The late Earth's accretion: Processes and materials

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In accord with the standard Earth accretion scenario, the late accretion supervened the last collision with a massive proto-planet, segregation of the core, and (partial) solidification of the magma ocean. These processes took place ≈ 40 Ma after Sun formation or somewhat later. Traces of the processes and respective materials have been preserved as specific elemental and isotopic abundances in the earth's mantle. Three groups of chemical elements, showing rather different behavior, allow the principal processes and materials to be restored: (i) involatile siderophile elements and the ^{182}Hf–^{182}W and ^{190}Pt–^{187}Re–^{186,187}Os isotopic systematics highlight the time scale of core formation, the late veneer materials, and post-core-formation interactions between the mantle and the core; (ii) involatile lithophile incompatible elements and the ^{147}Sm–^{143}Nd isotopic systematics indicate the early differentiation of the silicate Earth; ^{176}Lu–^{176}Hf one recorded the early crustal processes; (iii) highly volatile elements, noble gases, and the ^{238}U–^{235}U–^{232}Th–He–Ne and ^{244}Pu–^{238}U–^{129}I–Xe systematics trace the accreting materials and the rate of mantle mixing and degassing. Recently proposed interpretations of this last systematics appear to be precarious and are particularly discussed in this contribution. During the late accretion a terrestrial regolith, including chondritic and solar-wind-irradiated materials, was rapidly accumulating on the surface of the early thick basaltic crust, enriched in incompatible elements. This early crust had not been preserved. Its overturn(s) into the mantle during several 100th Ma after Sun formation and (partial) isolation from the mantle convection allow all principal observations, related to the informative systematics mentioned above, to be satisfied, providing the transfer of the crust&regolith "cake" was not accompanying by fractionation and degassing, in contrast to present-day slab subduction. *KEYWORDS:* Noble metals; noble gases; rare earth elements; isotope systematics; Earth; accretion; differentiation; degassing.

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1. Introduction

1.1. The Accreting Materials

This work is based on the standard model of accretion of terrestrial planets, which includes the following stages: (a) the ordered growth of the

planet's embryos, (b) the faster growth of the more massive proto-planets, and (c) the formation of the Earth through collisions with massive (up to the size of Mars) impactors [*Vityazev et al., 1990*; *Wetherill, 1990*; *Weidenschilling, 2000*].

There are many different arguments supporting the close-to-chondrite abundances of the Earth's refractory constituents [e.g., *Bond et al., 2010*; *Brandon et al., 2006*; *Dauphas et al., 2014*], even though alternative hypotheses about the Earth's matter, different from the chondritic composition, are also discussed in the literature [*Kostitsyn, 2004*]. A discussion of the proto-terrestrial matter is beyond the scope of this work. Chondrites are repeatedly used as unique carriers of elements and isotopes important for this contribution (see, for example, Sections 2.1, 2.2). Probably the chondrite material was the only one able to be formed in the earth's feeding zone. Therefore I accepted the "chondrite" Earth model.

Studies of meteorites show a clear correlation between the volatiles content and the heliocentric distance of the parental bodies; planetesimals in the Earth feeding zone were initially depleted in volatile components [*Albarede, 2009*; *Morbidelli et al., 2012*]. Numerous collisions of growing planets, including collisions with massive impactors of the lunar (or even Mars's) size, induced irreversible losses of volatiles and led to formation of extremely degassed terrestrial planets towards the end of accretion. Even if volatile-rich planetesimals were transferred from the asteroid belt (and/or from farther segments of the solar nebulae) to the Earth feeding zone, subsequent accretion processes (collisions, melting, degassing) minimized a residual contribution of their volatiles. The term "dry proto-earth", used in recent paper by *Caracausi et al.* [2016], probably also means a substantially degassed planet.

1.2. ^{182}Hf–^{182}W Chronometry of the Core Formation

The main accretion phase was completed by a giant collision and subsequent moon formation and core segregation [*Canup and Asphaug, 2001*; *Kleine et al., 2002*; *Stevenson, 1987*]. ^{182}Hf–^{182}W data indicate ≈ 40 Ma long time interval between formation of the Ca-Al-rich inclusions (CAI) in meteorites and the Earth's core. This interval could be somewhat longer, and the above minimum value corresponds to the following scenario [*Jacobsen, 2005*; *Kleine et al., 2002, 2009*; *Tolstikhin and Kramers, 2008*].

- At this time the proto-Earth collided with a massive protoplanet.

- The energy, released by the collision, resulted in almost complete melting and partial vaporization of the planetary matter, partitioning of siderophile elements (including W) into the metal phases, rapid segregation of these phases into the core, and depletion of the silicate Earth with siderophile elements, including W, yielding a high Hf/W ratio in this reservoir.

- A subsequent "late" slow accretion had not affected the isotopic compositions of Hf, W and Hf/W ratio in the mantle.

The giant collision and the final phase of core formation could take place somewhat later if: (i) the late accretion was sufficient to change the above parameters, (ii) mixing of the matter after the giant collision was not complete, or (iii) partitioning of siderophile elements into the metal phase(s) was not equilibrium [*Kramers, 1998*].

1.3. The Ancient Crust

After the giant impact and (partial) cooling of the magma's ocean, mantle temperatures significantly exceeded the present-day values, and as a result a thick, stagnant (the lifetime ≈ 100th Ma) dominantly mafic crust was formed. Hf isotope compositions in the most ancient (older than 4 Ga) zircons indeed indicate formation of the host rocks from such a crust [*Griffin et al., 2014*]. Continuing melting of the crust along with fractionation of the primary magmas could produce the hydrated magnesium-poor basalts, sources of the early tonalite-trondhjemite-granodiorite melts.

The base of the magnesium-rich crust was denser than the underlying complementary residual mantle and therefore gravitationally unstable at mantle temperatures greater than ≈ 1500°C. Such a crust would drip down into the mantle [*Johnson et al., 2014*] and its fragments could reside in the mantle. A stable crust slowed convection and thus pro-

vided a continued conservation of mantle heterogeneities, revealed, for example, as small deviations of ^{182}W and ^{142}Nd isotope abundance from the average mantle composition [e.g., *Walker, 2016*].

This scenario is shared by most researchers of the earliest Earth's tectonics [*Griffin et al., 2014*; *Johnson et al., 2014*; *O'Neill and Debaille, 2014*; *Van Hunen and Moyen, 2012*; *Van Thienen et al., 2004*]. The differences arise mainly in the choice of crust destruction processes and quantitative assessments (a crustal thickness, a composition, a life time, etc.).

Modeling of the late accretion shows that planetesimals, formed at greater distances from the Sun than the terrestrial planets (for example, in the asteroid belt), could cross the Earth's orbit and impact the Earth, thus delivering the "late" accretion materials, including those similar to chondrites [*Angor et al., 1999*; *Morbidelli et al., 2012*]. Later on these materials, the "terrestrial regolith", could be transported into the mantle by a submerging crust.

1.4. Terrestrial Reservoirs

The following main reservoirs of the Earth are considered in this paper. The bulk silicate earth (abbreviation BSE) is the silicate fraction of the Earth after the giant impact and the main stage of the core segregation, before differentiation of the silicate Earth and contribution of extraterrestrial matter during the "late accretion". The depleted with incompatible elements and gases mantle (DMM) is the main silicate reservoir of the Earth, a source of: (i) mid-ocean ridge basalts (MORB), feeding the oceanic crust (OCR); (ii) magmatic rocks in arc environments, feeding the continental crust (CCR); (iii) gases, including radiogenic isotopes of noble gases, which are transferring into the atmosphere (ATM). The depleted mantle, the crust and the atmosphere-hydrosphere are usually referred to as "accessible" reservoirs. A hypothetical isolated from mantle convection reservoir (DDP) could also occur in the mantle and contribute materials to the deep mantle plumes, forming ocean island basalts (OIB).

The main objective of this contribution is selection of "necessary and sufficient" geochemical observations that should be considered in order to understand the post-giant-impact evolution of solid Earth and to discuss the respective materials and processes. These observations should highlight the early history from different points of view and therefore include refractory siderophile, refractory lithophile and highly volatile elemental and isotopic systematics. Also important is to develop a relatively simple scenario, trying to follow the Occam's razor and avoid speculative hypothetical approaches. The sources and processes responsible for delivery of major volatile elements, mainly concentrated in the atmo-hydrosphere, are not considered here and the readers can find the respective data and discussions in recent papers by *Marty* [2012], *Albarede et al.* [2013], *Dauphas and Morbidelli* [2014], *Marty et al.* [2016, 2017], *Fischer-Gödde and Kleine* [2017].

2. Results and Discussion

2.1. Noble Metal Abundances in the Mantle

Among geochemical observations, directly related to the problems discussed in this contribution, one of the most important is chondrite-like relative abundances of noble metals (NM), i.e., refractory highly siderophile elements, in the earth's mantle (Figure 1). This is in contrast to the expectations from rather different and very large metal/silicate NM partition coefficients. The chondritic NM relative abundances also follow from ^{190}Pt–^{187}Re–$^{186,187}Os$ isotopic systematics [*Meisel et al., 2001*; *Walker, 2015*]. This feature of the mantle NM abundances is known since long [e.g., *Wanke et al., 1984*] and is repeatedly discussed in the literature [*Holzheid et al., 2000*; *Kramers, 1998*; *Maier et al., 2009*; *Walker, 2016*]. Recently it was emphasized, that the Hadean Os isotopic signature was preserved in the convecting mantle due to high recycling efficiencies for Os [*Jackson et al., 2016*].

