

Late veneer and the origins of volatiles of Earth

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Abstract Late veneer is an important paradigm in early Earth and planetary studies. It refers to the late addition of extraterrestrial materials to the Earth's mantle after the core formation, which leads to the overabundances of highly siderophile elements in the primitive upper mantle. In this review, the origin, evolution, and expansion of the late veneer hypothesis are summarized, including some unresolved problems. I hope this review would be helpful for the new entrants to this field.

Keywords Highly siderophile elements · Late veneer · Chondrites · Primitive mantle · Core formation · Volatile elements

1 Introduction

The mechanism of Earth “acquiring” its volatiles and finally evolving into a habitable planet is a problem under hot debate. For instance, at least in the last ten years, each Goldschmidt Conference had 2–3 sessions on this topic under themes including Solar System and Planets, Core and Mantle, or Early Earth. This devotion demonstrates that the origins and evolutions of volatile elements in the Earth are a complex issue that requires efforts from multiple perspectives of analyzations of natural samples, synthetizations of materials mimicking the building blocks of Earth

and its subsequent differentiation processes, simulations of planetary accretion stages, and observations of the on-going evolution of planetary disks of other stellar systems. A result of these efforts is that the hypothesis of late veneer has been widely employed to explain the origins of certain volatile elements of Earth, to a certain extent of Mars, Moon, and even Vesta (Dale et al. 2012).

In recent years (since 2006), our understanding of late veneer and the origins of volatile elements has been substantially improved. For instance, isotope dilution was widely used to obtain high precision data of element abundances (Becker et al. 2006; Wang and Becker 2013), mantle peridotites older than 3.5 Ga were carefully investigated (van de Löcht et al. 2018), nucleosynthetic anomalies have provided powerful evidence for tracing the origins of certain elements of Earth (Fischer-Gödde et al. 2020; Fischer-Gödde and Kleine 2017), magmatic dynamics were found to be able to amplify mass-dependent isotope fractionations to nucleosynthetic anomalies-like signatures (Zhang and Liu 2020), first-principles molecule dynamics were used to calculate the equilibrium isotope fractionation factors and element partition coefficients during extreme conditions such as core formation (Li et al. 2020; Wang et al. 2021a), etc. However, updated reviews on the late veneer and origins of volatile elements are still missing.

In this review, the themes are arranged roughly in the following order: the definitions of several confusing terms relating to the “last days” of Earth's growth, progress on the core arguments of late veneer, studies related to the origins of volatile elements of Earth, and finally some perspectives on the late veneer paradigm. I hope this review is useful, especially to the entrants to this field.

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2 Late heavy bombardment, late veneer, and late accretion

The most prevailing model of planet formation is called the Planetesimal Theory, which suggests that the planets formed in a disk-shaped protoplanetary nebula by accretion of small solids caused by electrostatic forces, gravity, and gravitational collapse of parts of the disk to form giant planets (Safronov 1969). Recent progress from astronomical observations of ultraviolet through near-infrared to millimeter wavelengths (Benisty et al. 2021; van der Marel et al., 2018, 2019), cosmochemical studies on meteorites (Braukmüller et al. 2019; Norris and Wood 2017), and space missions all confirmed and at the same time have refined the Planetesimal Theory. As time elapsed (Fig. 1), the solar nebula may have dispersed in the first 10 Myr after the formation of Calcium Aluminum Inclusions (CAIs; Bouvier and Wadhwa 2010; Russell et al. 2006; Wang et al. 2017). However, the growth of terrestrial planets continues until they, for instance, have cleared their orbits, respectively. In the case of Earth, its formation is suspected

to end at 200 Myr after the formation of CAIs (Connelly et al. 2008; Manhes et al. 1980; Patterson 1956). Although subsequent additions of meteorites, including the late heavy bombardment on the Moon and the late veneer on Earth, are not considered to have protracted the segregation of metal from silicates, these late accretion events may have greatly altered the environments and morphology of terrestrial bodies (Abramov and Mojzsis 2009; Bottke and Norman 2017; Cockell 2006). However, the three terms—late heavy bombardments, late veneer, and late accretion—are easily confused even in professional studies. Therefore, it is necessary to retrospect the evidence that was used to support these terms and thus understand the distinctions among them.

2.1 Late heavy bombardment

In 1949, Baldwin suggested that the circular structures on the surface of the Moon were produced by meteoritic bombardments (Baldwin 1949). In 1963, Beals and his colleagues recognized several meteoritic craters in the

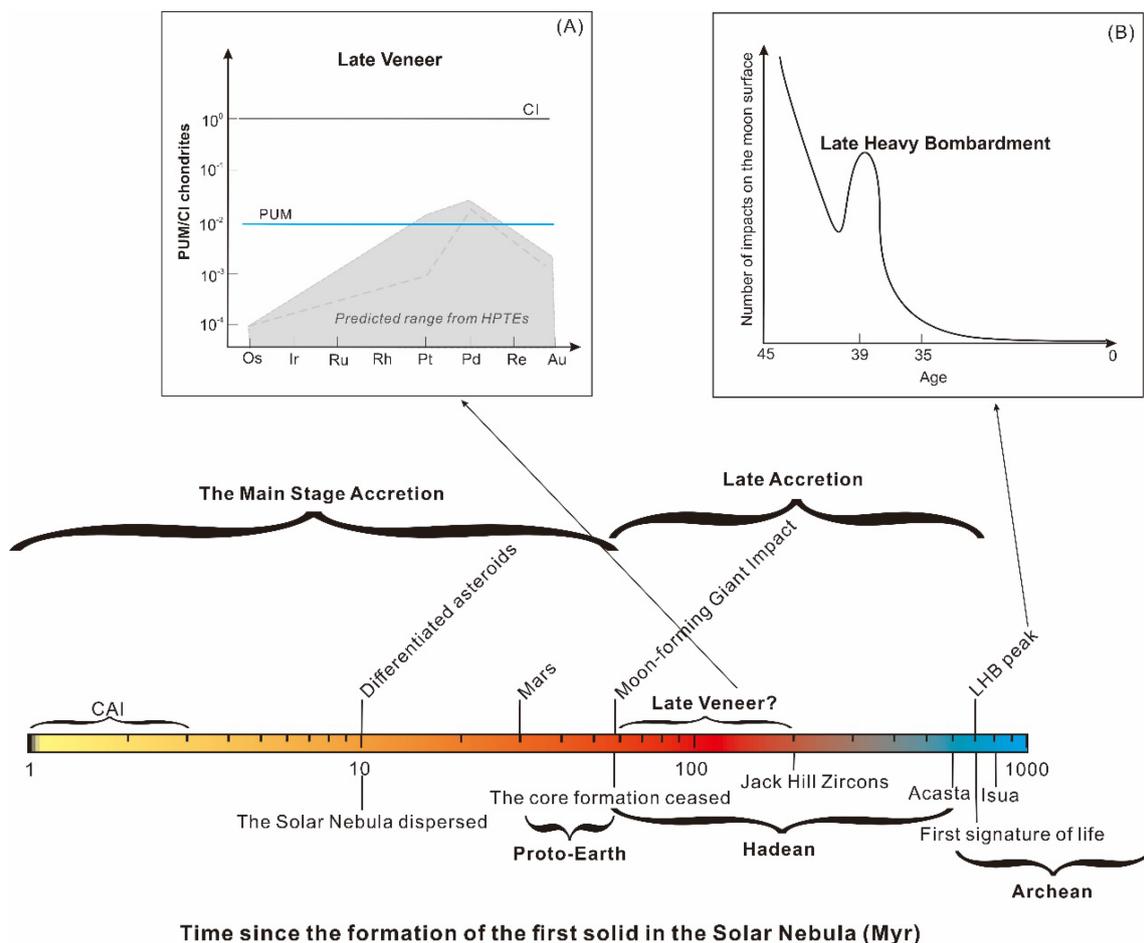


Fig. 1 Simplified illustration of the early Earth. The HSEs patterns of the PUM and CI are simplified to show the magnitude differences between chondrites, the PUM, and the predicted range from HPTEs

