Supporting Online Material for

**Heterogeneous Accretion and the Moderately Volatile Element Budget of Earth**


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Supporting Online Material

1. Analytical procedure

The details of the analytical procedure are described in (S1) and a summary is given in (S2). For this reason, only a brief description of the analytical method is given here.

Up to 10 g of basalt sample powder was digested in a closed Savillex Teflon beaker on a hotplate using HCl/HNO₃/HF and traces of boric acid following the procedure described in (S1). After the dissolution, a 10% aliquot was taken for the determination of Pd and Ag concentration by isotope dilution. The isotope dilution analyses were conducted following the procedure described by (S3), which is based on (S4).

A three-stage ion exchange procedure was used for the isolation and purification of Ag (S1). The yield of the three-stage procedure was usually ~ 99%. For some basalt samples, however, the yield was as low as 56% (Fig. S1). This was caused by the difficulties that arose while attempting to dissolve large amounts of basalt in 160 ml 0.5 M HCl prior to sample loading onto the first ion exchange column. If close to 10 g of dissolved sample was loaded, as e.g. for KS-87-05, a residue of 1 to 2 ml of gel was often observed. Some Ag was trapped in these residues as the yield for these basalt samples varied between 56 to 100%. However, no Ag isotope fractionation correlating with the yield was observed (Fig. S1). Meteorites and basalt samples for which less than 2 g of material was dissolved did not show this problem and the yield was constant at ~99%. Total procedural chemistry blanks, including sample dissolution and ion exchange chemistry were < 250 pg, while generally 50 – 100 ng Ag was analyzed for each sample.

The Axiom MC-ICPMS at the Department of Terrestrial Magnetism was used for the Ag isotope measurements. Shortly before the Ag analyses, Pd was added to monitor the instrumental mass bias. The sample was injected into the plasma by the means of a low-uptake Teflon nebulizer (Elemental Scientific, USA) in conjunction with a water-cooled glass cyclonic and impact bead spray-chamber. One measurement consumed about 110 μl per minute and yielded 22 V / ppm Ag. The use of a desolvating nebulization system would lead to larger analytical uncertainties because it induces changes in the mass bias that are not identical for both Ag and Pd (S1). As in previous work (S1, S2), the ¹⁰⁸Pd/¹⁰⁵Pd ratio was used to correct the ¹⁰⁷Ag/¹⁰⁹Ag ratio for instrumental mass fractionation applying the reference value of ¹⁰⁸Pd/¹⁰⁵Pd = 1.18899 (S5) and the exponential mass-fractionation law. Standard and samples were doped with equal amounts of NIST SRM3138 Pd in order to obtain ¹⁰⁶Pd/¹⁰⁷Ag signal intensity ratios of 1. The samples were measured interspersed between runs of Ag standard solutions at concentrations that were adjusted to match those of the sample within 20 %.

The isotopic measurements for 100 ppb Ag solutions yielded a reproducibility of typically 0.35 ε (2sd; standard deviation of the population) for ¹⁰⁷Ag/¹⁰⁹Ag over one measurement session and provided a long-term average ¹⁰⁷Ag/¹⁰⁹Ag = 1.07976 for the NIST SRM978a Ag standard (S1). This value is used for the model calculations in this work. The external reproducibility of our procedure is demonstrated by seven different dissolutions of Allende sample powder, which display an average ε¹⁰⁷Ag = -0.4 ± 0.5 (2sd) relative to the NIST SRM978a Ag standard (S1, S2). This external reproducibility
of ± 0.5 (2sd) provides a good estimate for the total uncertainty introduced through sample digestion, ion exchange chemistry and mass spectrometry. Replicated measurements of the basalt sample KOO49 yielded an average $\varepsilon^{107}$Ag of -9.35 ±0.68 (2sd) (S1). This Hawaiian basalt experienced significant weathering, which most likely induced a strong Ag isotope fractionation (-9.35 ±0.68). Its external reproducibility (±0.68) is slightly inferior to that obtained for Allende. This is attributed to the large amount of sample that was processed for the basalt. Based on this, a conservative external reproducibility of ± 0.7 (2sd) is adapted for basalt samples reported in this work.