The most popular explanation envisages addition of NM by a chondritic late veneer (arrived after core formation was ceased), which material was transferred into the mantle and mixed therein. Absolute chondritic contents of NM were "diluted" via mixing within the mantle, which had already lost NM (during the main stage of core segregation), but the relative chondritic concentration pattern was preserved.
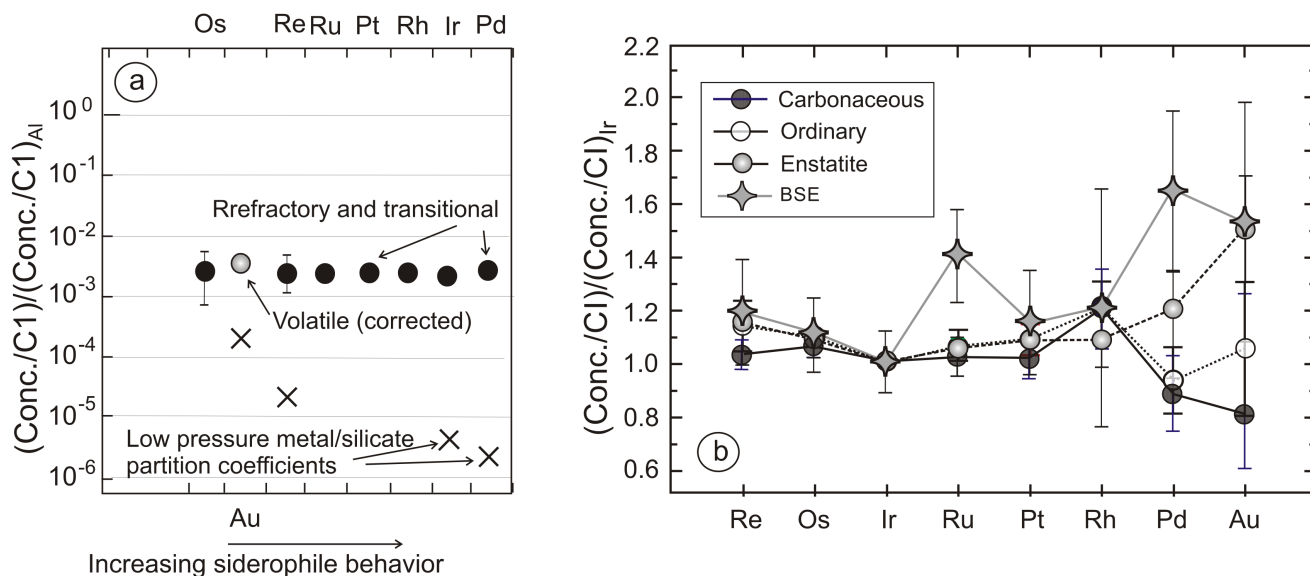
Figure 1. Normalised (to carbonaceous chondrites C1 and an involatile element, e.g., Al, Ir) abundances of highly siderophile elements (Noble Metals, NM) in the Earth's mantle. (a) Notice almost a chondrite-like concentration pattern in spite of the much lower concentrations compared with those in chondrites. However, the observed concentrations still (by orders of magnitude) exceed those, expected from equilibrium metal/silicate partitioning; moreover, such partitioning should result in rather different concentrations, in contract to those observed. Modified after *Righter and Drake* [2000]. (b) A comparison between terrestrial and chondritic abundances of noble metals. NM concentrations in enstatite chondrites are most similar to the terrestrial values. Modified after *Walker et al.* [2015].

To supply NM into the mantle, a contribution of the chondritic material $\approx 0.5\%$ of the Earth mass is required [*Walker, 2015*]. The relative abundances of NM seen in Figure 1b imply enstatite-like chondrites to be carriers of these species and thus a principal component of the late veneer. Study of the nucleosynthetic isotope anomalies showed a minimal difference between these meteorites and terrestrial rocks: the late veneer was derived from the inner Solar system material with a slightly higher contribution of the s-process nuclides compared with E-chondrites [*Bermingham and Walker, 2017*; *Burkhardt et al., 2016*; *Fischer-Gödde and Kleine, 2017*]. Ruthenium presents a clear isotopic evidence for an inner Solar System origin of the late veneer (Figure 2). Important constrain from the nucleosynthetic data is that the late veneer material could hardly source volatile elements for the Earth's atmo-hydrosphere, providing carbonaceous chondrites were the principal carriers of the volatiles. These new nucleosynthetic data are in contrast to proposals by e.g., *Lecuyer et al.* [1998], *Robert* [2001], *Kramers* [2003], *Marty* [2012]. Also along with NM the chondrite like late veneer ma-

terial should transfer into the mantle volatile elements, such as iodine (Section 2.4.2).

2.2. Planetary Xenon in the Mantle

Further supporting evidence on a contribution of chondrite like material during the late Earth's accretion follows from completely different group of elements, the noble gases (NG), i.e., highly-volatile chemically-inert elements. Even though chemical behavior of NM and NG is completely different, their common feature is very low abundances in the Earth's mantle, so that both groups are "sensitive detectors of the minor events".

The first precise measurement of the isotopic composition of mantle Xe by *Phinney et al.* [1978] revealed a contribution of meteoritic unfractionated Xe and ^{129}Xe(I). The sample was collected from CO_2 well gas (Harding County, New Mexico, USA) formed due to degassing of a basalt intrusion. The accuracy of their analysis was not high enough to distinguish between SOLAR-Xe and planetary Q-Xe components. Later on these results were sup-

ported by *Smith and Reynolds* [1981]. *Caffee et al.* [1999] and *Ballentine and Holand* [2008] observed a meteoritic Xe component in several CO_2 gas samples and *Holland et al.* [2009] discovered a meteoritic component of Kr. Recently *Caracausi et al.* [2016] analyzed noble gases of the mantle plume (Eifel, Germany) and identified the meteoritic Xe component as "planetary" (Q) xenon (Figure 3).

Carbonaceous chondrites (CC) are meteorite with the highest content of volatile elements, including planetary Xe and Kr [*Busemann et al.,* 2000]. According to the transport geochemical Earth's model [see Chapter 28 in *Tolstikhin and Kramers,* 2008], the minimal mass of the CC material, required to maintain Xe flux through the mantle during the whole Earth's history, approaches $\approx 5 \times 10^{-4}$ of the Earth's mass. This is by a factor of ≈ 10 less than the mass of the late veneer, which is needed to supply the Earth's mantle with noble metals. Because of such a small contribution, CC could be still their carriers even taken into account the nucleosynthetic constraint discussed in Section 2.1. Also Xe and I concentrations in some enstatite chondrites, e.g., in South Oman [*Pepin,* 1991] are only slightly (by a factor of ≈ 3) below those in CC and Xe isotopic compositions in these two meteorite groups are similar [*Crabb and Anders,* 1981]; hence, the enstatite-like chondrite material could carry both NM and Xe (and ^{129}I) constituents of the late veneer. It should be noted that Q-Xe could not be captured by the Earth from a hypothetical solar-gas atmosphere (Section 2.5).

2.3. Nucleogenic Xenon Isotopes in the Mantle

Precise measurements of the isotopic composition of Xe in mantle rocks and gases allowed ^{136}Xe(Pu) and ^{136}Xe(U) to be distinguished in samples of mantle plume and mid-ocean ridge basalts, but also in carbon dioxide gases [*Ballentine and Holand,* 2008; *Caracausi et al.,* 2016; *Parai and Mukhopadhyay,* 2015]. The parent isotopes, ^{129}I and ^{244}Pu, are short-life, so that they had decayed into the daughter species, ^{129}Xe(I) and ^{136}Xe(Pu), during the early Earth's evolution. *Caracausi et al.* [2016] and *Parai and Mukhopadhyay* [2015] showed that this early generated ratio in MORB, ^{129}Xe(I)/^{136}Xe(Pu)≈ 8, is somewhat higher than in the plume rocks, ≈ 2.
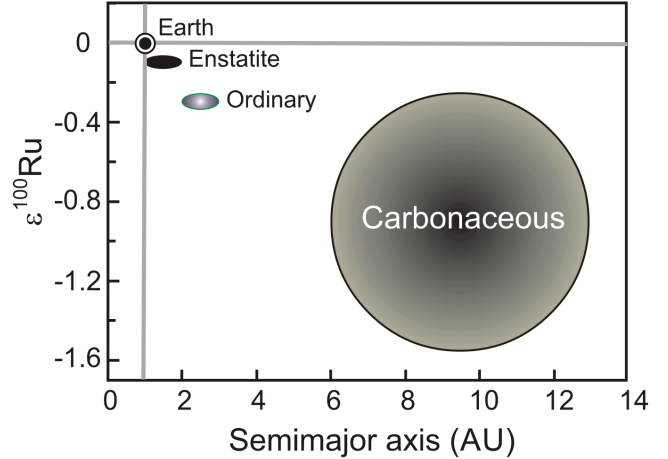

Figure 2. Contribution of the s-process isotope ^{100}Ru, ε^{100}Ru, increases with decreasing distance (in astronomical units, AU) from the Sun. More reduced materials like enstatite and ordinary chondrites have less negative ε^{100}Ru compared to more oxidized and volatile-rich materials, such as carbonaceous chondrites formed at greater heliocentric distance. ε^{100}Ru$=10,000\times\{[(\frac{^{100}Ru}{^{101}Ru})_{\mathrm{MET}}/(\frac{^{100}Ru}{^{101}Ru})_{\mathrm{STAND}}]-1\}$. Modified after *Fischer-Gödde and Kleine* [2017].