Canadian Craton (Beals et al. 1963). Such a direct observation led the community to accept the meteorite bombardments as a ubiquitous and important process in the Solar System. In 1965, Hartman proposed that the majority of craters on the Moon was formed before 3.6 Ga based on size-frequency distributions of craters (Hartmann 1965). He proposed “Early Intensive Cratering” as the name for this process. With the Apollo Program, the Wasserburg-Tera-Papannastassiou group published the first studies on the Rb–Sr and U–Pb ages of the craters on the Moon, demonstrating that at 3.95 Ga the Moon underwent an intensive meteoritic bombarding stage (Tera et al. 1974a, b, 1973). They named it Terminal Cataclysm. At the same time, another Ar–Ar dating study suggested the interval of the intensive cratering stage is between 3.88 and 4.0 Ga (Turner and Cadogan 1975). Wetherill (1975) first used Late Heavy Bombardment (LHB) to describe the event and pointed out that it refers to the same event as Terminal Cataclysm. The community of lunar researchers finally adopted LHB as the most used name. Although people have long been suspected that Earth also underwent such an intensive cratering stage, it is clear that LHB is a term based on radiometric dating of Apollo mission returned lunar samples and is not directly related to Earth.

2.2 Late veneer

Gottfried et al. (1972), Gottfried and Greenland (1972) and Laul et al. (1972) reported the abundances of Au and Ir in the oceanic and continental basalts. In 1974, scientists realized that the contents of some of the highly siderophile elements (Re, Os, Ir, Ru, Rh, Pt, Pd and Au; HSEs; The classification of elements are in Fig. 2) are much higher than the predictions from metal-silicate partition coefficients of these elements by High Temperature and Pressure Experiments (HTPEs; Kimura et al. 1974; Mao 1974). Chen-Lin Chou (1978) reported the first concurrent measurement of the abundances of HSEs in oceanic basalts and confirmed earlier discoveries. More importantly, Chou realized that the relative abundances of HSEs in the primitive upper mantle (PUM) are in the range of chondrites. Based on the two pieces of evidence—overabundances of HSEs and near-chondritic relative abundances of HSEs, Chou proposed that it was a late addition event that delivered chondrites to the PUM, increasing the HSEs in the PUM to a level of 200 times higher than the suggestions from HTPEs. Chou estimated the addition of carbonaceous chondrites of $1.0 \pm 0.4\%$. He and his colleagues refined this value to be $0.74 \pm 0.07\%$ of the Earth’s mass (M_{\oplus} ; Chou et al. 1983). At that time, the LHB was widely known to have added meteorites to the Moon, therefore Chou used LHB to explain the characterization of HSEs in the PUM. The reason for substituting LHB with late veneer lately in

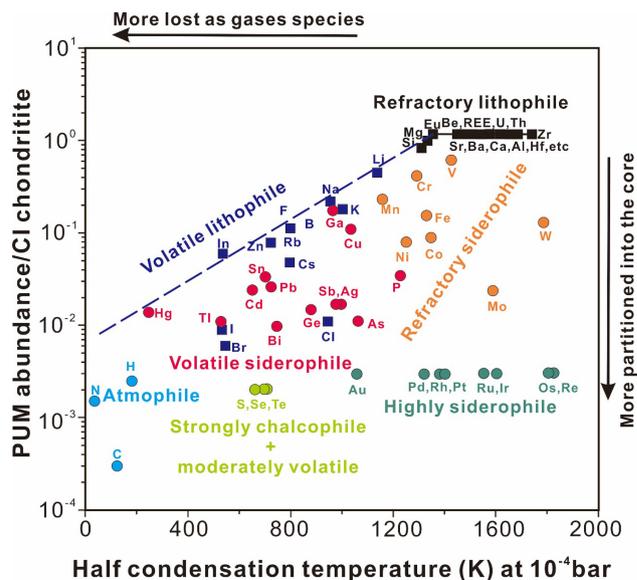


Fig. 2 The classification of elements based on half condensation temperature and metal-sulfide-silicate partition coefficients. Modified from Lodders (2003) and Wood et al. (2019)

the community studying the HSEs and related issues in the PUM was probably that the two terms were built on different foundations.

As emphasized in the last section, LHB describes a lunar event defined by radiometric dating, whereas the overabundances of HSEs and near-chondritic relative abundances of HSEs in the PUM is purely a phenomenon of Earth and have little to do with isotope geochronology. Therefore, late veneer was proposed to refer to the two characterizations of HSEs in the PUM. The reason for using “veneer” is that the abundances of HSEs in mantle-derived samples from different locations of Earth are rather homogeneous, it was suspected that the meteorites should have been evenly distributed as a thin layer on the entire surface of Earth (imagine it as spreading black peppers on your spaghetti; O’Neill 1991).

2.3 Late accretion

The growth of terrestrial planets is believed to begin from the sticking of dust and gases in the solar nebulae and continue to the collision, merging, and homogenization of planetesimals and planetary embryos (Chambers 2014). For the Earth, the last planetary collision is the Moon-forming Giant Impact. In the community of modeling planetary growth, the dynamical stage of Earth growing from 90% (just including the Moon-forming Giant Impact) of its final mass is called Late Accretion. Different of late veneer defined in geochemical factors from the Earth rocks and LHB from isotope geochronology considerations of Apollo samples, late accretion is used in numerical and

modeling communities (Morbidelli and Wood 2015), which requires data such as obtained from late veneer and LHB. Therefore, the results of late veneer and LHB could be input parameters in the late accretion modeling, whereas the results of late accretion modeling may not be direct constraints on late veneer and late accretion.

Therefore, it should be noted that the three terms are defined with “late”, but it refers to distinct scenarios: the LATE in LHB means after the solidification of the lunar magma ocean, the LATE in late veneer refers to the time after the terrestrial core formation, whereas the LATE in late accretion roughly defines the accretion stages after Earth growing to 90% of its final mass.

3 The two pillars of late veneer hypothesis

As mentioned above, the hypothesis of late veneer is supported by two pillars: (1) the abundances of HSEs in the PUM, and (2) the metal-silicate partition coefficients of HSEs during the terrestrial core formation. Although later studies support late veneer from other perspectives, the two footstones are indispensable. Therefore, in this section, some details regarding the two aspects are provided, while the supports from other insights are included in Sect. 4.

3.1 Early supports from oceanic basalts

As written in Sect. 2.2, the early studies tried to constrain the abundances of HSEs in the PUM by using oceanic basalts. There are two reasons. (1) Basalts could be viewed as simple partial melts of the mantle peridotites, as the silicate portion of Earth at that time had already been known roughly had a peridotite-like or pyrolite-like chemical composition (Ringwood 1966; Jagoutz et al. 1979). Therefore, the chemical compositions of basalts to some extent could stand for the chemical composition of the BSE or PUM. (2) Acquiring precise trace element abundances such as HSEs was a difficult issue. The detection limits of the mass spectrometer and the application of isotope dilution methods were not well prepared for resolving subtle differences, which were latterly recognized by e.g., Becker et al. (2006). For incompatible trace elements, they are enriched in partial melts (represented by basalts) relative to the parental peridotites. Therefore, in the 1980s and 1990s the trace element abundances measured from basalts were easier to be obtained and more reliable to use than those directly measured from mantle peridotites (e.g., Hofmann and White 1983). Although the origins and evolutions of oceanic basalts are eventually much more complex, Chou presented a great start. As mentioned in Sect. 2.2, Chou used LHB to refer to the addition of carbonaceous chondrites in the Earth’s mantle.