2. The Ag isotope composition of bulk silicate Earth

The Ag isotope composition of bulk silicate Earth (BSE) is estimated from new Ag isotope analyses obtained from unaltered mantle-derived igneous rocks, which originate from a broad variety of geological settings (Table S1). Sample descriptions are available in (S6-11). All samples yield identical Ag isotope compositions within the analytical uncertainty and they define an average $\varepsilon^{107}$Ag of -2.2 ± 0.7 (2sd) relative to the NIST SRM978a Ag standard. The standard deviation of the population is used as an uncertainty, which is a measure for the scatter of the data. The reason for choosing this conservative error is that the standard error of the mean is only valid if all samples possess identical Ag isotope compositions. Although all data overlap within analytical uncertainty (Table S1), we cannot exclude that some of them slightly differ in Ag isotope composition due to some very minor stable isotope fractionation (smaller than the uncertainty of the analytical procedure). Such small differences within igneous rocks were recently reported for Cd isotopes (S12). To account for such potential effects, a conservative error of ± 0.7 (2 sd) is adapted for the $\varepsilon^{107}$Ag estimate of BSE.

3. Two-stage core formation models

Two-stage core formation models have been widely used to model the Earth accretion and core formation (S13-15). The two stages are (i) the Earth before core formation, which is usually approximated by chondritic material and (ii) the Earth differentiated into core and mantle after an instantaneous core formation event. Two-stage models underestimate the complexity of the core forming process because core formation likely is a prolonged process occurring with the arrival of every large impactor. Moreover, the incoming core material may not have equilibrated perfectly with the silicate mantle (S16, S17). Keeping this limitation in mind, two-stage models represent a useful first approach to compare results provided by different chronometers. In Figure 1A we do not show the two-stage evolution of the Ag isotope composition of BSE with time for one specific core formation time, instead the expected $\varepsilon^{107}$Ag of BSE today is illustrated depending on the time of core formation. Such a diagram covers a much larger parameter space. For instance, if all Pd is efficiently sequestered into the core (BSE Pd/Ag = 0, Fig. 1A), the BSE records and preserves the isotopic composition of the precursor (chondritic) reservoir at the time of core formation, since the Earth’s mantle experiences no subsequent radiogenic in-growth from the decay of $^{107}$Pd. A viable model predicts an $\varepsilon^{107}$Ag of the present-day BSE that overlaps with the measured value of -2.2 ± 0.7 (2sd). More details about two-stage models can be found in e.g., (S17, S18).
4. The continuous core formation model

The continuous core formation model employed in this study follows the model described in (S16). The core is assumed to grow in approximately constant proportion to the Earth’s mass. An exponential growth curve for the Earth is adapted, which is then approximated by a step function [see Fig. 1 in (S16)]. These steps simulate the impact-driven growth of the Earth. The accretion starts with a runaway growth that produces objects with sizes of about 1 % of the Earth current mass. The further growth is dominated by stochastic collisions between these objects, which the model simulates by successive addition of objects of increasing size, starting with objects of 1 % of the present-day Earth mass until the Earth reaches 10 % of its mass today, then 2 % objects up to 30 %, followed by 4 % objects up to 90 %. The Moon-forming giant impact is approximated by an increment of a further 9 % such that the Earth reaches 99 % of its total mass. At this point in time, core formation stops and a subsequent late veneer adds another 1 % of material. The timing of each increment (or impact) is calculated from the time of the Moon-forming giant impact, in order to achieve an exponentially decreasing rate of growth, which is broadly consistent with dynamic calculations. The model also assumes that the impactors and their cores grow by step-wise accretion and at the same rate as the Earth did when of equivalent size.

The model has the advantage that the isotopic evolution of metal and silicate reservoirs in the proto-Earth and also in the impacting planetesimals and proto-planets can be tracked within each accretion step. The volatile element content can be varied for each impactor (for heterogeneous accretion) as well as the degree of metal-silicate equilibration (f) between the impactors core and BSE (f = 0 to 1 corresponds to 0 to 100 % equilibration, respectively). The newly set-up model calculations were verified by applying the model to the Hf-W decay system and the results reproduced those reported in (S16).