Interpreting these data, *Caracausi et al.* [2016] used a simple two-stage degassing model, based on the assumption of total losses of radiogenic isotopes of Xe(I, Pu) from a Deep-seated Distinct mantle reservoir (source of the Plume, hereafter DDP), until time t_{DDP}, when its degassing ceased and it was "closed" to Xe loss until the total decay of the parent isotopes, ^{129}I and ^{244}Pu:

$$t_{\mathrm{DDP}} = [1/(\lambda_{244} - \lambda_{129})]\times$$

$$\ln[(^{129}\mathrm{Xe(I)}/^{136}\mathrm{Xe(Pu)})_{\mathrm{DDP}}\times$$

$$(^{238}\mathrm{U}/^{127}\mathrm{I}_{\mathrm{DDP},0}) \times (^{244}\mathrm{Pu}/^{238}\mathrm{U}_{\mathrm{DDP},0})\times$$

$$(^{127}\mathrm{I}/^{129}\mathrm{I}_{\mathrm{DDP},0}) \times \mathrm{B}_{244} \times \mathrm{Y}_{244}] \qquad (1)$$

Parameters in (1) are: the initial concentration of ^{238}U$_{\mathrm{DDP}}$ =^{238}U$_{\mathrm{BSE}}$ = 1.6×10^{-10} mol g^{-1} [see Table 17.1 in *Tolstikhin and Kramers,* 2008]; the ratios of ^{129}Xe(I)/^{136}Xe(Pu)$_{\mathrm{DDP}}$ = 2.1 (Figure 3b), ^{244}Pu/^{238}U$_{\mathrm{DDP},0}$ = 0.007 [*Hudson et al.,* 1989], ^{127}I/^{129}I$_{\mathrm{DDP},0}$ = 9090 [see Figure 11.9 in *Tolstikhin and Kramers,* 2008, and references therein]; the decay constants $\lambda_{244} = 8.41$ Ga^{-1}, $\lambda_{129} = 44.1$ Ga^{-1};
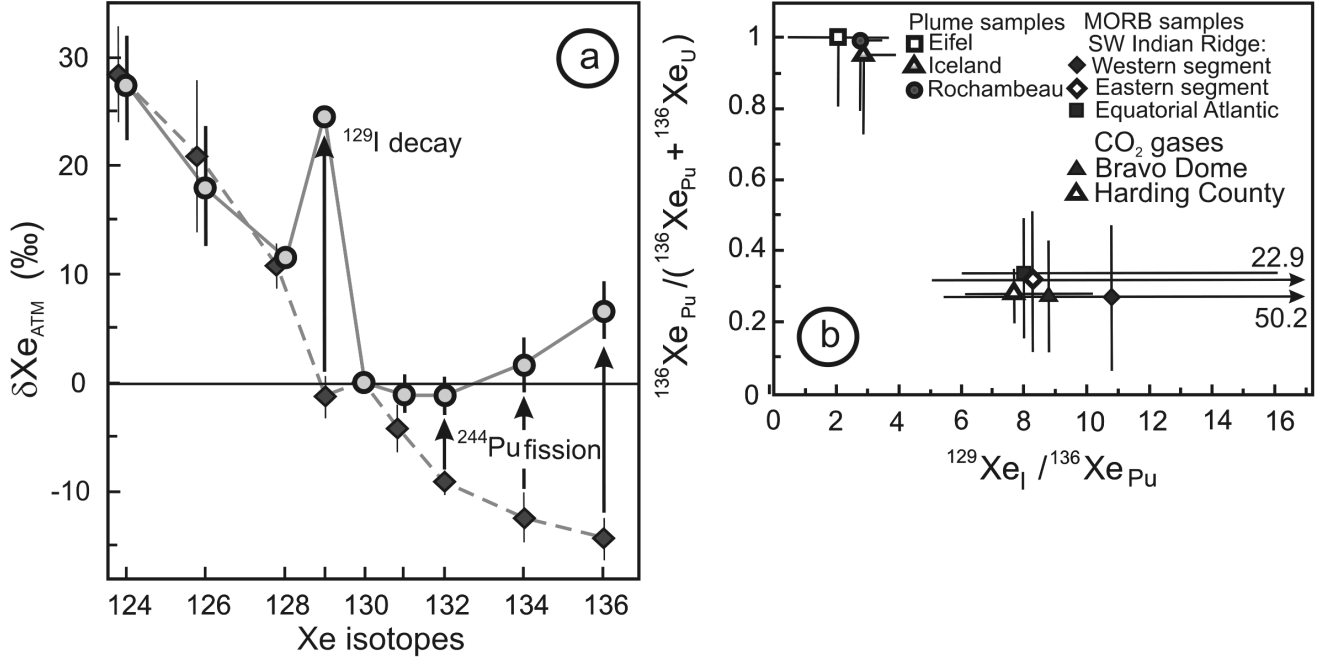
Figure 3. Xe isotope in mantle derivates. (a) Isotope composition of Xe from Victoriaquelle gas (Eifel, Germany), presented relative to air Xe: $\delta^i Xe = 1000 \times \{[(^i Xe/^{130} Xe)_{SAMPLE}/^i Xe/^{130} Xe)_{AIR}] - 1\}$, parts per mil (‰). For comparison a three-component model of mantle Xe is presented, which includes: (1) subducted unfractionated air Xe (84%); (2) carbonaceous chondrite Q-Xe (16%); this mixture is shown by rhombs; (3) radiogenic ^{129}Xe(I) and fission $^{131-136}$Xe(Pu) isotopes are shown by arrows. Modified after *Caracausi et al.* [2016]. (b) The radiogenic Xe isotope ratios in mantle rocks and gases, calculated relative to isotope composition of the average carbonaceous chondrite xenon after *Parai and Mukhopadhyay* [2015] and *Caracausi et al.* [2016]. These authors considered the different ^{129}Xe(I)/^{136}Xe(Pu) ratios in MORB-source and PLUMR-source materials as indication of different formation and evolution of the respective mantle reservoirs. The interpretation proposed in this contribution takes into account rather different "initial" ^{129}Xe(I)/^{136}Xe(Pu) ratios in the terrestrial regolith and the early crust (Section 2.4) and on this ground envisages some heterogeneity of the PLUME-source reservoir, in accord with data of the U-Th-He isotope systematics (Section 2.5.3).

the branching ratio $B_{244} = 1.25 \times 10^{-3}$; the yield $Y(^{136}Xe)_{244} = 5.6 \times 10^{-2}$. *Caracausi et al.* [2016] varied a poorly known content of $^{127}I_{DDP}$ from 2.4×10^{-11} mol g^{-1} to 1×10^{-10} mol g^{-1} and obtained from (1) the "closure" time of the DDP $75 \leq t_{DDP} \leq 120$ Ma after CAI formation.

Because of several reasons I doubt validity of this time estimate.

2.3.1. There is a discrepancy between (i) the assumption on the complete losses of radiogenic isotopes ^{129}Xe(I) and ^{136}Xe(Pu) from DDP before t_{DDP} and (ii) the retention of planetary Q-Xe seen in Figure 3a. An additional assumption is

required: after the complete decay of the parent isotopes (about 4200 Ma ago or later on) ^{129}Xe(I) and ^{136}Xe(Pu) were released from DDP and mixed with Q-Xe in a hypothetical reservoir, which did not contain the radiogenic species.

2.3.2. The above discrepancy between the chronological interpretation of the ^{129}Xe(I)/^{136}Xe(Pu)$_{DDP}$ ratio and the observation on planetary Xe is not the only one. Substitution of a higher value of ^{129}Xe(I)/^{136}Xe(Pu)$_{DMM}$ (Figure 3b) into (1) had led to another paradox: $t_{DDP} < t_{DMM}$, i.e., an isolated PLUME-source reservoir had already been "opened" for degassing,

while a MORB-source depleted mantle, including DDP, was still closed.

To overcome this second contradiction, *Caracausi et al.* [2016] abandoned the two-stage model for the depleted mantle and suggested "an increase in the I/Pu ratio due to the gradual addition of volatile rich components to the initially dry proto-earth." This dualistic interpretation envisages "two late veneers", separated by time and required different interaction(s) between the veneers and the Earth's materials.

2.4. Materials with Different ^{129}I/^{244}Pu and ^{129}Xe(I)/^{136}Xe(Pu) Ratios

A much more simple and self-consistent interpretation implies mixing of two materials, the late veneer and the early crust, after their transfer into the mantle (Section 1.3). To simplify the estimates presented below, I assume a single transfer of the materials from the Earth's surface to its interior, about 80 million years after CAI (about one half-life of ^{244}Pu and five half-lives of ^{129}I). This assumption will not affect the conclusions (Section 2.4.3).

2.4.1. According to Sections 2.1 and 2.2, the late veneer included chondrite material (CH), carrier of volatile components. The maximum ^{129}Xe(I)/^{136}Xe(Pu) ratio in this material can be calculated assuming a total retention of radiogenic Xe isotopes. Indeed, a large number of chondrites of various classes (including E-chondrites, Section 2.1) retained a significant fraction of ^{129}Xe(I) to the present [see Figure 11.9 in *Tolstikhin and Kramers,* 2008]. During the time scale discussed here, the retention of Xe should be better, because some fraction could have been lost during a 4500 Ma long evolution of chondrite parent bodies. Substituting the initial abundances of ^{129}I and ^{244}Pu, which determine the yield of radiogenic isotopes of Xe, i.e. ^{127}I$_{CH}$ = 3.4 × 10^{-9} mol g^{-1}, ^{129}I/^{127}I$_{CH}$ = 1.1 × 10^{-4}; ^{238}U$_{CH}$ = 6.7×10^{-11} mol g^{-1}, ^{244}Pu/^{238}U$_{CH}$ = 0.007 [see Tables 3.3 and 11.2 in *Tolstikhin and Kramers,* 2008] into (2) gives, after complete decay of these short-lived nuclides,

$$^{129}\text{Xe(I)}/^{136}\text{Xe(Pu)}_{CH} =$$

$$^{129}\text{I}_{CH}/(\text{B}_{244} \times \text{Y}_{244} \times ^{244}\text{Pu}_{CH}) = 11 \times 10^3 \quad (2)$$

It should be noted that the value calculated in (2) is the upper limit and can be somewhat decreased by using another set of parameters involved. Thus, new estimate of the average iodine concentration in carbonaceous chondrites, ^{127}I$_{CH}$ = 4.5 × 10^{-10} mol g^{-1} [*Clay et al.,* 2017], gives ^{129}Xe(I)/^{136}Xe(Pu)$_{CH}$ = 1.5 × 10^3, which is quite a large value still.