However, the two footstones of late veneer were well established: the absolute and relative abundances of HSEs in the Earth’s mantle, and the partition coefficients of HSEs during core-mantle differentiation.

3.2 High precision HSE abundances from mantle peridotites

It is known that basalts as partial melts of the mantle that ascends from the deep mantle to the surface, which eventually solidify into rocks after fractional crystallization and/or mixing with other materials including wall-rocks or recycled surface substances. For the relatively incompatible Pt and Pd, fractional crystallization of HSE-bearing phases and contamination from heterologous materials will modify the signatures of HSEs in the resultant basalts (Gannoun et al. 2016). These complexities make the basalts not suitable samples to derive the abundances of HSE in the PUM. Based on the HSEs abundances determined by isotope dilution-field sector-ICP-MS from 50 mantle peridotites of diverse tectonic settings, Becker et al. (2006) reported, up to date, the most precise and best estimates of HSEs abundances in the PUM (to a certain sense the whole mantle). Because this work made several important progresses of late veneer, it is necessary to retell the methodology in Becker et al. (2006). This might be helpful for new entrants to understand several disputes that were caused by the application of the methodology to other elements.

First of all, the contents of Al_2O_3 in mantle peridotites are used as the lithophile melt extraction indicator (Aluminum is an incompatible element during melt extraction from peridotites). (2) It was found that the contents of Ir in the studied peridotites, including both fertile and depleted peridotites, keep invariant with changes of Al_2O_3 . The most straightforward conclusion is that the contents of Ir in the mantle peridotites are not influenced by melt extraction, and thus the average Ir content (3.5 ± 0.4 ng/g, 1σ) of the investigated rocks can represent the value of PUM. (3) Becker et al. (2006) noticed that Os/Ir and Ru/Ir ratios of the mantle peridotites are constants (1.12 ± 0.09 , 1σ ; 2.03 ± 0.12 , 1σ) with increasing Al_2O_3 contents, then they calculated the Os (3.9 ± 0.5 ng/g; 1σ) and Ru (7.0 ± 0.9 ng/g; 1σ) contents of the PUM. (4) Different from Os, Ir, and Ru which are compatible during partial melting, Pt and Pd are enriched in partial melts. Becker et al. (2006) found that Pt/Ir and Pd/Ir ratios display a positive linear relationship with Al_2O_3 , and calculated the abundances of Pt and Pd in the PUM to be 7.6 ± 1.3 and 7.1 ± 1.3 ng/g, respectively, at $\text{Al}_2\text{O}_3 = 4.3$ wt. % (the Al_2O_3 content of the PUM). (5) The abundance of Re in the PUM was calculated from a different approach because Re-Os is a radio-decay system. Becker et al. (2006) used the

$^{187}\text{Os}/^{188}\text{Os}_{\text{PUM}} = 0.1296 \pm 0.0008$ and $^{187}\text{Re}/^{188}\text{Os}_{\text{PUM}} = 0.435 \pm 0.0010$ (1σ ; Meisel et al. 1996) to calculate that the Re content of the PUM is 0.35 ± 0.06 ng/g (1σ). Through the above five steps, Becker et al. (2006) obtained the reliable estimates of the HSEs abundances of the PUM and thus presented a detailed discussion on the origins of HSEs in the Earth's mantle by comparing with HSEs abundances of chondrites as well as the signatures of HSEs of the lunar mantle.

It should be noted that there were still two HSEs, Rh and Au, not included in Becker et al. (2006): Rh and Au have no isotope, therefore the isotope dilution method cannot be applied. This issue was lately solved by Fischer-Gödde et al. (2011). Fischer-Gödde et al. (2011) used the Rh/Ir ratio (0.34 ± 0.03 , 1σ) and obtained the Rh content of the PUM of 1.2 ± 0.2 ng/g (1σ). The positive linear correlation between Au/Ir and Al_2O_3 and the positive linear correlation between Au and Re were used to calculate the Au content of PUM to be 1.7 ± 0.5 ng/g (1σ).

Besides the verification of the results of Chou (1978) and Chou et al. (1983) that the abundances of HSEs in the PUM require late additions of chondrites of $\sim 0.5\%$ Earth-mass, the first-order observation of the two studies (Becker et al. 2006; Fischer-Gödde et al. 2011) is that although the relative abundances of some HSEs are similar to certain types of chondrites, Pd/Ir and Ru/Ir are higher than all the investigated types of chondrites. This at least implies that the measured chondrites solely are not the materials that were added into the mantle and thus increased the HSEs abundances of the PUM.

3.3 HSEs partitioning between the core and mantle

The abundances of HSEs in the mantle are one pillar of the late veneer hypothesis, the other one is the partition coefficients of HSEs between metal and silicates ($D_{\text{HSE}}^{\text{metal/silicate}}$) at the terrestrial core formation conditions.

As mentioned in Sect. 2.2, the earlier studies checking the HSEs as well as other siderophile elements partitioning coefficients during core formation include Kimura et al. (1974) and Mao (1974). Since then, there have been essentially two leagues on the issue of whether the $D_{\text{HSE}}^{\text{metal/silicate}}$ are high enough to require late veneer to explain the abundances of HSEs in the PUM. A general difference between the two leagues is that the pros usually measured the partition coefficients of several HSEs in one investigation, whereas the cons normally measured only one or two HSEs in one study. Here I only present one of the studies supporting the late veneer hypothesis, leaving the cons in Sect. 5.2.

Mann et al. (2012) provided the partition coefficients simultaneously determined for Ir, Ru, Rh, Pt, Pd, and Re between metal and silicate over a range of 2.5–18 GPa and

2423–2773 K. They found that the $D_{\text{HSE}}^{\text{metal/silicate}}$ values decrease with increasing pressure and to a greater extent with increasing temperature. They extrapolated the $D_{\text{HSE}}^{\text{metal/silicate}}$ values obtained at ≤ 18 GPa and ≤ 2773 K and to ≥ 60 GPa and ≥ 3560 K, covering the potential range of conditions for core-mantle segregation. The extrapolated $D_{\text{HSE}}^{\text{metal/silicate}}$ values are higher than those at lower T-P conditions, but they are still insufficient to account for the HSEs abundances in the PUM if the core and mantle were equilibrated at oxygen fugacity of IW-2 \sim IW-4 (Mann et al. 2012). Even considering the uncertainties of the extrapolations, the high P-T equilibrium core formation would almost completely remove the HSEs from the mantle (Fig. 1). This means that the HSEs in the PUM need a late veneer process.

4 Recent progress

The progress here is referred to those obtained under the acceptance of late veneer as the explanation of the over-abundances of HSEs in the PUM. The results which are not in favor of late veneer will be presented in Sect. 5.

If one accepts late veneer, a series of questions arise, including which kinds of chondrites they are, in which fashion they got the surface of Earth, how much chondrites were added, when these added materials were homogenized in the mantle, what the influences of late veneer on other elements. In this section, I will present some important achievements in the last decades.

4.1 What extraterrestrial materials were added?

Meisel et al. (1996) extrapolated a PUM value of $^{187}\text{Os}/^{188}\text{Os}$ of 0.1290 ± 0.0009 (1σ) from the correlation between $^{187}\text{Os}/^{188}\text{Os}$ and Al_2O_3 of variably melt-extracted mantle peridotite xenoliths. The Os isotope composition of PUM is similar to those of enstatite or ordinary chondrites (0.1286 ± 0.0010), but distinct from carbonaceous chondrites (0.1258 ± 0.0005). Therefore, they suggested that the majority of chondrites added during late veneer could be enstatite or ordinary chondrites, or a mixture of the two types.