5. The building blocks of the Earth (precursor material)

The modeling here is based on the initial $^{107}$Ag/$^{109}$Ag and $^{107}$Pd/$^{108}$Pd ratio obtained from carbonaceous chondrites and iron meteorites, which are consistent with one other (S2). It is assumed that the solar system started with homogeneous Ag and Pd isotopic compositions and that major volatile deletion took place in the solar nebula as suggested from carbonaceous chondrites (S2, S19-23). We do not claim that the Earth was built from carbonaceous chondrites, but from materials that experienced the same depletion (compared to CI chondrites and the sun) of moderately volatile elements as carbonaceous chondrites. This depletion trend is called the nebular trend because it follows the condensation sequences calculated for the solar nebula [e.g., (S24, S25)]. The Earth and carbonaceous chondrites fall on the nebular trend [e.g., (S26-29)], hence, it is likely that the material that built up the Earth experienced the same kind of nebular depletion.

In contrast, there are several lines of evidence that ordinary chondrites do not fall on the nebular depletion trend. Several studies (some based on chemical equilibrium calculations [e.g., (S25)], other on isotopic data [e.g., (S2, S30, S31)]) have shown that the volatile element budget of ordinary chondrites is best explained by volatile depletion that resulted from open system thermal metamorphism (or more precisely a nebular depletion...
trend that was modified by open system thermal metamorphism). Thermal metamorphism most likely also gave rise to the large Ag isotope effects observed in these rocks, which cannot be explained by radiogenic ingrowth (S2). Therefore, ordinary chondrites display locally disturbed Pd-Ag systematics and are not well suited to approximate the building blocks of the Earth.

6. The late veneer

The similarity in the Ag isotope composition of the BSE with CI chondrites raises the question of whether Ag delivered by the late veneer completely dominates the BSE Ag budget. In the end member case where core formation leaves the mantle devoid of any highly siderophile elements like Pd, the 3.27 ppb (S29) estimated concentration of Pd in the current BSE restricts the amount of a CI-like (with Pd = 556 ppb, Ag = 197 ppb) late veneer to no more than 0.4% of the Earth’s mass. Addition of this amount of CI-like material would increase the Ag concentration of the BSE by 1.16 ppb, assuming that none of the added Ag went into the core. This is at most 30% of the estimated BSE Ag concentration (4-8 ppb). Assuming that the CI-like veneer (added after $^{107}$Pd was extinct) had the $^{107}$Ag/$^{109}$Ag measured for the CI chondrite Orgueil ($^{107}$Ag = -2.1), the mantle to which this veneer was added must have had an $^{107}$Ag lower than -1.3. Admixing of a CI-like veneer cannot reduce any higher mantle values to -1.5, the maximum allowed value from our $^{107}$Ag = -2.2 ± 0.7 value measured for mantle-derived samples. From Figure 1, a mantle $^{107}$Ag of -1.3 would restrict core formation to no later than 11 Myr (2-stage) or 14 Myr (continuous core formation). Consequently, the late veneer does not significantly modify the observation of the mis-match between core formation ages derived from Pd-Ag and Hf-W.

7. Model parameters

All calculations used the following parameters: $^{107}$Ag(solar system initial) = -3.1, calculated relative to the NIST SRM978a standard solution ($^{107}$Ag/$^{109}$Ag = 1.07976); an initial $^{107}$Pd/$^{108}$Pd ratio of the solar system = 5.9 (±2.2) x 10$^{-5}$(S2) and the decay constant $\lambda^{107}$Pd = 0.106 x 10$^{-6}$ yr$^{-1}$ (S32).