2.4.2. To estimate the ^{129}I/^{244}Pu ratio in another material of interest, the early Earth's crust composed by basalts or komatiites, I take the iodine content in mantle peridotites of the bulk silicate Earth ^{127}I$_{BSE}$ = 1 × 10^{-9} g g^{-1}. There are three independent reasons for choosing such a low concentration of iodine.

(a) Investigation of a one-reservoir mantle degassing model based on xenology [*Tolstikhin et al.,* 2014] showed that the solutions can be found for ^{127}I$_{BSE}$ ≥ 2 × 10^{-9} g g^{-1}, the content of U$_{BSE}$ and Pu/U ratio from Section 2.3, and the ratio of ^{129}Xe(I)/^{136}Xe(Pu)$_{DMM}$ = 23 ± 5 in the present day depleted mantle [*Pepin and Porcelli,* 2006]. The low value of ^{129}Xe(I)/^{136}Xe(Pu)$_{DMM}$ ≈ 8 (Figure 3b), proposed in *Caracausi et al.* [2016], allows a solution for the above ^{127}I$_{BSE}$ concentration to be obtained as well.

(b) After the transfer into the mantle the chondrite material amount, required by the NM abundances (Section 2.1), the ^{127}I concentration in this reservoir increased by ≈ 2 × 10^{-9} g g^{-1}; then the post-veneer iodine concentration would be ≈ 3×10^{-9} g g^{-1}, i.e., the value, used as a lower limit by *Caracausi et al.* [2016]. Regarding the abundance and source of terrestrial iodine, it should be noted that to provide the planet with volatile components, it is necessary to add ≈ 0.015× M$_{EARTH}$ of a chondrites-like material [*Clay et al.,* 2017; *Kramers,* 2003; *Marty,* 2012]. Such an amount corresponds to ^{127}I$_{BSE}$ ≈ 10 × 10^{-9} g g^{-1}, which is close to the maximum value used by *Caracausi et al.* [2016]. Thus, it is possible that "surface materials" were an important source of halogens on the Earth and their concentrations in the mantle could be (partially) provided by transporting these elements from near-surface reservoirs into the mantle, similar to air Xe [*Holland and Ballentine,* 2006; *Tolstikhin and Marty,* 1998].

(c) Considering that I, U and Pu are all incompatible elements and taking into account their ini-

tial concentrations in mantle peridotites, $^{127}I_{BSE} \approx 1 \times 10^{-9}$ g g^{-1}, $^{238}U_{BSE} = 38 \times 10^{-9}$ g g^{-1}, then, after 80 Ma passed by, $^{244}Pu_{BSE} \approx (1/2) \times 0.007 \times {}^{238}U_{BSE} = 5.6 \times 10^{-13}$ mol g^{-1}; $^{129}I_{BSE} \approx (1/32) \times 1.1 \times 10^{-4} \times {}^{127}I_{BSE} = 3 \times 10^{-17}$ mol g^{-1}, and after their decay, the ratio of the daughter Xe isotopes in the early crust turns out to be

$$^{129}Xe(I)/^{136}Xe(Pu)_{CRUST} \approx$$

$$^{129}I_{CRUST}/(B_{244} \times Y_{244} \times {}^{244}Pu_{CRUST}) \approx 0.7 \quad (3)$$

It should be noted that the above estimate does not take into account the degassing of iodine from mantle melts in the course of crust formation [*Bureau et al., 2016*]: the iodine condensation temperature, $\approx 400°C$, is significantly lower than the temperature of silicate melts $\approx 1400°C$. This again confirms the correct choice of a low concentration of $^{127}I_{BSE}$, and, accordingly, the low value of $^{129}Xe(I)/^{136}Xe(Pu)_{CRUST}$.

2.4.3. The ratio $^{129}Xe(I)/^{136}Xe(Pu)$ in the coexisting materials, the ancient crust and the chondrite-like regolith on its surface (see (2) and (3)) could differ by $\approx 10,000$ times (!). This impressive difference is the maximum and it can be somewhat reduced. However, taking into account the fundamentally different behavior of the parent elements, I and Pu, as well as the composition and evolution of the two transfer materials, their $^{129}I/^{244}Pu$ and $^{129}Xe(I)/^{136}Xe(Pu)$ ratios will always remain very different and the mixing proportions would cover a wide range of $^{129}Xe(I)/^{136}Xe(Pu)$ ratios, from < 1 to $\approx 10,000$.

Because of this wide range, a plume source (after ≈ 4500 Ma long evolution) could preserved some heterogeneity (rather small relative to the initial one) and thus supply the DMM with Xe characterized by slightly different $^{129}Xe(I)/^{136}Xe(Pu)$. This is in accord with observations on the plume-derived light noble gases (Section 2.5.3).

Also, because of the very different behavior of the parent elements and different evolution of their carriers before they were mixed in the mantle reservoir(s), $^{129}Xe(I)/^{136}Xe(Pu)$ observed in mantle rocks and gases do not contain any information about the "closure time" of any terrestrial (extraterrestrial) reservoir, in contrast to the proposals by *Avice and Marty* [2014] and *Caracausi et al.* [2016].

Instead, abundances of Xe isotopes in the mantle recorded:

(a) a flux of chondrite-like material that transferred highly volatile Xe and I into the mantle at the late stages of accretion;

(b) a rate of convection (which governs mixing) in mantle reservoirs, including the depleted MORB-source mantle and the apparently isolated mantle reservoir–source of PLUME noble gases;

(c) fluxes (of materials and/or species) from these reservoirs;

(d) transfer of volatile elements from the mantle reservoirs into the atmosphere and hydrosphere (degassing);

(e) transfer of atmospheric noble gases into the mantle.

It should be emphasized that all these mass fluxes were time-dependent. The first of them (a) can be considered as a global injection of an isotope tracer, which allows modeling other mass/atom fluxes. Many aspects of the above interpretation are also valid for the light noble gases (Section 2.5).

2.5. Sources of the Light Noble Gases in the Mantle

Regarding the light noble gases (He and Ne) of extraterrestrial origin in the Earth's mantle, it was suggested that they were captured from the nebular atmosphere "during the early stages of terrestrial accretion before gas dissipation" [*Caracausi et al., 2016*; *Tucker and Mukhopadhyay, 2014*]. Such a proposal is in contrast with (i) the nebula life time (2.5.1); (ii) the light noble gas abundances available in meteorites "before gas dissipation" and thus applies to yet unknown processes (2.5.2); (iii) discovery of mantle Q-Xe, which cannot be captured from solar gas atmosphere (Section 2.2). Meanwhile another well known source of the light extraterrestrial noble gases is available (2.5.3).

2.5.1. The dissipation time of the solar nebula is determined by the age of the chondrules, major constituents of chondrite meteorites: chondrules had been produced in the gas/dust nebula and their formation ceased along with the nebula dissipation. The time intervals of the chondrule formation are measured by isotope chronometers, including the short-lived isotope systematics, first of all $^{26}Al–^{26}Mg$, and the long-lived ones,

^{238}U_^{235}U_^{206,207}Pb. According to both chronometers, these intervals are within 4 Ma after the CAI formation [see *Amelin et al.,* 2002; *Krot et al.,* 2009; Figures 11.7, 13.1 and 13.2 in *Tolstikhin and Kramers,* 2008].

2.5.2. During this short interval, the chondrites captured minor amounts of the light noble gases from the (shielded from the solar wind) solar nebula [*Eugster et al.,* 2007; *Scherer and Schultz,* 2000]: ^{4}He$< 5 \times 10^{-10}$ mol g^{-1}. Such a low content is comparable to the accumulation of radiogenic ^{4}He(!).

2.5.3. In contrast, high concentrations of the light noble gases are observed in NG-rich meteorites (both chondrites and achondrites), which are the most suitable carriers of the light NG onto the early Earth. These meteorites were irradiated by the solar wind after the dissipation of the gas-dust nebula. "The presence of an implanted solar wind is usually considered a sign of a matter occurred on the surface of the meteorite parent bodies" [*Beyersdorf-Kuis et al.,* 2015] or other bodies (e.g. regolith on the lunar surface). Concentrations of He and Ne in such "solar-gas-rich" materials are very high [*Eugster et al.,* 2007; *Pedroni and Begemann,* 1994; *Scherer and Schultz,* 2000], ^{4}He$_{SW} \approx 5 \times 10^{-7}$ mol g^{-1}, and up to $\approx 5 \times 10^{-5}$ mol g^{-1} in the lunar regolith [*Benkert et al.,* 1993]. Such concentrations could occur in terrestrial regolith, especially taking into account that during the time period under consideration the accretion was still continuing and the solar-wind-irradiated regolith could be quickly accumulating on the surface of the early crust.