Becker et al. (2006) and Fischer-Gödde et al. (2011) found that although the PUM has Os/Ir, Pt/Ir, Au/Ir, and Rh/Ir ratios in the range of chondrites, including enstatite chondrites, the Ru/Ir and Pd/Ir ratios of the PUM are remarkably higher than any reported chondrites. They suggested that the materials added by late veneer are not in the current collection of chondrites.

Fischer-Gödde caught a key point that the suprachondritic Ru/Ir ratio of the PUM. Fischer-Gödde and Kleine (2017) found that the $\epsilon^{100}\text{Ru}$ value (the parts per 10,000

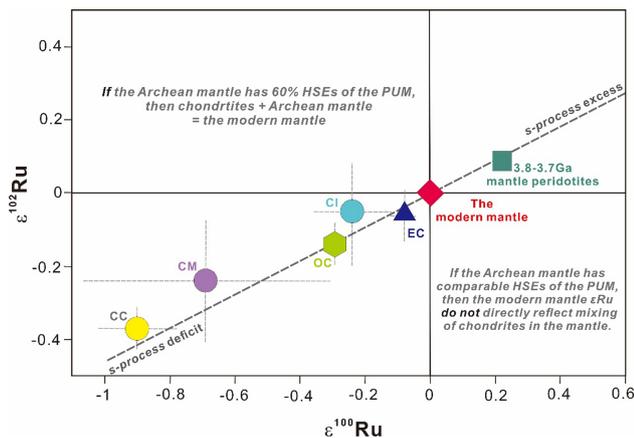


Fig. 3 The Ru isotope anomalies reported by Fischer-Gödde et al. (2017 and 2020). Modified from Fischer-Gödde et al. (2020)

deviation of the $^{100}\text{Ru}/^{101}\text{Ru}$ ratio from the terrestrial standard value) of modern terrestrial rocks ($\epsilon^{100}\text{Ru} = 0$) are much higher than those of carbonaceous chondrites ($\epsilon^{100}\text{Ru} = -0.9 \pm 0.6$, 2σ), enstatite chondrites ($\epsilon^{100}\text{Ru} = -0.08 \pm 0.04$, 95% confidence interval) and ordinary chondrites ($\epsilon^{100}\text{Ru} = -0.29 \pm 0.03$, 95% confidence interval). Since the effects of mass-dependent isotope fractionation were corrected, the higher $\epsilon^{100}\text{Ru}$ value of Earth represents the enrichments of s-process in the materials added by the late veneer. These materials are distinct from the investigated chondrites. This conclusion is essentially the same as Becker et al. (2006) and Fischer-Gödde et al. (2011). However, Fischer-Gödde et al. (2020) discovered that the 3.8–3.7 Ga mantle peridotites (the reason why Archean mantle rocks are important is given in Sect. 4.4) from various localities of the Itsaq Gneiss complex in southwest Greenland have $\epsilon^{100}\text{Ru}$ values of $+0.22 \pm 0.04$ (95% confidence interval). Taking the PUM with $\epsilon^{100}\text{Ru} = 0$ and carbonaceous chondrites with $\epsilon^{100}\text{Ru} = -0.9 \pm 0.6$ (2σ) into consideration, Fischer-Gödde et al. (2020) suggested that the majority of late veneer materials could be carbonaceous chondrite-like (Fig. 3). The reason why Fischer-Gödde et al. (2020) considered carbonaceous chondrites is provided in Sect. 4.4.

Scientists have used radiogenic isotopic systematic of Re-Os, the relative element abundances of HSEs, stable isotope compositions of HSEs (see detailed discussions in Sect. 6.2), and nucleosynthetic anomalies of Ru to constrain exactly which type of chondrites is the main one during late veneer. One should have already realized that almost all types of chondrites, even differentiated meteorites, were suggested as candidates for late veneer based on this or that piece of evidence.

4.2 How the extraterrestrial materials were added?

As explained in Sect. 2.2, late veneer was used to refer to the addition of chondrites to enhance the HSEs abundances in the mantle after the core formation since mantle rocks from different localities have essentially homogeneous HSEs abundances. It should be noted that the mass delivered by late veneer is classically estimated to be $0.5\% M_{\oplus}$, which equals roughly the current mass of the Earth's crust including continental and crustal (an equivalent planet-wide thickness of 5–20 km). Therefore, it was a reasonable assumption that the chondrites should have been evenly spread on the surface of Earth as a thin layer, and thus can they be homogenized in the mantle on the global scale.

However, the results of dynamic modeling of planetary accretion do not suggest the necessity of the “veneer” form. Bottke et al. (2010) suggests that if the late veneer was dominated by materials from the inner asteroid belt, the largest impactors can be up to 2500 to 3000 km in diameter, which may not lead to the form of veneer on the surface of Earth. Furthermore, Bottke et al. (2010) provide an explanation for the lower abundances of HSEs in the Moon and Mars relative to the PUM by employing smaller size impactors (250–300 km in diameter).

Besides Bottke et al. (2010), Genda et al. (2017) proposed that a singular, immense (~ 3000 km in diameter) impactor of chondritic compositions would also be able to explain the HSEs abundances in the PUM. Such an impactor would be in the lunar size and should have been differentiated into a metallic core and a silicate mantle. In an oblique collision, the impactor's core would be disintegrated into a metallic hail of small droplets (~ 10 m). Most of the metallic droplets would be re-accreted to Earth's mantle and thus increase the HSEs abundances. Marchi et al. (2018) discovered that planetesimal-size impacts could additionally explain both the negative and positive ^{182}W isotopic anomalies in distinct domains of Earth's mantle.

Bottke et al. (2010), Genda et al. (2017) and Marchi et al. (2018) treat late veneer as an independent event, Sleep (2016) suggests that most of the terrestrial veneer is the core of the Moon-forming impactor, Theia. Essentially, materials rich in HSEs are still needed to increase the HSEs abundances in the mantle, but such a late addition does not inevitably refer to an independent event (also see Sect. 6.1).

4.3 How many extraterrestrial materials were added?

The mass that could have been added to Earth by late veneer is generally estimated under distinct assumptions or parameters, which include $D_{\text{HSE}}^{\text{metal/silicate}}$ and the

dynamics of late veneer. (1) From the consideration of mass balance, if only chondrites were chosen as the candidates for late veneer, the amount of late veneer should be 0.09–0.5% M_{\oplus} (the geochemical estimate). (2) As suggested by Marchi et al. (2018), the late veneer mass may be 1–2.5% M_{\oplus} . (3) In the scenario of Sleep (2016), the overall materials added to the Earth would be $\sim 10\%$ M_{\oplus} . The latter two estimates can be viewed as dynamical estimates.

It should be noted that the geochemical estimates, especially those based on newly determined $D_{\text{HSE}}^{\text{metal/silicate}}$, tend to decrease the amount of late veneer (in some studies even late veneer is not required, see Sect. 5.2), whereas the dynamical estimates generally suggest a higher mass of late veneer. This discrepancy may be caused by the fact that the geochemical estimates are obtained on equilibrium core-mantle segregation scenarios of various pressure, temperature, and oxygen fugacity conditions, whereas the dynamical estimates are suggested from unequilibrated metal-silicate separations. Therefore, the geochemical estimates can be viewed as the most conservative ones, providing a base for the discussion of how much late veneer materials were added to the mantle.

4.4 When the late veneer materials were added and homogenized in the mantle?

The timing of late veneer and the survival duration of these chondritic blocks in the mantle are important parameters for constraining the thermal state of early Earth.