7.1 Estimates for the Pd, Ag, Mn and Cr concentrations in the Earth and Mars

Accretion and core formation models using the Pd-Ag and Mn-Cr chronometers require an estimate for the Pd/Ag and Mn/Cr ratios of the BSE and the core. There are different types of models that can be applied to obtain this information (S26, S27). For example, the composition of chondritic meteorites can be used to obtain an estimate for the elemental composition of bulk Earth and together with either (i) experimental metal-silicate partition coefficient or (ii) BSE estimates based on the analyses of terrestrial samples, the elemental abundances of the BSE and the core can be obtained. For this work, we estimated the Pd/Ag and Cr/Mn ratios of bulk Earth from their correlation with U/K in chondrites (Fig. S2). These correlations yield a Pd/Ag and Mn/Cr ratio for bulk Earth of 12.9 and 0.30, respectively. The bulk Earth Mn/Cr ratio of 0.30 is in good agreement with previous work [Mn/Cr = 0.34 ± 0.07 (S23)]. McDonough (S27), however, proposed a lower value of 0.17. The Pd/Ag ratio estimated here is lower than previous
estimates \([\text{Pd/Ag} = 19.2 \ (S26); \text{Pd/Ag} = 20 \ (S27)]\). A higher bulk Earth Pd/Ag ratio of 
\(~20\) results in an even shorter timescale (a few Myr) for terrestrial core formation, if the 
Earth accreted from volatile-deleted material only (Fig. 1). Although such a high Pd-Ag 
ratio would reinforce our reasoning, we prefer the lower estimate of 12.9, because of the 
well-defined U/K - Pd/Ag correlation for carbonaceous chondrites (Fig, S2; \(R=0.9954\)). 

The Ag concentration of the bulk Earth was estimated based on Na, which is an 
element with a similar half mass condensation temperature as Ag \([\text{Ag}= 996\text{K} \text{ and} \ \text{Na}=958 \text{ K} \ (S24)]\). Using the depletion trend of Na relative to the refractory element Ti in 
chondrites \((S27)\), a value of 46 ppb for Ag in the bulk Earth was obtained, in agreement 
with previous work \((S26, S27)\). This Ag concentration corresponds to a bulk Earth Pd of 
592 ppb based on the U/K correlation (Table S2). Interestingly, McDonough \((S27)\) 
obtained lower Mn and higher Pd concentrations (Table S2) than the estimates that use 
elemental abundances in meteorites \([e.g., \ (S26, this \ study)]\). This is most likely because 
McDonough \((S27)\) took a different approach that is based on the iron content of the core, 
the BSE abundances for Fe, Cr and V and chondritic ratios of these elements in the bulk 
Earth. If our heterogeneous accretion model is calculated using the Pd, Ag, Mn and Cr 
values recommended by McDonough \((S27)\), this does not jeopardize the heterogeneous 
accretion scenario, but it increase the amount of volatile-rich material required at the end 
of accretion from \(~13\% \text{ to } ~21\%\).

The bulk composition of Mars is clouded in large uncertainties due to the limited 
availability of Martian samples. We adopted the Mn and Cr values from \((S33)\), which are 
in good agreement with other studies \((S34, S35)\) and propose a volatile-rich Martian bulk 
composition. A bulk Mars Pd/Ag ratio of 4.1 was estimated from the Pd/Ag - Cr/Mn 
correlation and the Ag concentration was estimated from the chondritic Pd/Ag - 1/Ag 
correlation (Fig. S3).

7.2 Parameters used in Figure 1, 2 and 3:

The effect of variations in the Pd/Ag ratios and Pd and Ag concentrations of BSE 
(Fig. 1A): Figure 1A shows two solid curves for BSE Pd/Ag ratios of 0 and 2, 
respectively, which yield slightly different ages for terrestrial core formation. These small 
variations, however, do not affect our model conclusion. The illustrated variations in BSE 
Pd/Ag ratios can account for two end member scenarios: (i) all the Pd in the mantle 
originates from the late veneer \((\text{Pd/Ag} = 0 \text{ for the mantle prior to the late veneer}) \ [e.g., 
(S36)]) or (ii) the current Pd in the mantle is left from incomplete partitioning into the core 
[e.g., \((S37)]\). Moreover, variations in the Pd/Ag ratio of BSE between 0 and 2 can account 
for BSE Ag contents \(\geq 3\) ppb. Current estimates of BSE Ag contents range from 4 to 8 
ppb \((S27, S29, S38)\), but could also be higher as suggested from Table S1, where mantle 
rocks display Ag contents up to 22 ppb Ag, potentially due to the inhomogeneous 
distribution of Ag-rich sulfides. Our model calculations (Fig. 1) are not sensitive to 
variations of BSE Ag contents above the 3 ppb limit. The exclusive accretion of volatile 
depleted materials, therefore, yields exceedingly short core formation ages (compared to 
the Hf-W ages), regardless of the uncertainties in Pd/Ag ratios or in the efficiency of core 
segregation of Pd.