Again there are two different materials: a solar wind irradiated regolith with implanted solar wind He, ^{3}He/^{4}He$_{REG} = 4.3 \times 10^{-4}$, and a crustal basalt with gradually accumulating radiogenic He, ^{3}He/^{4}He$_{MORB} \approx 2 \times 10^{-8}$, and the difference, $\approx 10,000$, is of the same order as for ^{129}Xe(I)/^{136}Xe(Pu) ratios. In PLUME rocks and gases ^{3}He/^{4}He$_{PLUME}$ ratios generally vary within $(> 1$ to $\approx 6) \times 10^{-5}$ [*Graham,* 2002; *Jackson et al.,* 2010], i.e., by a factor of about 6, similar to that for Xe isotopes in mantle materials (Figure 3). Some ocean island hotspots, such as Réunion, show relatively constant distinct ^{3}He/^{4}He ratios during long time intervals, up to 10^8 years. These observations "suggest the possibility of deep mantle reser-

voirs having variable ^{3}He/^{4}He" [*Graham,* 2002] or "different time integrated (U and Th)/^{3}He ratios in different regions of the DDP" [*Tolstikhin and Hofmann,* 2005]; these conclusions are in accord with interpretation of Xe data presented in Section 2.4.3.

It should also be mentioned that isotope compositions of Ne in the solar wind and the Sun (or Solar nebula) are similar, ^{20}Ne/^{22}Ne ratios are within 13.5 to 13.8 [*Heber et al.,* 2012], and can hardly be distinguished by the study of terrestrial samples. However these ratios in the natural targets (solar wind irradiated meteorites or lunar regolith) are systematically lower, varying around 12.5; similar values are typical for mantle samples [*Moreira and Charnoz,* 2016; *Peron et al.,* 2017]: the SW irradiated "natural targets" are the most suitable carrier of the light noble gases onto the Earth, as it was proposed earlier by [*Tolstikhin and Hofmann,* 2005, see Figure 3 in their paper]. The ^{3}He/^{22}Ne$_{SW}$ ratio, 4.2 [*Heber et al.,* 2007], is slightly below that observed in the MORB-source depleted mantle, ≈ 7. This discrepancy is discussed in Section 2.6 below.

2.6. He/Ne Ratios in the Mantle and in the Solar Wind

The ratio of the extraterrestrial light noble gas isotopes in mantle rocks and gases, ^{3}He/^{22}Ne$_{EXT}$, correlates (with a slope ≈ 1) with the nucleogenic ^{4}He/^{21}Ne$^*_{NUC}$ ratio within almost 4 orders of magnitude; both ratios vary in the course of recent partial melting/degassing processes [*Honda and Pattrson,* 1999]. Within the frame of this correlation a projection of the known mantle production ratio ^{4}He/^{21}Ne$^* = 2.2 \times 10^7$ [*Yatsevich and Honda,* 1997] onto the ^{3}He/^{22}Ne$_{EXT}$ axis corresponds to ^{3}He/^{22}Ne$_{EXT} \approx 7$, same as measured in the popping rocks (gas rich MORB basalt glasses). In PLUME derived materials, rocks and gases, lower ratios are generally observed, $0.1 <$ ^{3}He/^{22}Ne$_{EXT,PLUME} < 7$; in contrast, enhanced values, $7 \leq$ ^{3}He/^{22}Ne$_{EXT,MORB} < 100$ are typical for MORB glasses [*Graham,* 2002; *Honda and Patterson,* 1999; *Moreira et al.,* 1998; *Tucker and Mukhopadhyay,* 2014].

The mantle values should be compared with those observed in the solar wind. SW-irradiated foils on the Earth's satellites show ^{3}He/^{22}Ne$_{SW} = 4.2$ [*Heber et al.,* 2007]. In natural materials these

ratios are usually somewhat lower; for example, $^3\text{He}/^{22}\text{Ne}_{\text{SW}} \approx 3$ in chondrite Acfer 111 [*Pedroni and Begemann,* 1994], ≈ 1.4 in samples of lunar ilmenite [*Palma et al.,* 2002]. The difference results from a preferential loss of readily migrating He during the long evolution of natural targets.

Considering these relationships, *Tucker and Mukhopadhyay* [2014] put forward a fantastic proposal: "The increase in the ratio $^3\text{He}/^{22}\text{Ne}...$ in the depleted mantle requires at least two episodes of atmospheric outburst and degassing of magmatic oceans associated with giant collisions during ongoing earth accretion." Without going into the discussion of this dramatic scenario, I note that the increased ratios of $^3\text{He}/^{22}\text{Ne}_{\text{EXT}}$ (relative to SW values) in MORB-source mantle can be explained without invoking any new hypothesis, in full accord with the Ockham's rule.

As a solar-noble-gas rich plume (having similar to SW $^3\text{He}/^{22}\text{Ne}_{\text{EXT}} \approx 4$) ascends, the mobile He is expected to migrate from the plume into the surrounding (depleted and degassed) MORB-source mantle much faster than Ne. This specific behavior of He atoms in silicate rocks (minerals) increases $^3\text{He}/^{22}\text{Ne}_{\text{EXT}}$ in the mantle. However, some fraction of PLUME can be mixed with mantle matter, which process surves to set in the mantle the SW-value. Another PLUME fraction is degassed nearby the earth's surface. Within the frame of this simple concept the "average" (corrected for subsequent fractionation [*Honda and Pattrson,* 1999]) $^3\text{He}/^{22}\text{Ne}_{\text{EXT,MORB}} \approx 7$ could result from some "natural balance" of these processes.

A rough estimate below illustrates this explanation. "The diffusion coefficients of He in quartz are 5–7 orders of magnitude greater than those for Ne in the temperature range up to $400°\text{C}$" [*Shuster and Farley,* 2005]. Estimates of the He diffusion coefficient in olivine vary widely up to $D(\text{He}) \approx 10^{-3} \text{ cm}^2 \text{ s}^{-1}$ at magmatic temperatures, $1350°\text{C}$ [*Trull and Kurz,* 1993], similar to He diffusion through basaltic melts [*Lux,* 1987]. Unfortunately, data on Ne diffusion rate in mantle materials at magmatic temperature are not available, and I assume that Ne migrates much slower than the He. A plume rise time (from the core/mantle boundary to the Earth's surface) ≈ 10 Ma [*Zharkov,* 1983], and the above diffusion coefficient give the diffusion radius ≈ 5 km or $\approx 1/20$ of the plume radius

[*Sleep,* 1990]. According to these estimates, an appreciable part of the plume material can lose He by diffusion. Studies of the mobility of He and Ne at "magmatic" temperatures in minerals typical for the Earth's mantle will allow us to check this simple explanation, and also to use such data to model the evolution of plumes.

According to this brief discussion, the implanted solar wind appears to be the most adequate source of light noble gases in the Earth's mantle. The minimal mass of the SW-irradiated material, required to maintain $^3\text{He}_{\text{SW}}$ flux through the mantle during the whole Earth's history, is similar to that obtained for Xe isotopes, $\approx 10^{-4}$ of the Earth's mass (Section 2.2).

2.7. Radiogenic Nd Isotope Inventory in Terrestrial Reservoirs

The late veneer, transferred NM and NG, first interacted with the massive ancient crust (Sections 1.3, 2.4.2), which formation and evolution was recorded by involatile incompatible lithophile elements, of all $^{147}\text{Sm}–^{143}\text{Nd}$ isotope systematics. Comparison of the abundances of Nd isotopes in the earth's silicate reservoirs within the frame of a chondritic earth's model shows that all these reservoirs are depleted with Nd, which is more incompatible than Sm.

The balance of radiogenic $^{143}\text{Nd}^*$ in silicate reservoirs is determined by the equation [*Allegre,* 1997]:

$$\text{M}_{\text{CCR}}[^{143}\text{Nd}^*]_{\text{CCR}} + \text{M}_{\text{DMM}}[^{143}\text{Nd}^*]_{\text{DMM}} =$$

$$(\text{M}_{\text{CCR}} + \text{M}_{\text{DMM}})[^{143}\text{Nd}^*]_{\text{BSE}} \qquad (4)$$

Usually the contribution of $^{143}\text{Nd}^*$ in reservoir "i" is expressed as

$$\varepsilon^{143}\text{Nd} = 10,000 \times \left\{ \left[\left(\frac{^{143}\text{Nd}}{^{144}\text{Nd}} \right)_{\text{I}} \Big/ \left(\frac{^{143}\text{Nd}}{^{144}\text{Nd}} \right)_{\text{BSE}} \right] - 1 \right\}. \qquad (5)$$

Substituting (5) into (4) and taking into account that within the frame of the chondritic earth model $\varepsilon^{143}\text{Nd}_{\text{BSE}} \equiv 0$ reduce (4) to

$$\text{M}_{\text{DMM}}[\text{Nd}]_{\text{DMM}} \varepsilon^{143}\text{Nd}_{\text{DMM}} =$$

$$- \text{M}_{\text{CCR}}[\text{Nd}]_{\text{CCR}} \varepsilon^{143}\text{Nd}_{\text{CCR}} \qquad (6)$$

Substituting the mass of the continental crust $M_{CCR} = 2.26 \times 10^{25}$ g, the (average for the reservoirs) concentrations of $[Nd]_{CCR} = 22 \times 10^{-6}$ g g^{-1}, $[Nd]_{DMM} = 0.7 \times 10^{-6}$ g g^{-1}, and the ε-values, $\varepsilon^{143}Nd_{CCR} = -17$, $\varepsilon^{143}Nd_{DMM} = 9$ [see Figure 27.18 and Tables 17.1 and 28.2 in *Tolstikhin and Kramers, 2008*], into (6), as small mass M_{DMM} is derived as $\approx 1.2 \times 10^{27}$ g, which is $\approx 30\%$ of the mass of the silicate Earth. To ensure the balance of the ^{147}Sm–^{143}Nd isotope systematics, a complementary reservoir is required, either a large ($\approx 2/3$ of the silicate Earth) with chondritic isotope abundances of Sm and Nd, or a smaller one, consisting of an enriched material (for example, the ancient crust) isolated from the mantle convection of [e.g., *Tolstikhin and Hofmann, 2005*].