Based on the suggestions that the late veneer is the major contributor to the budgets of the moderate to highly volatile elements in the modern terrestrial mantle, Albarède (2009) suggested that the U–Pb chronology (half condensation temperature of Pb is ~ 725 K, a moderately volatile element), I–Xe and Pu–Xe chronology can be used to

determine the timing of Earth acquiring volatiles. It was found that the “ages of Earth” constrained by U–Pb, I–Xe, and Pu–Xe are 50–160 Ma younger than the age of the Solar System. Therefore the late veneer might have occurred at ~ 100 Ma after the collapse of the solar nebula. However, Wood et al. (2010) commented that the younger age of Pb–Pb chronology of Earth records the terrestrial core formation because Pb is a highly chalcophile and siderophile element that would be partitioned into the core. Even if the U–Pb chronology is complicated by metal-silicate segregation (marked by the Moon-forming Giant Impact), the younger ages of Earth suggested from I–Xe and Pu–Xe chronology should have not to be affected by the core formation and thus potentially represent the arrival of volatiles to Earth via late veneer. It should be mentioned here that if the younger ages (~ 100 Ma after the collapse of the solar nebula; ~ 4.4 Ga) of I–Xe and Pu–Xe are accepted to represent the timing of late veneer, it would overlap some estimates of the timing of the Moon formation.

Nevertheless, it seems that the late veneer occurred rather earlier (4.4 Ga), which poses a question of how long it took to homogenize these late added materials in the entire mantle. Maier et al. (2009) found that the Pt abundances increase from 3 ng/g in 3.5 Ga komatiites to 10 ng/g 2.9 Ga komatiites, and since 2.9 Ga on, the Pt abundances in komatiites remain invariant (Fig. 4). The Ru abundances of komatiites display the same pattern. Because komatiites are normally accepted as high-degree partial melts from the deep mantle, Maier et al. (2009) suggested that the late veneer materials should have not been homogenized in the mantle until 2.9 Ga. This suggests a rather sluggish Hadean and Archean mantle, which needs to be reconciled into the models where short-lived radiogenic isotopes, impacts, and the fast-involving core generate much more heat for the mantle of early Earth.

However, Puchtel et al. reported several studies on the abundances of HSEs and Pt–Re–Os isotopic systematics of Archean komatiites, including 2.7 Ga Belingwe komatiites, 2.7 Ga Aibitibi komatiites (Puchtel et al. 2009b), 3.5 Ga Weltevreden komatiites, 3.5 Ga Komati formation (Puchtel et al. 2013), and 3.5 Ga Schapenburg komatiites (Puchtel et al. 2009a). The essential argument of Puchtel et al. is that the abundances of HSEs in the Archean mantle changed little from 3.5 to 2.7 Ga, which means the Archean mantle has HSEs abundances similar to the PUM. Puchtel et al. did not offer a definitive explanation for the discrepancy between their work and Maier et al. (2009).

Since the issue of the HSEs abundances in the Archean mantle cannot be solved based on Archean komatiites, other types of old rocks needed to be considered. Li et al. (2014) reported the HSEs abundances of the Acasta Gneiss Complex from northwest Canada. The oldest rock of the

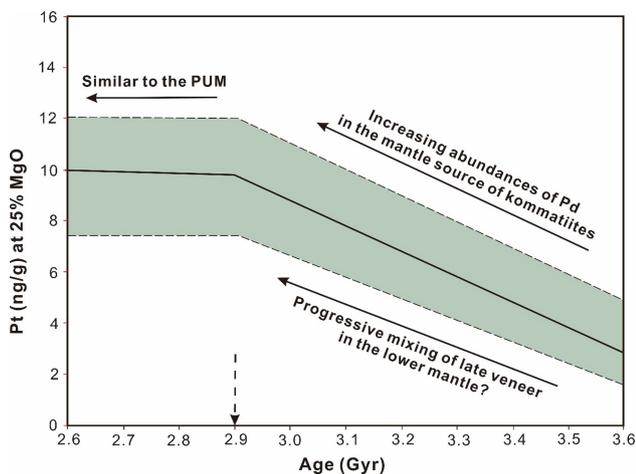


Fig. 4 The abundances of Pt calculated for the mantle source of Archean komatiites. Modified from Maier et al. (2009)

Acasta Gneiss Complex is dated as 4.2 Ga, while the majority of these crustal rocks (both felsic and mafic) are aged at 4.0–3.8 Ga (Bowring and Housh, 1995; Iizuka et al., 2006; Mojzsis et al., 2014). It was found that the HSEs abundances of the Acasta samples are similar to their post-Archean equivalents. This means at least the late veneer materials had been homogenized in the mantle of the Acasta rocks before 4.0 Ga (Li et al., 2014). van de Löcht et al. (2018) presented the HSEs abundances of 3.8 Ga mantle peridotites from the Eoarchean terrains of western Greenland (the same samples were used by Fischer-Gödde et al. (2020); picking up the issue left in Sect. 4.1). They found that the 3.8 Ga mantle peridotites show an entire record of late veneer (van de Löcht et al. 2018). Therefore, the late veneer blocks may have been homogenized in the major parts of the mantle by at least 3.8 Ga. It appears that it took ~ 0.5 Ga to homogenize the late veneer materials in the mantle, instead of ~ 1.7 Ga indicated by Maier et al. (2009). This would suggest a much more active mantle of early Earth.

Returning to the issue left in Sect. 4.1 about Fischer-Gödde et al. (2020) and van de Löcht et al. (2018) paper is titled “Earth’s oldest mantle peridotites show entire record of late accretion” and clearly states that “probably as much as 100% of late accretion component was mixed into the sampled mantle domains.” Fischer-Gödde et al. (2020) used some of the 3.8–3.7 Ga mantle peridotites and conclude that the $\epsilon^{100}\text{Ru}$ of the modern mantle could be a mixture of $\epsilon^{100}\text{Ru}$ of $\sim +0.22$ represented by the 3.8–3.7 Ga mantle peridotites and $\epsilon^{100}\text{Ru}$ of ~ -0.9 of carbonaceous chondrites by “assuming a minimum late accretion contribution of 60% for the ≥ 3.8 -Gyr-old Itsaq mantle source” and cited van de Löcht et al. (2018). If one accepts the conclusion of van de Löcht et al. (2018), the positive $\epsilon^{100}\text{Ru}$ of the 3.8–3.7 Ga mantle peridotites can be explained in the same way as Fischer-Gödde et al. (2017) that the late veneer materials in the mantle source of 3.8-Gyr-old Itsaq mantle peridotites are distinct from the current collections of chondrites. This would mean that there possibly some rocks of Earth are characterized by negative $\epsilon^{100}\text{Ru}$, which may be or may not be in the ranges of chondrites. It has occurred to ^{182}W anomalies, where both positive and negative values have been found from the terrestrial rocks (Mundl-Petermeier et al. 2020; Willbold et al. 2015).

5 Late veneer and the origins of volatiles of Earth

Expanding the connotation of late veneer to the origins of volatile elements of Earth is major progress. The connection between late veneer and origins of volatiles on Earth is established under the assumption that the Moon-forming

Giant Impact is such a violent event that causes substantial loss of volatiles in Earth and Moon. Therefore, the budgets of volatile elements in the PUM should have been brought by late additions of volatile-rich extraterrestrial materials, for instance, chondrites. Because there are a least 30 elements are categorized as volatile elements (Fig. 2) and up to 10 of them in the PUM are contributed by the late veneer. Since I am not able to dedicate all these elements, I will focus on the strongly chalcophile and moderately volatile elements (S–Se–Te) and highly volatile elements (C–N–H).

5.1 The strongly chalcophile and moderately volatile elements (S–Se–Te)

Using the same approach of Becker et al. (2006), Wang and Becker (2013) reported that the abundances of S, Se, and Te in the PUM are 200 times higher than the predictions of HPTEs, and the relative abundances of S, Se and Te are in the range of CM chondrites (a type of carbonaceous chondrites). They invoked that the budgets of the three elements in the Earth’s mantle were established by a volatile-rich late veneer (Wang and Becker, 2013). This suggestion caused controversies with Labidi et al. (2013) and König et al. (2014).

