

Partitioning of palladium at high pressures and temperatures during core formation

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An early equilibration of the Earth's mantle with the metals that later formed the core may explain the concentrations of iron-loving (siderophile) elements in the mantle. However, a subset of these elements, the highly siderophile elements including palladium, are present in greater concentrations than expected. Moreover, their relative ratios are similar to those found in chondrites, that is, primitive solar-system materials^{1–4}. On the basis of very high partition coefficients for these elements derived from experiments at low pressures and temperatures (for example, a coefficient for palladium $> 10^4$), it has been argued that the high mantle concentrations of the highly siderophile elements and also of volatile elements originated from the addition of chondritic material after core formation as a 'late veneer'^{1–4}. Here we present experiments at higher pressures and temperatures that approximate the conditions of early Earth, and find much lower partition coefficients for palladium, about 480, consistent with an equilibration scenario. This obviates the need for a late veneer to explain the terrestrial-mantle palladium content, and calls into question traditional explanations for the origin of the Earth's volatile elements.

One of the most elusive geochemical aspects of the early Earth has been explaining the near-chondritic relative abundances of the highly siderophile elements (HSEs; Au, Re and the platinum-group elements) in Earth's primitive upper mantle (PUM). Perhaps they were delivered to the Earth after core formation, by late addition of carbonaceous chondrite material (see refs 1–4 and references therein). Furthermore, this late chondritic material is commonly cited as the source of the Earth's volatiles, such as water and carbon (see, for example, refs 1,2). However, many moderately siderophile elements (for example Ni, Co, W) can be explained by high-pressure-and-temperature (PT) metal–silicate equilibrium⁵. In addition, suprachondritic Pd/Ir and Ru/Ir ratios have been documented in a number of primitive mantle peridotites, suggesting Pd was not necessarily added with the late veneer^{6,7}. These two lines of evidence lead to the question of whether high-PT equilibrium can also explain the HSE concentrations.

Answers to this question have been slowed by experimental difficulties (nugget effect and very low solubilities⁸), but two different perspectives have emerged from recent studies. One perspective is that metal/silicate partition coefficients D (M/S) for HSEs at high PT are not low enough to explain terrestrial mantle depletions of these elements (for Pd and Pt (refs 9,10)). A second perspective is that D (M/S) values are reduced substantially at high PT and even low enough to explain terrestrial mantle depletions (for Au and Pt (refs 11,12)). Issues complicating interpretation of

all experiments include use of MgO- and FeO-free silicate melts, and S-free and FeNi-metal-free (and HSE-metal-rich) systems. In addition, conclusions for Pt rest on an interpretation that the tiny metallic nuggets plaguing many such experiments were formed on quench¹². There is no agreement on this issue, and the general question of HSE solubility at high PT remains unresolved.

Key to resolution of this problem is the ability to work in nugget-free, uncompromised conditions, and to use experimental compositions that approximate those of the early Earth (that is, peridotitic melts and S- and C-bearing FeNi metallic liquids). In order to address this problem, we have undertaken a new series of experiments with the HSE Pd. Pd was chosen for two reasons. First, it is well understood at low pressures, with several studies across a range of temperatures and oxygen fugacities (f_{O_2}) (refs 13,14), silicate melt compositional effects are thought to be small¹⁴ and its behaviour in S-bearing systems is well known¹⁵. Second, nugget formation is not reported down to low f_{O_2} , equivalent to IW-1 (ref. 13), making analysis and interpretation more straightforward than other nugget-affected elements such as Pt (refs 9,10,12). New experiments at high pressure and temperature were conducted at NASA Johnson Space Center (see the Supplementary Information), and analysed for Pd at low concentration levels using laser-ablation inductively-coupled-plasma mass spectrometry at Florida State University (FSU) (see the Supplementary Information). Experimental runs were devised to study the effect of temperature, pressure and melt composition, with Fe-rich metal and FeO-bearing and MgO-rich silicate melts.