2.8. The Late Accretion

Three specific features of the late accretion are required in order to explain all different observations considered in Sections 2.1–2.7: impacts of the late veneer bodies with the Earth (2.8.1) as well as transfer of the early Earth's crust along with the chondrite-like and solar wind irradiated regolith into the mantle (2.8.2) were not accompanied by fractionation of noble metals and degassing of noble gases; some fraction of the transferred material was mixed with the mantle rocks, while another one was isolated from mantle convection and mixing (2.8.3).

2.8.1. The models of the late accretion are to be developed and at present there is no consensus about size(s) of impactors constituting the late veneer and the post-impact processes. In case of meter-scale sizes [*Rivera-Valentin and Barr, 2014*; *Schlichting et al., 2012*], fallout of small debris did not cause their melting, fractionation, and degassing, by analogy with meteorites collected on the Earth's surface at present. Such a proposal envisages preservation of both NM and NG in the regolith material. Future modeling should show whether the flow of such debris would be intense enough to transfer a sufficient mass of an unfractionated and un-degassed regolith on the surface of the early crust.

In case of large (up to $\approx 10^3$ km) impactors [*Raymond et al., 2013*] melting and evaporation of impactor, crustal and mantle materials are the principal processes [*Kraus et al., 2015*]. To prevent fractionation of NM, special additional features of these processes are considered. For example, evaporation was followed by condensation of the cooling matter and its deposition on the surface of the ancient crust; it is assumed that these processes do not fractionate the NM [*Albarede et al., 2013*]. Another possibility is that impact-generating melting (of the impactor's core and mantle along with the earth's crust and mantle) resulted in "atomization" of NM in the melt. Subsequent mixing with (almost) NM-free mantle was fast enough to prevent the segregation of metal [*Puchtel et al., 2017*].

The two "end-member" proposals are not completely incompatible, especially taken into account the different contributions of the late veneer materials, required to supply NM ($\approx 5 \times 10^{-3} \times M_{EARTH}$) and NG ($\approx 5 \times 10^{-4} \times M_{EARTH}$). The heavy impacts caused explosions and (partially) disintegrate colliding materials; small debris, produced by disintegration (e.g., "earth-earth meteorites"), could preserve the noble gases and even be SW irradiated.

2.8.2. The transfer of the ancient crust with NM- and NG-rich regolith on its surface into the mantle without melting, fractionation and degassing has not been studied yet. The simplest assumption proposed by *Tolstikhin and Hofmann* [*2005*] envisaged the early (subduction-like) transfer when water was absent on the earth surface. However recent models of the early crust indicate its relatively long life time (Section 1.3). Thus, *Mojzsis et al.* [*2001*] studied ancient (up to 4300 Ma old) zircons and postulate that they were formed from "magmas containing a significant component of re-worked continental crust that formed in the presence of water near the Earth's surface." These data are therefore consistent with the presence of a hydro-sphere ≈ 4300 Ma ago.

The mechanisms of transfer of the early crust (occurred before ≈ 4000 Ma) into the mantle could have no analogues with those operated during the "geological history". For example, *Marchi et al.* [*2014*] considered flux of extraterrestrial bodies, early terrestrial impacts, and their effects on the crustal growth and evolution. The surface of the Hadean Earth was widely reprocessed by impacts through mixing and burial of impact-generated melts. Existing oceans would have repeatedly boiled away into steam atmospheres as a result of large collisions.

2.8.3. Within the convective depleted mantle the sunken crust + regolith were (i) partially mixed with the mantle materials, thus providing the occurrence of NM in the Earth's mantle in chondritic relationships [*Walker,* 2016]; (ii) partially preserved as an isolated mantle reservoir [*Jackson et al.,* 2010; *Tolstikhin and Hofmann,* 2005], thus providing the contributions of solar He, Ne [*Graham,* 2002], ^{129}Xe(I), ^{136}Xe(Pu), Q-Xe [*Caracausi et al.,* 2016; *Parai and Mukhopadhyay,* 2015] and meteoritic Kr [*Holland et al.,* 2009] in mantle rocks and gases.

3. Concluding Remarks

Sinking of the ancient crust with the chondritic and solar-wind-irradiated regolith into the mantle allows several independent observations (on the concentrations and isotopic compositions of volatile, lithophile and siderophile elements in the observable terrestrial reservoirs) to be explained, providing this process was not accompanied by fractionation and degassing of the respective species.

Following this scenario transport models, based on evolution of the radioactive and radiogenic isotopes in the Earth's principal reservoirs, allow estimates of the fluxes of masses and species between and within the reservoirs. Thus, the rate of partial melting of mantle rocks through time, i.e., the degassing flux, constrains the convection in the silicate Earth, and also the time of Earth's atmosphere closure to Xe loss. The validity of the transport models should be verified by more complicated physical modeling.

Regarding the late Earth's accretion, the most important problems, to be studied by physical modeling, are: (i) the accumulation of sufficient amounts of undegassed and unfractionated chondrite and SW-irradiated materials (the late veneer) on the early crust; (ii) transfer of these materials along with the early crust into the mantle without fractionation and degassing; (iii) the mechanism(s) and degree(s) of mixing of the transferred crust with terrestrial regolith within mantle reservoir(s). Solution of these problems would help to understand the post-giant-impact evolution of the Earth, and respective observations, including difference in ^{129}Xe(I)/^{136}Xe(Pu) in MORB and PLUME rocks and fluids.

References

Albarede, F. (2009), Volatile accretion history of the terrestrial planets and dynamic implications, *Nature*, *461,* 1227–1233, https://doi.org/10.1038/nature08 477

Albarede, F., C. Ballhaus, J. Blichert-Toft, C.-T. Lee, B. Marty, F. Moynier, Q.-Z. Yin (2013), Asteroidal impacts and the origin of terrestrial and lunar volatiles, *Icarus*, *222,* 44–52, https://doi.org/10.10 16/j.icarus.2012.10.026

Allegre, C. J. (1997), Limitation on the mass exchange between the upper and lower mantle: the evolving convection regime of the Earth, *Earth Planet. Sci. Lett.*, *150,* 1–6, https://doi.org/10.1016/S0012-821X(97)00072-1

Amelin, Y., et al. (2002), Lead isotope ages of chondrules and calcium-aluminum-rich inclusions, *Science*, *297,* 1678–1683, https://doi.org/10.1126/science.1073950

Angor, C. B., R. M. Canup, H. Levison (1999), On the character and consequences of large impacts in the late stage of terrestrial planet formation, *Icarus*, *142,* 219–237, https://doi.org/10.1006/icar.1999.6201

Avice, G., B. Marty (2014), The iodine-plutonium-xenon age of the Moon–Earth system revisited, *Phil. Trans. Royal Soc. Lond.*, *A 372,* 20130260, https://doi.org/10.1098/rsta.2013.0260

Ballentine, C. J., G. Holland (2008), What CO_2 well gases tell us about the origin of noble gases in the mantle and their relationship to the atmosphere, *Phil. Trans. Royal Soc. Math. Phys. and Engineering Sci.*, *366,* 4183–4203, https://doi.org/10.1098/rsta.2008.0150

Benkert, J.-P., H. Baur, P. Signer, R. Wieler (1993), He, Ne, and Ar from the solar wind and solar energetic particles in lunar ilmenites and pyroxenes, *J. Geophys. Res.*, *98,* 13147–13162, https://doi.org/10.1029/93JE01460

Bermingham, K. R., R. J. Walker (2017), The ruthenium isotopic composition of the oceanic mantle, *Earth Planet. Sci. Lett.*, *474,* 466–473, https://doi.org/10.1016/j.epsl.2017.06.052

Beyersdorf-Kuis, U., U. Ott, M. Trieloff (2015),

Early cosmic ray irradiation of chondrules and prolonged accretion ofprimitive meteorites, *Earth Planet. Sci. Lett.*, *423*, 13–22, https://doi.org/10.1016/j.epsl.2015.04.024

Bond, J. C., D. S. Lauretta, D. P. O'Brien (2010), Making the Earth: Combining dynamics and chemistry in the Solar System, *Icarus*, *205*, 321–337, https://doi.org/10.1016/j.icarus.2009.07.037

Brandon, A. D., R. J. Walker, I. S. Puchtel (2006), Platinum-osmium isotope evolution of the Earth's mantle: Constraints from chondrites and Os-rich alloys, *Geochim. Cosmochim. Acta*, *70*, 2093–2103, https://doi.org/10.1016/j.gca.2006.01.005

Bureau, H., A.-L. Auzende, M. Marocchi (2016), Modern and past volcanic degassing of iodine, *Geoch. Cosmochim. Acta*, *173*, 114–125, https://doi.org/10.1016/j.gca.2015.10.017

Burkhardt, C., et al. (2016), A nucleosynthetic origin for the earth's anomalous 142Nd composition, *Nature*, *537*, 194–198, https://doi.org/10.1038/nature18956