Labidi et al. (2013) determined the $\delta^{34/32}\text{S}$, Rb–Sr, and Sm–Nd isotopic systematics in Mid-Ocean Ridge Basalts (MORBs) and calculated the $\delta^{34/32}\text{S}$ of the most depleted mantle source of MORB to be ~ -1.3 ‰. This value is much lower than those of chondrites. The non-chondritic $\delta^{34/32}\text{S}$ value of the Earth’s mantle does not support the budget of S in the mantle established by late veneer, but core formation extracting heavier S isotopes into the core. Labidi et al. (2016) carried out experiments to determine the equilibrium S isotope fractionation factors between metal and silicate during the core formation conditions. The results reinforce the suggestion of Labidi et al. (2013). Recent progress provides a method of constraining the S isotope composition of bulk Earth, which suggests that the Earth’s sulfur is related to the planetesimal evaporation rather than core formation or late veneer (Wang et al. 2021a, b).

König et al. (2014) measured the abundances of S, Se, and Te in mantle peridotites and also obtained the near-chondritic S–Se–Te ratios, but they suggested that the near-chondritic S–Se–Te ratios reflect the complex history of melt depletion and re-enrichment in the mantle instead of primitive signatures of the mantle. This argument was refuted by Wang and Becker (2015), which was again replied to by König et al. (2015). Both groups admitted that the S–Se–Te ratios in the Earth’s mantle are chondritic, the discrepancy is what they should be represented. If the indication of Wang et al. (2021a, b) is considered in the

explanations of Se isotopes of Earth's mantle rocks, it could be possible that the Se isotope compositions of Earth are also related to planetesimal evaporation in the solar nebula.

Varas-Reus et al. (2019; Stephan König co-authored) reported the Se isotope compositions of mantle peridotites and found the PUM is probably characterized by carbonaceous chondrite-like Se isotope composition. This eventually leads to the conclusion that the Se budget in the PUM was a result of volatile-rich late veneer (Varas-Reus et al. 2019). The Te isotope compositions of terrestrial samples (standard solutions, sediments, and ore samples) are similar to the investigated carbonaceous chondrites (Fehr et al. 2018). The authors carefully implied that the similarity suggests a late veneer origin of Te in the Earth's mantle. It should be noted that Te isotope compositions of terrestrial magmatic rocks, for instance, mantle peridotites and MORB, have not to be determined. Te isotope compositions of basalts, komatiites, and mantle peridotites are needed to discuss the origins of Te in the terrestrial mantle.

The overall impression is that, although there is a chance of S–Se–Te in the mantle having a late veneer origin, the obvious sub-chondritic S isotope composition of the PUM suggests a much earlier process modifying the isotopes of volatile elements in the solar nebula conditions. Because Se and Te have a similar geochemical affinity of S, the two elements may be also influenced by planetesimal evaporation. However, currently, only the equilibrium S isotope fractionation factors between metal and silicate during the core formation conditions were determined, where those of Se and Te have not been investigated. Future work needs to evaluate the relative effects of volatility and core formation on the isotope of Se, Te, and other similar elements.

5.2 The highly volatile elements (C–N–H)

Carbon, nitrogen, and hydrogen have much lower half condensation temperatures than S, Se, and Te, therefore in the light of Albarède (2009), C, N, and H would be severely lost in the proto dry Earth. The current budgets of the three highly volatile elements in the mantle should have extraterrestrial contributions after the core formation.

Hirschmann (2016) summarized that the C/H ratio of the PUM is 2–15 times lower than those of chondrites, whereas the C/N ratio is superchondritic. Because carbon is the most siderophile among the three elements, the high C/N in the PUM probably reflects the addition of carbon after core formation or atmospheric blow-off of nitrogen. The sub-chondritic C/H ratio on the other hand implies an appreciable amount of H in the mantle of the Earth after the Moon-forming Giant Impact but before the late veneer. Taking the C/H and C/N ratios of the PUM together, it is certainly a combination of events are required to explain

the element ratios, including parent body processing, core formation, catastrophic atmospheric loss, and partial replenishment by a late veneer. It seems that element ratios cannot provide definitive constraints on the origins of C, N, and H in the mantle, therefore comparisons of the isotope compositions of the PUM and potential Earth-building blocks may contain crucial information.

The C isotope composition of the PUM ($\delta^{13}\text{C}_{\text{PDB}} = -5\text{‰}$) is much higher than those of chondrites ($\delta^{13}\text{C}_{\text{PDB}} \leq -15\text{‰}$; Wood et al. 2013), displaying the low chance of late veneer establishing the budget of C in the mantle. Li et al. (2021) checked the effect of sublimation on carbon during the evolution of protoplanetary disks. They found that the carbon-rich materials can move to 1 astronomical unit without much carbon sublimated. This means that the major building blocks of Earth much be depleted in the accretional processes to explain the low C content of Earth ($0.4 \pm 0.2\%$). This work eventually suggests that the C in Earth is probably not related to the late veneer. It appears that at the current collection of evidence, the carbon of Earth is not directly related to the late veneer.

The N isotope composition of the PUM ($\delta^{15}\text{N}_{\text{air}} = -5\text{‰}$) is between that of the enstatite chondrites ($\delta^{15}\text{N}_{\text{air}} = -30 \pm 10\text{‰}$), ordinary chondrites ($\delta^{15}\text{N}_{\text{air}} = 0\text{‰}$) and carbonaceous chondrites ($\delta^{15}\text{N}_{\text{air}} = +40\text{‰}$) (Li et al. 2016). Li et al. (2016) determined the metal-silicate isotope fractionation factors of N at 1.5 to 7.0 GPa and 1600 to 1800 °C. Their results suggested that the light N isotopes were more likely partitioned in the metallic core, leaving the silicate mantle with heavier $\delta^{15}\text{N}_{\text{air}}$ value and thus supporting the model that enstatite chondrites are the main building blocks of the Earth. Dalou et al. (2019) additionally explored the effects of oxygen fugacity on N isotope fractionation between metal and silicate. They found that at IW0-IW-3, the $\delta^{15}\text{N}_{\text{air}}$ of the mantle could have increased by 20 ‰ during the core formation because of the light N isotopes segregated into the core. Grewal et al. (2021) further studied the relative roles of degassing and the nature of siderophile on the N budget of Earth. They found that if the rate of differentiation (core-mantle segregation) is greater than the rate of accretion (accompanied by volatile loss of N), then a late veneer scenario would be permitted to satisfy the N budget of Earth; however, if the rate of differentiation is smaller than the rate of accretion, the Earth's nitrogen can be solely the result of accretion of planetary embryos without requiring a late veneer. Considering the evidence above, it seems that the late veneer is not needed to explain the N abundance and N isotope composition of the PUM.

The origin of water on Earth is complicated by the disputes about whether the silicate mantle represented by the PUM is the major reservoir compared to the Earth's deeper layers or portions. Li et al. (2020) used ab initio

molecular dynamics and thermodynamic integration techniques to calculate the partition coefficients of water between core and mantle. They found that the Earth's core is a major reservoir that contains most of the Earth's water. Wang et al. (2021a, b) further indicated that even the solid inner core could contain substantial amounts of hydrogen. These calculations are in good agreement with the most recent HPTEs (Tagawa et al. 2021; Yuan and Steinle-Neumann 2020). Therefore, the issue turns into whether the deep layers of Earth have similar D/H ratios to the surface materials.