Metal-silicate partitioning coefficients of Ag and Pd (Fig. 1B): the calculations 
for the continuous core formation model used metal-silicate partitioning coefficients of 
\(D_{\text{Ag}} = 15\) and \(D_{\text{Pd}} = 500\). The metal-silicate partitioning coefficients of \(D_{\text{Pd}} = 500\) may
seem low, given that there is evidence that $D_{Pd}$ could be as high as $10^5$ to $10^6$ [e.g., (S36)]. The latter corresponds to the case where all the Pd is delivered by the late veneer, while $D_{Pd} = 500$ describes the other end-member scenario (no Pd delivered by the late veneer). Our model output remains the same regardless if $D_{Pd} = 500$ or a higher value is applied. This is because the resultant changes in the total terrestrial Pd budget are small: the modeling is little affected if 99.6% ($D_{Pd} = 500$) or 99.97% ($D_{Pd} = 10^4$) of the Pd resides in the core.

**Metal-silicate equilibration (Fig. 1B and Fig. 2):** two-stage models automatically assume complete isotopic equilibration between the mantle and the core. For the more realistic continuous core formation model, accreting materials equilibrate only with the terrestrial mantle and the degree of equilibration can be varied ($f = 0$ to 1). The model curves in Fig. 1B were calculated for complete metal-silicate equilibration ($f = 1$), while Fig. 2 investigates the effect of incomplete metal-silicate equilibration assuming volatile-depleted precursor material with Pd/Ag$_{(precursor)} = 8.5$. Model parameters are the same as in (S16). Core formation ages (= the time of the giant impact) and the corresponding degrees of metal - silicate equilibration obtained from Hf-W are shown in Fig 2A. Figure 2B provides the $\varepsilon^{107}_{\text{Ag}}$ of the BSE that results from using a given pair of these parameters. For example, equilibration of 50% ($f = 0.5$) of the metal from each impactor with BSE results in a Hf-W model age of ~ 60 Myr (Fig. 2A, line with crosses). Using this 60 Myr core formation age and $f =0.5$ for the Pd-Ag model yields a BSE $\varepsilon^{107}_{\text{Ag}}$ today of -0.9. The Ag isotope composition of the BSE measured today (Fig. 2B, hatched area) does not overlap with any of the model results, suggesting that incomplete metal-silicate equilibration cannot reconcile the apparently short Pd-Ag core formation ages with the Hf-W constraints, if a similar degree of disequilibrium for both Ag and W isotopes under identical accretion conditions is assumed.

**Parameters for heterogeneous accretion (Fig. 3):** All calculations for the heterogeneous accretion scenario used the continuous core formation model. The calculations assume complete metal-silicate equilibration and use metal-silicate partitioning coefficients of $D_{\text{Mn}} = 1.1$ and $D_{\text{Cr}} = 3$, except for metal-silicate partitioning within Theia, where $D_{\text{Mn}} = D_{\text{Cr}} = 0$, because Cr is expected to remain lithophile in a Mars-size body (S39). For the Pd-Ag system, metal-silicate partition coefficients of $D_{\text{Ag}} = 15$ and $D_{\text{Pd}} = 500$ were applied throughout. Parameters for the precursor material are: volatile-poor material: Pd/Ag = 12.9 and Mn/Cr = 0.30, CI-like precursor: Pd/Ag = 2.8 and Mn/Cr = 0.73, Mars-like precursor: Pd/Ag = 4.1 and Mn/Cr = 0.61. Also used was the decay constant $\lambda^{53}\text{Mn} = 0.1873 \times 10^{-6} \text{ yr}^{-1}$ and $\varepsilon^{53}\text{Mn}_{(\text{solar system initial})} = -0.16$. 