Busemann, H., H. Baur, R. Wieler (2000), Primordial noble gas in "phase Q" in carbonaceous and ordinary chondrites studied by closed-system stepped etching, *Meteorit. Planet. Sci.*, *35*, 949–973, https://doi.org/10.1111/j.1945-5100.2000.tb01485.x

Caffee, M. W., G. B. Hudson, C. Velsko, G. R. Huss, E. C. Alexander, Jr., A. R. Chivas (1999), Primordial noble gases from Earth's mantle: Identification of a primitive volatile component, *Science*, *285*, 2115–2118, https://doi.org/10.1126/science.285.5436.2115

Canup, R. M., E. Asphaug (2001), Origin of the Moon in a giant impact near the end of the Earth's formation, *Nature*, *412*, 708–713, https://doi.org/10.1038/35089010

Caracausi, A., G. Avice, P. G. Burnard, E. Fuery, B. Marty (2016), Chondritic xenon in the Earth's mantle, *Nature*, *533*, 82–85, https://doi.org/10.1038/nature17434

Clay, P. L., et al. (2017), Halogens in chondritic meteorites and terrestrial accretion, *Nature*, *551*, 614–618, https://doi.org/10.1038/nature24625

Crabb, J., E. Anders (1981), Noble gases in E-chondrites, *Geochim. Cosmochim. Acta*, *45*, 2443–2464, https://doi.org/10.1016/0016-7037(81)90097-1

Dauphas, N., A. Morbidelli (2014), Geochemical and planetary dynamical views on the origin of Earth' atmosphere and oceans, *Treatise Geochem.*, *6*, 1–35.

Dauphas, N., et al. (2014), Calcium-48 isotopic anomalies in bulk chondrites and achondrites: Evidence for a uniform isotopic reservoir in the inner protoplanetary disk, *Earth Planet. Sci. Lett.*, *407*, 96–108, https://doi.org/10.1016/j.epsl.2014.09.015

Eugster, O., S. Lorenzetti, U. Krähenbühl, K. Marti (2007), Comparison of cosmic-ray exposure ages and trapped noble gases in chondrule and matrix samples of ordinary, enstatite, and carbonaceous chondrites, *Meteoritics Planet. Sci.*, *42*, 1351–1371, https://doi.org/10.1111/j.1945-5100.2007.tb00579.x

Fischer-Gödde, M., T. Kleine (2017), Ruthenium isotopic evidence for an inner Solar System origin of the late veneer, *Nature*, *541*, 525–527, https://doi.org/10.1038/nature21045

Graham, D. W. (2002), Noble gas isotope geochemistry of mid-ocean ridges and ocean island basalts: characterization of mantle source reservoirs, *Noble gases in geochemistry and cosmochemistry (Eds. Porcelli D., Ballentine C. J., and Wieler R.)* p. 247–318, Mineral. Soc. Amer., Washington. https://doi.org/10.2138/rmg.2002.47.8

Griffin, W. L., et al. (2014), The world turns over: Hadean-Archean crust-mantle evolution, *Lithos*, *189*, 2–15, https://doi.org/10.1016/j.lithos.2013.08.018

Heber, V. S., et al. (2007), The Genesis solar wind concentrator target: mass fractionation characterised by neon isotopes, *Space Sci. Rev.*, *130*, 309–316, https://doi.org/10.1007/s11214-007-9179-1

Heber, V. S., H. Baur, K. McKeegan, M. Neugebauer, D. Reisenfeld, R. Wieler, R. Wiens (2012), Isotopic fractionation of solar wind: evidence from fast and slow solar wind collected by the Genesis Mission, *Astrophys. J.*, *759*, 121–133, https://doi.org/10.1088/0004-637X/759/2/121

Holland, G., C. J. Ballentine (2006), Seawater subduction controls the heavy noble gas composition of the mantle, *Nature*, *441*, 186–191, https://doi.org/10.1038/nature04761

Holland, G., M. Cassidy, C. Ballentine (2009), Meteorite Kr in earth's mantle suggests a late accretionary source for the atmosphere, *Science*, *326*, 1522–1525, https://doi.org/10.1126/science.1179518

Holzheid, A., P. Sylvester, H. S. O'Neill, D. C. Rubie, H. Palme (2000), Evidence for a late chondritic veneer in the Earth' mantle from high-pressure partitioning of palladium and platinum, *Nature*, *406*, 396–399, https://doi.org/10.1038/35019050

Honda, M., D. B. Patterson (1999), Systematic elemental fractionation of mantle-derived helium, neon and argon in mid-oceanic ridge glasses, *Geochim. Cosmochim. Acta*, *63*, 2863–2874, https://doi.org/10.1016/S0016-7037(99)00206-9

Hudson, G. B., B. M. Kennedy, F. A. Podosek, C. M. Hohenberg (1989), The early solar system abundance of ^{244}Pu as inferred from the St. Severin chondrite, *Proc. Lunar Planet. Sci. Conf.*, *19*, 547–555.

Jackson, M. G., et al. (2010), Evidence for the survival of the oldest terrestrial mantle reservoir, *Nature*, *466*, 853–856, https://doi.org/10.1038/nature09287

Jackson, M. G., et al. (2016), j.gca.2016.02.011 Peridotite xenoliths from the Polynesian Austral and Samoa hotspots: Implications for the destruction of ancient ^{187}Os and ^{142}Nd isotopic domains and the preservation of Hadean ^{129}Xe in the modern convecting mantle, *Geochim. Cosmochim. Acta*, *185*, 21–43, https://doi.org/10.1016/

Jacobsen, S. B. (2005),   The Hf-W isotopic system and the origin of the Earth and Moon, *Ann. Rev. Earth Planet. Sci.*, *33*, 18.1–18.40.

Johnson, T. E., et al.   (2014),   Delamination and re-cycling of Archaean crust caused by gravitational instabilities, *Nat. Geosci.*, *7*, 47–52, https://doi.org/10.1038/ngeo2019

Kleine, T., C. Munker, K. Mezger, H. Palme (2002), Rapid accretion and early core formation on asteroids and the terrestrial planets from Hf-W chronometry, *Nature*, *418*, 952–955, https://doi.org/10.1038/nature00982

Kleine, T., M. Touboul, B. Bourdon, F. Nimmo, K. Mezger, H. Palme, S. B. Jacobsen, Q.-Z. Yin, A. N. Halliday (2009), Hf-W chronology of the accretion and early evolution of asteroids and terrestrial planets, *Geochim. Cosmochim. Acta*, *73*, 5150–5188, https://doi.org/10.1016/j.gca.2008.11.047

Kostitsyn, Yu. A. (2004),   Sm-Nd and Lu-Hf isotope systematics of the Earth: do they respond to chondrites?, *Petrology*, *12*, 451–466.

Kramers, J. D. (1998),   Reconciling siderophile element data in the Earth and Moon, W isotopes and the upper lunar age limit in a simple model of homogeneous accretion, *Chem. Geol.*, *145*, 461–478, https://doi.org/10.1016/S0009-2541(97)00155-1

Kramers, J. D. (2003),   Volatile element abundance patterns and the early liquid water ocean on Earth, *Precambrian Res.*, *126*, 379–394, https://doi.org/10.1016/S0301-9268(03)00106-2

Kraus, R. G., S. Root, R. W. Lemke, S. T. Stewart, S. B. Jacobsen, T. R. Mattsson (2015), Impact vaporization of planetesimal cores in the late stages of planet formation, *Nature Geoscience*, 1–4, https://doi.org/10.1038/ngeo2369

Krot, A. N., et al.   (2009),   Origin and chronology of chondritic components: A review, *Geochim. Cosmochim. Acta*, *73*, 4963–4997, https://doi.org/10.1016/j.gca.2008.09.039

Lecuyer, C., P. Gillet, F. Robert (1998),   The hydrogen isotope composition of seawater and the global water cycle, *Chem. Geol.*, *145*, 249–261, https://doi.org/10.1016/S0009-2541(97)00146-0

Lux, G. (1987),   The behavior of noble gases in silicate liquids: solution, diffusion, bubbles and surface effects, with implications to natural samples, *Geochim. Cosmochim. Acta*, *51*, 1549–1560, https://doi.org/10.1016/0016-7037(87)90336-X

Maier, W. D., et al.   (2009),   Progressive mixing of meteoritic veneer into the early Earth's deep mantle, *Nature*, *460*, 620–623, https://doi.org/10.1038/nature08205

Marchi, S., et al.   (2014),   Widespread mixing and burial of Earth's Hadean crust by asteroid impacts, *Nature*, *511*, 578–582, https://doi.org/10.1038/nature13539

Marty, B. (2012),   The origins and concentrations of water, carbon, nitrogen and noble gases on Earth, *Earth Planet. Sci. Lett.*, *313–314*, 56–66, https://doi.org/10.1016/j.epsl.2011.10.040

Marty, B., G. Avice, Y. Sano, K. Altwegg, H. Balsiger, M. Hässig, A. Morbidelli, O. Mousis, M. Rubin (2016),   Origins of volatile elements (H, C, N, noble gases) on Earth and Mars in light of recent results from the ROSETTA cometary mission, *Earth Planet. Sci. Lett.*, *441*, 91–102, https://doi.org/10.1016/j.epsl.2016.02.031

Marty, B., et al.   (2017),   Xenon isotopes in 67P/Churyumov-Gerasimenko show that comets contributed to Earth's atmosphere, *Science*, *356*, 1069–1072, https://doi.org/10.1126/science.aal3496

Meisel, T., R. J. Walker, A. J. Irving, J.-P. Lorand (2001),   Osmium isotopic compositions of mantle xenoltiths: A global perspective, *Geochim. Cosmochim. Acta*, *65*, 1311–1323, https://doi.org/10.1016/S0016-7037(00)00566-4