Clog et al. (2012, 2013) measured the D/H ratios of basalts from the southern Pacific ridge and the Middle Atlantic Ridge and suggested that the most depleted mantle source of MORB is $\delta D = -60 \pm 5 \text{ ‰}$. However, Hallis et al. (2015) found that the olivine crystals from the Baffin Island and Icelandic lavas (mantle plume systems) have δD lower than -218 ‰ , approaching to the δD of the solar wind ($\delta D = -870 \text{ ‰}$). Therefore, the PUM may have a distinct δD compared to the deeper mantle and core. The δD of the PUM is close to those of chondrites and some comets, suggesting the contribution of extraterrestrial materials possibly by late veneer. More recent work suggests that these lower δD values in mantle-derived rocks may be a result of a multi-stage melting history of the upper mantle where minor D/H fractionation could be associated with hydrogen retention in nominally anhydrous residual minerals (Loewen et al. 2019). At present, the true meaning of the extremely low δD is not demonstrated, however, if one accepts that the proto-solar-like δD in the deep mantle may be a result of the incorporation of the solar nebula during the growth of Earth, it would imply that Earth acquired its water in the core and deep mantle in the first 10 Ma after the formation CAIs and the Moon-forming Giant Impact did not affect the D/H in the deep mantle.

In conclusion, there is a tendency that the S, Se, and Te of Earth could be related to the late veneer, whereas that a late veneer origin of Earth's C, N, and H is not supported at least by the present arguments. The reason behind this discrepancy is that studies on the origins of highly volatile C, N, and H have investigated the volatile loss during the main accretion stage and the Moon-forming Giant Impact (Grewal et al. 2019), whereas this process is less considered in the work on the origins of moderately volatile elements of Earth.

6 Unsolved issues weakening the late veneer

In Sect. 3, I presented the evidence in favor of having a late veneer; in Sect. 4, I listed four issues if there was a late veneer; and in Sect. 5, I provided a rather simple summary on the current understanding of the origins of different

volatile elements of Earth. The studies and investigations that provided evidence that does not support the late veneer as explanations of the overabundances of HSEs and other relevant elements are presented below.

6.1 Metal-silicate partitioning experiments for HSEs

As shown in Sect. 3.3, some studies reported partition coefficients of HSEs between metal and silicate supporting the late veneer hypothesis, but there are also reports providing $D_{\text{HSE}}^{\text{metal/silicate}}$ values that imply that the HSEs budgets in the mantle can be satisfied solely by the core formation.

Righter et al. (2008) suggested that the very high $D_{\text{HSE}}^{\text{metal/silicate}}$ obtained from experiments at low pressures and temperatures (for instance $D_{\text{Pd}}^{\text{metal/silicate}} > 10^4$) may be decreased at higher P–T conditions ($D_{\text{Pd}}^{\text{metal/silicate}} > \sim 480$). Together with earlier work reporting relatively low $D_{\text{Au}}^{\text{metal/silicate}}$ and $D_{\text{Pt}}^{\text{metal/silicate}}$ values at elevated pressures and temperatures (Cottrell and Walker, 2006), Righter et al. (2008) implied that no late veneer is needed to explain the abundances of at least some HSEs (for instance Pt, Pd, and Au) in the PUM. This suggestion was lately confirmed by (Brenan and McDonough 2009). More recent work found that Pt nanonuggets in silicate glass quenched in the HPTEs is a reason for the low $D_{\text{Pt}}^{\text{metal/silicate}}$ values in previous work (Médard et al. 2015). Malavergne et al. (2016) systematically studied the nanonuggets of HSEs found in the quenched glass at HPTEs and suggested that the nanonuggets formed predate the quench. HSE nuggets were present within mineral crystals and acted as nucleation sites. A new study determined the $D_{\text{Pt}}^{\text{metal/silicate}}$ using laser-heated diamond anvil cell equipment and found that $D_{\text{Pt}}^{\text{metal/silicate}}$ is rather small at $> 40 \text{ GPa}$ and 3900 K (Suer et al. 2021). This means that additional reduction processes such as sulfide segregation are required to reduce the Pt abundances in the mantle. It is unclear up to now whether the late veneer is needed to explain the Pt abundance in the PUM.

Another issue is that the core is not a pure iron metal, it contains $\sim 9\%$ light elements. The role of light elements in the core on the $D_{\text{HSE}}^{\text{metal/silicate}}$ must be evaluated. Jana and Walker (1997) did not investigate HSEs directly, but they found that the carbon in the metal would decrease $D_{\text{metal/silicate}}$ for the moderate siderophile elements. Rubie et al. (2016) found the pure metal-silicate equilibration at the core formation conditions would increase the HSEs abundances in the mantle. Therefore, a subsequent step called Hadean matte (iron sulfide segregation from silicate mantle) is needed to strip the magma oceans of HSEs before late veneer. These two studies leave us in a difficult situation: the core has carbon and sulfur, but it is uncertain

how much of each of the two is in the core respectively. Therefore, it is not clear how the HSEs behave in the true core formation scenario if the light elements exert opposite roles on $D_{\text{HSE}}^{\text{metal/silicate}}$. Besides, another point causing uncertainties in the Hadean Matte hypothesis: sulfur is a highly siderophile element that would be segregated into the core completely during the pure metal-silicate segregation, leading to a sulfur-poor mantle and thus inhibiting the formation of an independent iron sulfide phase being segregated from the mantle to the core.

Besides the HSEs, there are also disputes on the metal-silicate partition coefficients of S, Se, and Te at the core formation conditions. Rose-Weston et al. (2009) found that the three elements are highly siderophile and the abundances of the three elements in the PUM require the late addition of volatile-rich chondrites. Boujibar et al. (2014), however, reported that the $D_{\text{S}}^{\text{metal/silicate}}$ is not so high as Rose-Weston et al. (2009) and the budget of S in the mantle can be explained by core-mantle differentiation. Brennan (2015) reported sulfide-silicate partition coefficients of Se and Te and suggested a late veneer origin of the two elements in the mantle.

From the perspectives of HPTEs, there is much to be investigated, such as multiple light elements in the metal, achieving metal-silicate equilibration in laser-heated diamond anvil cell experiments, as well as the nanonugget effect, to obtain definitive answers on the $D_{\text{HSE}}^{\text{metal/silicate}}$ at the core formation conditions. Other approaches, for instance, ab initio molecular dynamics and thermodynamic integration techniques, may be useful in future studies.

6.2 Effects of the core formation on stable isotopes of HSEs

It is straightforward that if the HSEs budgets in the mantle are established by late veneer, the stable isotope compositions of HSEs of mantle rocks should be chondrite-like. The results are presented in Fig. 5.

Creech et al. (2016) found that the $\delta^{198}\text{Pt}/^{194}\text{Pt}$ of post-Archean mantle peridotites are in the range of chondrites ($\delta^{198}\text{Pt} = -0.14 \pm 0.03 \text{ ‰}$, 2σ), whereas the Archean mantle samples record superchondritic $\delta^{198}\text{Pt}/^{194}\text{Pt}$ values ($\delta^{198}\text{Pt}$ up to $+0.4 \text{ ‰}$, 2σ ; Fig. 5C). Creech et al. (2016) suggested that the super-chondritic $\delta^{198}\text{Pt}/^{194}\text{Pt}$ values represent the mantle domain without receiving the late veneer materials. However, in Creech et al. (2017) the $\delta^{106}\text{Pd}/^{105}\text{Pd}$ isotope compositions of both Archean and post-Archean mantle peridotites are in the range of chondrites ($\delta^{106}\text{Pd} = -0.19 \pm 0.05 \text{ ‰}$, 2σ ; Fig. 5B). It should be mentioned here that the Archean samples investigated in the two studies are the same suite. This is also in contrast to the fact that the Pd/Ir ratio of the PUM is super-chondritic, whereas the Pt/Ir ratio is chondritic (Becker et al. 2006).

Hopp and Kleine (2018) reported that the mass-dependent Ru isotopes of mantle peridotites and chondrites are in the same range (Fig. 5A).

