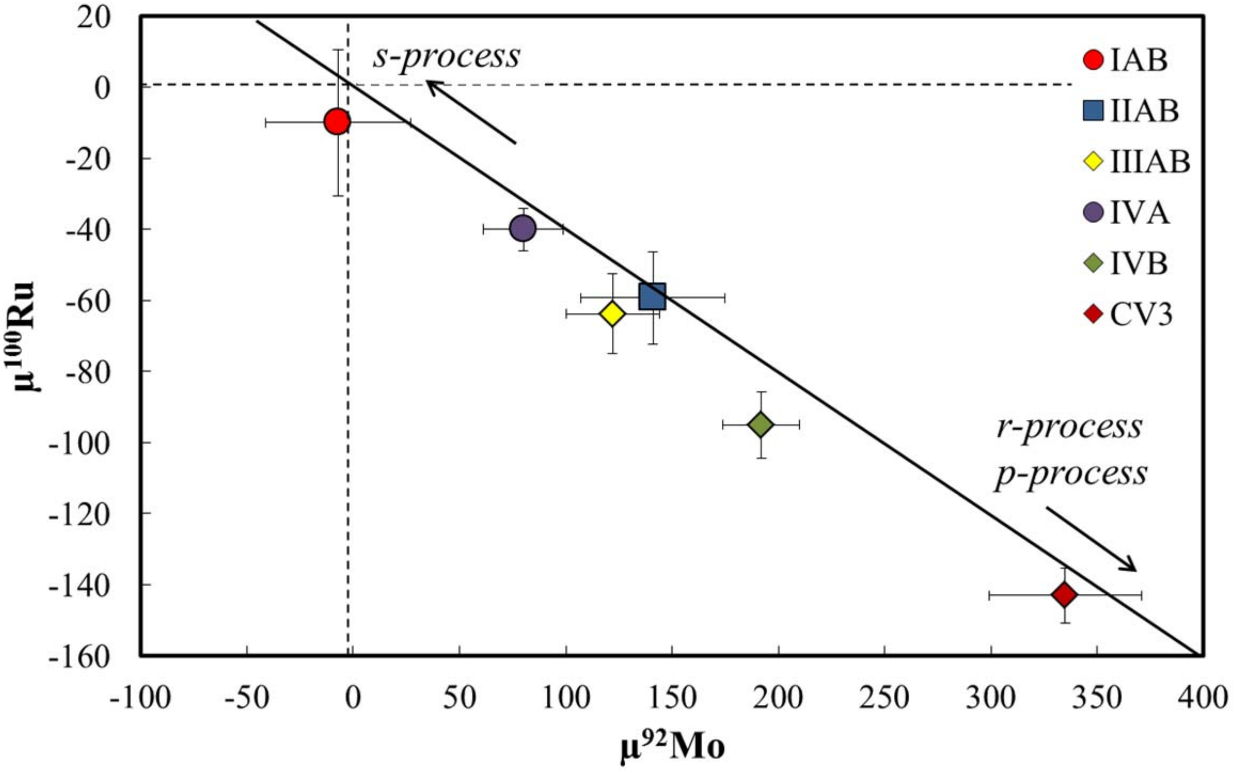

s-process
r-process
p-process
● IAB
■ IIAB
◆ IIIAB
● IVA
◆ IVB
◆ CV3
μ^{100}Ru
μ^{92}Mo
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-100
-50
0
50
100
150
200
250
300
350
400

Figure 11.

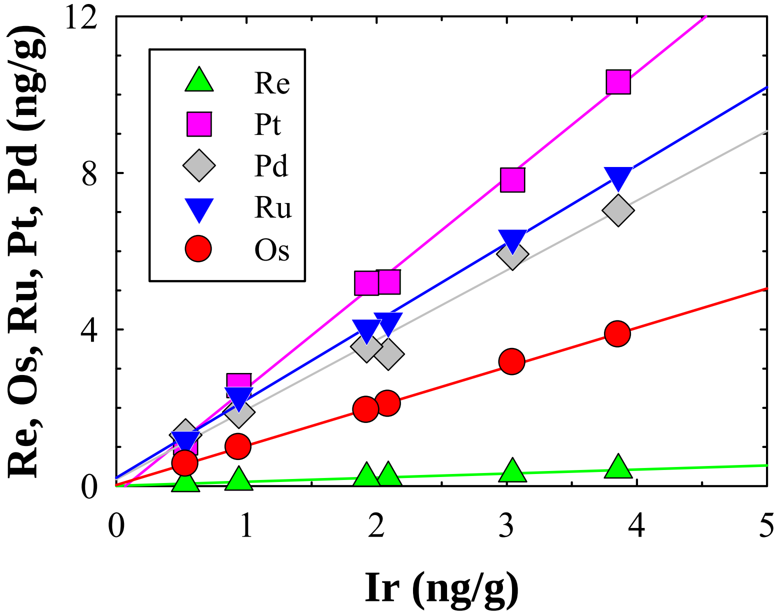


Figure 12.