Mojzsis, S. J., T. M. Harrison, R. T. Pidgeon (2001), Oxygen-isotope evidence from ancient zircons for liquid water at the Earth's surface 4,300 Myr ago, *Nature*, *409*, 178–181, https://doi.org/10.1038/35051557

Morbidelli, A., et al.   (2012),   Building terrestrial planets, *Ann. Rev. Earth Planet. Sci.*, *40*, 251–275, https://doi.org/10.1146/annurev-earth-042711-105319

Moreira, M., S. Charnoz (2016),   The origin of the neon isotopes in chondrites and on Earth, *Earth Planet. Sci. Lett.*, *433*, 249–256, https://doi.org/10.1016/j.epsl.2015.11.002

Moreira, M., J. Kunz, C. Allegre (1998),   Rare gas systematics in popping rock: Isotopic and elemental compositions in the upper mantle, *Science*, *279*, 1178–1181, https://doi.org/10.1126/science.279.5354.1178

O'Neill, C., C. V. Debaille (2014),   The evolution of Hadean-Eoarchaean geodynamics, *Earth Planet. Sci. Lett.*, *406*, 49–58, https://doi.org/10.1016/j.epsl.2014.08.034

Palma, R. L., et al.   (2002),   Irradiation records in regolith materials, II: Solar wind and solar energetic particle components in helium, neon, and argon extracted from single lunar mineral grains and from the Kapoeta howardite by stepwise pulse heating, *Geochim. Cosmochim. Acta*, *66*, 2929–2958, https://doi.org/10.1016/S0016-7037(02)00853-0

Parai, R., S. Mukhopadhyay (2015),   The evolution of MORB and plume mantle volatile budgets: Constraints from fission Xe isotopes in Southwest Indian Ridge basalts, *G Cubed*, 719–735, https://doi.org/10.1002/2014GC005566

Pedroni, A., F. Begemann (1994),   On unfractionated solar gasses in the H3-6 meteorite Acfer 111, *Meteoritics*, *29*, 632–642, https://doi.org/10.1111/j.1945-5100.1994.tb00776.x

Pepin, R. O. (1991),   On the origin and early evolution of terrestrial planet atmospheres and meteoritic volatiles, *Icarus*, *92*, 2–79, https://doi.org/10.1016/0019-1035(91)90036-S

Pepin, R. O., D. Porcelli (2006),   Xenon isotope systematics, giant impacts, and mantle degassing on

the early Earth, *Earth Planet. Sci. Lett.*, *250,* 470–485, https://doi.org/10.1016/j.epsl.2006.08.014

Peron, S., M. Moreira, B. Putlitz, M. D. Kurz (2017), Solar wind implantation supplied light volatiles during the first stage of earth accretion, *Geochem. Persp. Let.*, *3,* 151–159, https://doi.org/10.7185/geochemlet.1718

Phinney, D., J. Tennyson, U. Frick (1978), Xenon in CO_2 well gas revisited, *J. Geophys. Res.*, *83,* 2313–2319, https://doi.org/10.1029/JB083iB05p02313

Puchtel, I. S., et al. (2017), *Mixing times of the Archean mantle: evidence from 2.7 Ga komatiites*, Goldschmidt Conference 2017, Paris.

Raymond, S. N., H. Schlichting, F. Hersant, F. Selsis (2013), Dynamical and collisional constraints on a stochastic late veneer on the terrestrial planets, *Icarus*, *226,* 671–681, https://doi.org/10.1016/j.icarus.2013.06.019

Righter, K., M. J. Drake (2000), Metal-silicate equilibrium in the early Earth-New constraints from the volatile moderately siderophile elements Ga, Cu, P, and Sn, *Geochim. Cosmochim. Acta*, *64,* 3581–3597, https://doi.org/10.1016/S0016-7037(00)00466-X

Rivera-Valentin, E. G., A. C. Barr (2014), Estimating the sizes of late veneer impactors from impact-induced mixing on Mercury, *The Astrophys. J. Lett.* p. 1–6, AAS DSP meeting #46 id.205.01, U.S.A. https://doi.org/10.1088/2041-8205/782/1/L8

Robert, F. (2001), The origin of water on Earth, *Science*, *293,* 1056–1058, https://doi.org/10.1126/science.1064051

Scherer, P., L. Schultz (2000), Noble gas record, collisional history, and pairing of CV, CO, CK, and other carbonaceous chondrites, *Meteorit. Planet. Sci.*, *35,* 145–153, https://doi.org/10.1111/j.1945-5100.2000.tb01981.x

Schlichting, H. E., P. H. Warren, Q.-Z. Yin (2012), The last stages of terrestrial planet formation: Dynamical friction and the late veneer, *Astrophys. J.*, *752,* https://doi.org/10.1088/0004-637X/752/1/8

Shuster, D. L., K. A. Farley (2005), Diffusion kinetics of proton-induced ^{21}Ne, ^{3}He, and ^{4}He in quartz, *Geochim. Cosmochim. Acta*, *69,* 2349–2359, https://doi.org/10.1016/j.gca.2004.11.002

Sleep, N. H. (1990), Hotspots and mantle plume: Some phenomenology, *J. Geophys. Res.*, *95,* 6715–6736, https://doi.org/10.1029/JB095iB05p06715

Smith, S. P., J. H. Reynolds (1981), Excess ^{129}Xe in a terrestrial sample as measured in a pristine system, *Earth Planet. Sci. Lett.*, *54,* 236–238, https://doi.org/10.1016/0012-821X(81)90006-6

Stevenson, D. J. (1987), Origin of the Moon – the collision hypothesis, *Ann. Rev. Earth Planet. Sci.*, *15,* 271–315, https://doi.org/10.1146/annurev.ea.15.050187.001415

Tolstikhin, I. N., B. Marty (1998), The evolution of terrestrial volatiles: A view from helium, neon, argon and nitrogen isotope modeling, *Chem. Geol.*, *147,* 27–52, https://doi.org/10.1016/S0009-2541(97)00170-8

Tolstikhin, I., A. Hofmann (2005), Early crust on top of the Earth's core, *Phys. Earth Planet. Inter.*, *148,* 109–130, https://doi.org/10.1016/j.pepi.2004.05.011

Tolstikhin, I. N., J. D. Kramers (2008), *The Evolution of Matter (from the Big Bang to the present-day Earth)*, 521 pp., Cambridge University Press, Cambridge.

Tolstikhin, I., B. Marty, D. Porcelli, A. Hofmann (2014), Evolution of volatile species in the earth's mantle: A view from xenology, *Geochim. Cosmochim. Acta*, *136,* 229–246, https://doi.org/10.1016/j.gca.2013.08.034

Trull, T. W., M. D. Kurz (1993), Experimental measurements of He-3 and He-4 mobility in olivine and clinopyroxene at magmatic temperatures, *Geochim. Cosmochim. Acta*, *57,* 1313–1324, https://doi.org/10.1016/0016-7037(93)90068-8

Tucker, J. M., S. Mukhopadhyay (2014), Evidence for multiple magma ocean outgassing and atmospheric loss episodes from mantle noble gases, *Earth Planet. Sci. Lett.*, *393,* 254–265, https://doi.org/10.1016/j.epsl.2014.02.050

Van Hunen, J., J.-F. Moyen (2012), Archean subduction: fact or fiction?, *Annu. Rev. Earth Planet. Sci.*, *40,* 195–219, https://doi.org/10.1146/annurev-earth-042711-105255

Van Thienen, P., A. P. Van den Berg, N. J. Vlaar (2004), Production and recycling of oceanic crust in the early Earth, *Tectonophysics*, *386,* 41–65, https://doi.org/10.1016/j.tecto.2004.04.027

Vityazev, A. V., G. V. Pechernikova, V. S. Safronov (1990), *Earth Planets: Origin and Early Evolution*, 296 pp., Nauka, Moscow.

Walker, R. J. (2016), Siderophile elements in tracing planetary formation and evolution, *Geochemical Perspectives*, *5,* 1–145, https://doi.org/10.7185/geochemperv.5.1

Walker, R. J., K. Bermingham, J. Liu, I. S. Puchtel, M. Touboul, E. A. Worsham (2015), In search of late-stage planetary building blocks, *Chem. Geol.*, *411,* 125–142, https://doi.org/10.1016/j.chemgeo.2015.06.028

Wanke, H., G. Dreibus, E. Jagoutz (1984), Mantle chemistry and Accretion History of the Earth, *Archaean Geochemistry (Eds. A. Kroner, G. N. Hanson, and A. M. Goodwin)* Springer-Verlag, Berlin. https://doi.org/10.1007/978-3-642-70001-9_1

Weidenschilling, S. J. (2000), Formation of planetesimals and accretion of the terrestrial planets, *From Dust to Terrestrial Planets (Eds. W. Benz, R. Kallenbach, and G. W. Lugmair)* p. 295–310, Kluwer Academic Publisher, Dordrecht. https://doi.org/10.1007/978-94-011-4146-8_19

Wetherill, G. W. (1990), Formation of the earth, *Ann. Rev. Earth Planet. Sci.*, *18,* 205–256, https://doi.org/10.1146/annurev.ea.18.050190.001225

Yatsevich, I., M. Honda (1997), Production of nucleogenic neon in the Earth from natural radioactive decay, *J. Geophys. Res.*, *102,* 10,291–10,298, https://doi.org/10.1029/97JB00395

Zharkov, V. N. (1983), *Internal Structure of the Earth and Planets*, 416 pp., Nauka, Moscow.

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