It should be noted that the equilibrium isotope fractionation factors of Ru, Pt, and Pd between metal and silicate at the core formation conditions ($\Delta^{102}\text{Ru}^{\text{metal-silicate}}$, $\Delta^{198}\text{Pt}^{\text{metal-silicate}}$, and $\Delta^{106}\text{Pd}^{\text{metal-silicate}}$) have been determined neither by HPTEs nor first principles calculations. Therefore, future work is required to obtain these values, and the nuclear volume effect on these stable isotopes should also be considered.

6.3 The cloud on the nucleosynthesis

Nucleosynthetic anomalies are free of the influences of processes, including mass-dependent and mass-independent, and serve as the best constraints on the origins of materials. Nucleosynthetic anomalies are common in heavy elements because that the formation of their isotopes is disproportionately related to the s-process, r-process, and p-process. As shown in Sects. 4.1 and 4.4, nucleosynthetic anomalies were used to reveal the origins of HSEs in the PUM as well as (possibly) the mixing history of the late veneer materials in the Hadean and Archean mantle.

Based on the nuclear field shift effect, however, Zhang and Liu (2020) produced some of the ppm-level ^{182}W anomalies (both positive and negative) in Archean and modern mantle-derived rocks using a multistage close-system melting and crystallization evolution model, combined with ab-initio calculations and Monte Carlo simulations. This work demonstrates that the accumulative effect of mass-dependent isotope fractionation at the mantle temperatures can be amplified into isotope anomalies. This work implies that some of the isotope anomalies (including nucleosynthesis) of heavy elements could be a product of complex mantle evolution history and cannot be directly used to constrain the origins of elements in the mantle. It is necessary to evaluate the effects reported by Zhang and Liu (2020) on the Ru and other isotope anomalies.

7 Conclusion and perspective

In this review, the most important points of late veneer have been checked. There are much more studies on this topic, but it is impossible and not necessary to include all the literature in this review. The review will be ended here by listing the most reliable observations and the unresolved problems, respectively.

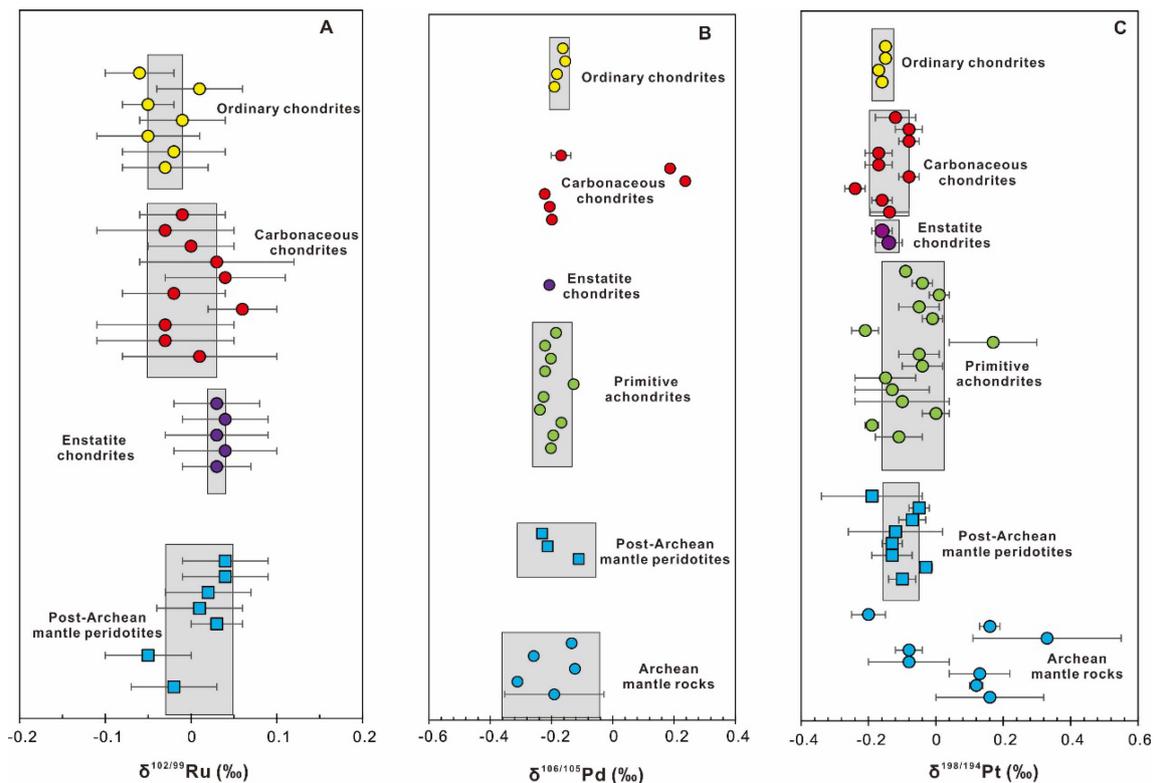


Fig. 5 Stable isotopes of Ru, Pd, and Pt in terrestrial and meteoritic materials. Data are from Creech et al. (2016, 2017) and Hopp and Kleine (2018)

7.1 The most reliable observation

(1) The abundances of HSEs in the primitive upper mantle have been precisely determined by Becker et al. (2006). (2) The nucleosynthetic anomalies of Ru in the Archean mantle, the present mantle, and the chondrites are measured (Fischer-Gödde et al. 2020; Fischer-Gödde and Kleine 2017). (3) Light elements and more extreme conditions have been taken into consideration in HPTEs in addition to pure iron metal-silicate core formation scenarios (Rubie et al. 2016; Suer et al. 2021). (4) The stable isotope compositions of HSEs in terrestrial rocks and chondrites have been reported (Creech et al. 2016, 2017; Hopp and Kleine 2018). (5) Increasing studies about the effects of the Moon-forming Giant Impact on origins of volatiles in the Earth (e.g., Grewal et al. 2021; Marchi et al. 2018; Sleep 2016). (6) New methods of calculating the equilibrium isotope fractionation factors between metal and silicate melts at the terrestrial core formation conditions (Wang et al. 2021a, b).

7.2 The problems requiring further investigations

7.2.1 The metal-silicate partition coefficients of HSEs at the core formation conditions

(1) In the future the laser-heated diamond anvil cell equipment that can achieve much higher temperatures and pressures should be used to investigate the metal-silicate partition coefficients of several HSEs (not only one) at the same time. (2) more than one type of light element should be considered to simulate the true core formation conditions. (3) Ab initio molecular dynamics and thermodynamic integration techniques should be developed for the HSEs.

7.2.2 Equilibrium and nonequilibrium core formations

The current estimates of how much chondrites were added into the mantle after the core formation are different from the equilibrium core formation conditions (named as the geochemical estimate) and nonequilibrium metal-silicate separation during the growth of Earth (named as the dynamical estimate). In the future, the two estimates should be reconciled.

7.2.3 Isotope effects

The stable isotopes of Pt and Pd, the nucleosynthetic anomalies of Ru have been used to study the origins and the mixing history of HSEs in the mantle. However, some of the isotope effects have been not investigated carefully. (1) Future work may need to determine the metal (containing light elements)-silicate equilibrium stable isotope fractionation factors of HSEs at the core formation conditions by HPTEs and ab initio methods. (2) It is necessary to evaluate the effects of the multistage close-system melting and crystallization evolution model on the nucleosynthetic anomalies of relevant elements.

7.2.4 Origins of volatile elements

Unfortunately, many volatile elements are both siderophile (entering the metallic core) and volatile (lost to the space during accretion). (1) Currently it is unclear about the relative rates of terrestrial planetary differentiation and accretion. There are some new investigations (Grewal et al. 2021; Wang et al. 2021a, b), which may be better continued. (2) One also needs to consider the effects of violent events, such as the Moon-forming Giant Impact.

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