S6
Figure S1: No correlation is observed between the chemistry yield of the basalt samples and their Ag isotope compositions.
Figure S2: The Pd/Ag ratios correlate with U/K in carbonaceous chondrites. The best-fit line is calculated for the carbonaceous chondrite data only. Data from (S2, S26, S40).
Figure S3: Left diagram shows that Cr/Mn ratios correlate with Pd/Ag in carbonaceous chondrites. The data for Mars was excluded from the regression calculation. The right diagram illustrates the linear correlation between Pd/Ag ratios and inverse Ag concentrations of CI, CM and CV chondrites. Data from (S2, S21, S23).
Table S1: Silver isotope compositions and Pd and Ag concentrations for different terrestrial rocks

<table>
<thead>
<tr>
<th>Sample</th>
<th>Type and location</th>
<th>Pd (ppb)</th>
<th>Ag (ppb)</th>
<th>Pd/Ag</th>
<th>2 sd</th>
<th>ε$^{107}$Ag</th>
<th>2 sd</th>
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<td>PM16A</td>
<td>Spinel lherzolite, San Carlos, Arizona</td>
<td>1.4</td>
<td>1.6</td>
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<td>PM251A</td>
<td>Spinel lherzolite, San Carlos, Arizona</td>
<td>1.9</td>
<td>5.5</td>
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<td>0.003</td>
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<tr>
<td>LS-33</td>
<td>Garnet lherzolite, Patagonia</td>
<td>3.4</td>
<td>22</td>
<td>0.156</td>
<td>0.002</td>
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<td>ALV 519-4-1</td>
<td>MORB glass, Mid-Atlantic Ridge</td>
<td>8.3</td>
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<td>0.003</td>
<td>-2.6</td>
<td>0.7</td>
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<tr>
<td>AII0093-6-11-1</td>
<td>MORB glass, Southeast Indian Ridge</td>
<td>0.5</td>
<td>15</td>
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<td>0.007</td>
<td>-2.3</td>
<td>0.7</td>
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<td>ML-2-50</td>
<td>Picrite, Mauna Loa, Hawaii</td>
<td>3.2</td>
<td>33</td>
<td>0.096</td>
<td>0.001</td>
<td>-2.5</td>
<td>0.7</td>
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<td>KS-87-03</td>
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<td>0.097</td>
<td>0.001</td>
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<td>0.7</td>
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<tr>
<td>duplicate</td>
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<td>H11</td>
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<td>0.001</td>
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<tr>
<td>LO-02-02</td>
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<td>42</td>
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<td>0.7</td>
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<td>85-41b</td>
<td>Magnesian andesite, Mt. Shasta, California</td>
<td>1.5</td>
<td>60</td>
<td>0.025</td>
<td>0.005</td>
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<tr>
<td>85-44</td>
<td>Basaltic andesite, Mt Shasta, California</td>
<td>11.3</td>
<td>38</td>
<td>0.297</td>
<td>0.003</td>
<td>-2.5</td>
<td>0.7</td>
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<td>BCR2</td>
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<td>35.3</td>
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<td></td>
<td></td>
<td></td>
<td>-2.2</td>
<td>0.7</td>
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</table>

The Ag isotope composition is expressed in ε$^{107}$Ag, which is the deviation from the terrestrial NIST SRM978a Ag standard in parts per 10$^4$. The average of the ε$^{107}$Ag values for all samples is shown together with the 2-sigma standard deviation. An analytical uncertainty of ± 0.7 is adapted for ε$^{107}$Ag based on replicate measurements of a terrestrial basalt (S1).
Table S2: The Pd, Ag, Mn and Cr concentrations for bulk Earth and Mars

<table>
<thead>
<tr>
<th></th>
<th>Pd</th>
<th>Ag</th>
<th>Pd/Ag</th>
<th>Mn</th>
<th>Cr</th>
<th>Mn/Cr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk Earth&lt;sup&gt;a&lt;/sup&gt;</td>
<td>592</td>
<td>46</td>
<td>12.9</td>
<td>1275</td>
<td>4250</td>
<td>0.30</td>
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<tr>
<td>Bulk Earth&lt;sup&gt;b&lt;/sup&gt;</td>
<td>1000</td>
<td>50</td>
<td>20.0</td>
<td>800</td>
<td>4700</td>
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<tr>
<td>Bulk Mars&lt;sup&gt;a&lt;/sup&gt;</td>
<td>620</td>
<td>150</td>
<td>4.1</td>
<td>2250</td>
<td>3680</td>
<td>0.61</td>
</tr>
</tbody>
</table>

<sup>a</sup>Values used for modeling  <sup>b</sup>Data from (S27)  <sup>c</sup>Data from (S33)

References to Supporting Online Material