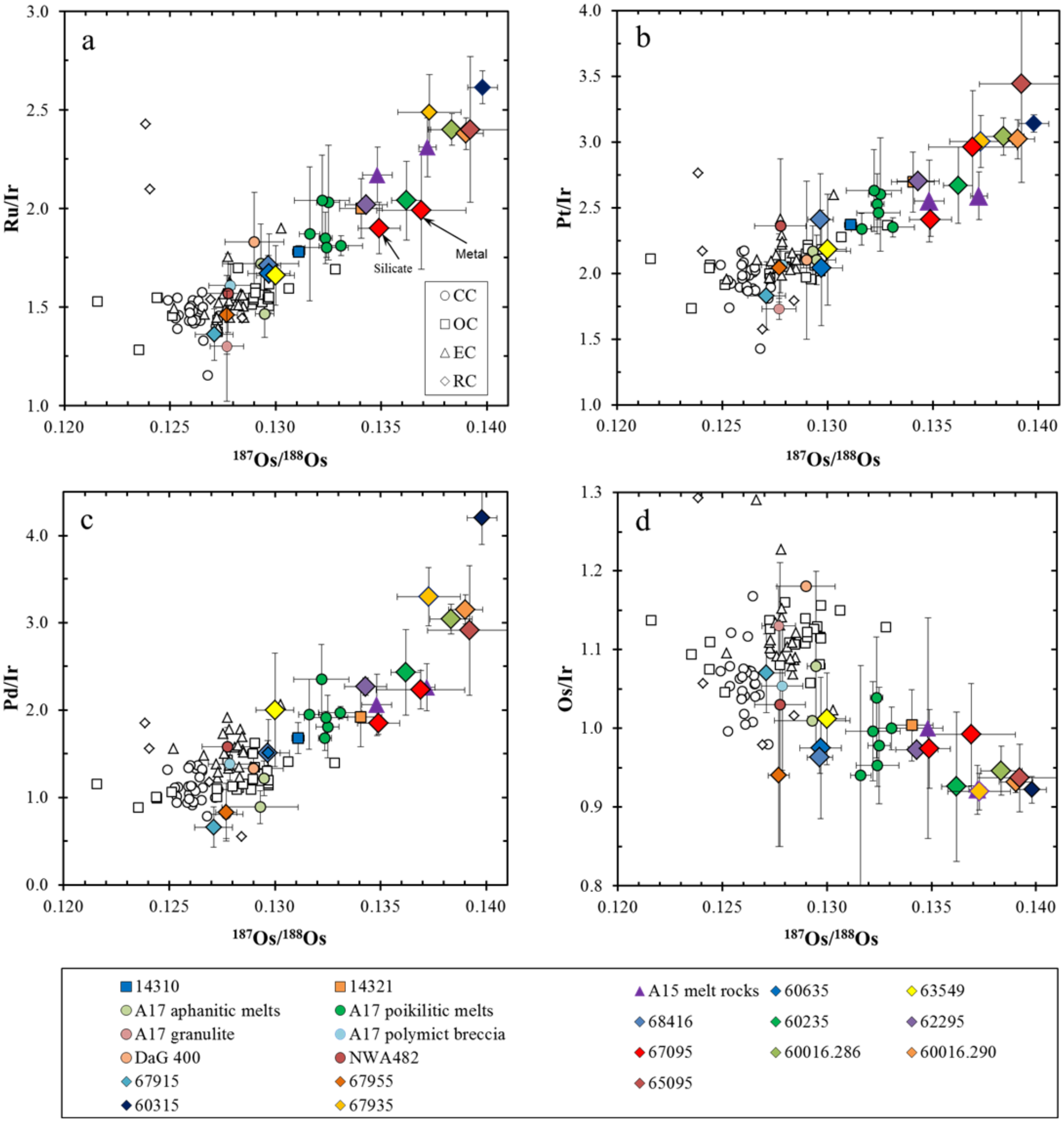

a
Ru/Ir
3.0
2.5
2.0
1.5
1.0
Silicate
Metal
○ CC
□ OC
△ EC
◇ RC
b
Pt/Ir
4.0
3.5
3.0
2.5
2.0
1.5
1.0
c
Pd/Ir
4.0
3.0
2.0
1.0
0.0
d
Os/Ir
1.3
1.2
1.1
1.0
0.9
0.8
0.120
0.125
0.130
0.135
0.140
$^{187}Os/^{188}Os$
■ 14310
■ 14321
● A17 aphanitic melts
● A17 poikilitic melts
● A17 granulite
● A17 polymict breccia
● DaG 400
● NWA482
◆ 67915
◆ 67955
◆ 60315
◆ 67935
▲ A15 melt rocks
◆ 60635
◆ 63549
◆ 68416
◆ 60235
◆ 62295
◆ 67095
◆ 60016.286
◆ 60016.290
◆ 65095

Figure 13a-d.