Metal/silicate partition coefficients for Pd (or D (Pd) M/S = wt% Pd in metal/wt% Pd in silicate melt) have been measured for 11 experimental runs at pressures between 1.5 and 15.0 GPa, and temperatures from 1,400 to 2,150 °C (see Supplementary Information, Table S1). Experiments in graphite capsules have lower D (Pd) owing to equilibration at a slightly higher oxygen fugacity, and also owing to smaller affinity for Pd in C-bearing metallic melt¹⁶. Those in MgO capsules equilibrated at lower f_{O_2} and have higher D values (Fig. 1). Both series show important variation in D ; the C-capsule series shows a small increase with increasing temperature, whereas the MgO-capsule series shows a large decrease with temperature. The greater decrease in the MgO-capsule series is due to increasing depolymerization of the silicate melt, an effect also observed over a small melt compositional range in ref. 14. The very high-pressure (and temperature) runs show even lower values, as low as 500. These new results show that D (Pd) M/S decreases substantially at higher pressures and temperatures, and approaches the value

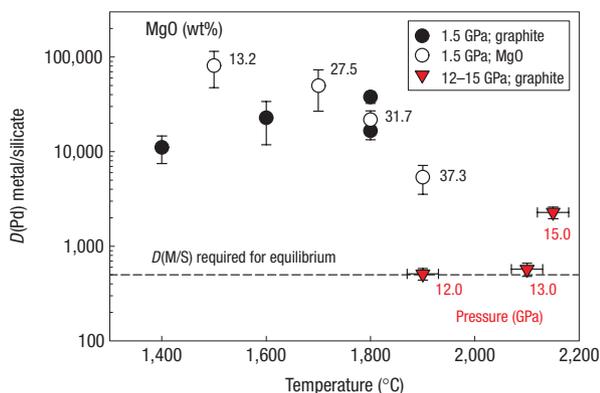


Figure 1 Temperature variation of $D(\text{Pd})$ M/S. New $D(\text{Pd})$ M/S results showing variations in D with temperature, pressure and melt composition. The series of experiments at 1.5 GPa in C capsules shows only a small increase with temperature. The series with MgO capsules shows a large decrease with temperature, reflecting silicate melt compositional changes from MgO = 13 to 37 wt% from 1,500 to 1,900 °C. All three experiments at high pressures (12–15 GPa) have lower $D(\text{Pd})$ than all 1.5 GPa experiments, illustrating the significant pressure effect. The horizontal line shows the value of $D(\text{Pd})$ required to explain the primitive upper mantle concentration of Pd by an equilibrium process ($D = 480 \pm 80$). Error bars for $D(\text{Pd})$ are based on two-sigma error on Pd measurements in metal and silicate, and those for temperature are based on uncertainties discussed in the Supplementary Information.

(~ 480 ; see Supplementary Information, Table S2) required to explain the upper-mantle Pd content (Fig. 1; also predicted by ref. 8 on the basis of a more limited dataset).

The new $D(\text{Pd})$ values reported here are lower than those from high-PT experiments reported previously⁹, which can be attributed to several differences. First, there are large compositional differences: experiments of ref. 9 involved K_2O - and SiO_2 -rich, FeO-poor and MgO-free silicate melts, whereas the current study uses FeO-bearing and MgO-rich silicate melts, which would be expected in an extensively molten terrestrial mantle. Second, the differences in melt composition lead to very different high-PT volumetric properties of the melts. For example, the partial molar volume of K_2O in silicate melt is 47.28, compared with 12.02 for MgO (ref. 17), and there are similar large differences between the compressibilities of K_2O - and MgO-rich silicate melts (-1.3 versus $-14.5 \times 10^{-7} \text{ mol cm}^{-3} \text{ bar}^{-1} \text{ K}^{-1}$) (ref. 18)). As a result, the high-PT experiments of ref. 9 report a much stronger pressure effect compared with the current work, owing to different volumetric properties of the melts. Third, the experiments of ref. 9 involve S- and C-free metallic liquids, and the current study uses FeS and Fe–S–C liquids. The participation of light elements S and C is known to decrease $D(\text{Pd})$ ¹⁶ and is also expected in natural systems. All of these factors combined lead to different results between the current study and previous work, and highlight the importance of using experimental materials and conditions that more closely approach those expected in nature.

It is possible to combine our new data with previous work to derive a predictive expression for $D(\text{Pd})$ M/S as a function of pressure P , temperature T , $f\text{O}_2$, silicate melt and metallic liquid composition. The temperature dependence of $D(\text{Pd})$ is based on ref. 13 and this study, the oxygen-fugacity dependence is based on refs 13,14, the effect of metallic liquid S is based on ref. 15 (also known from ref. 15), the effect of melt composition is based

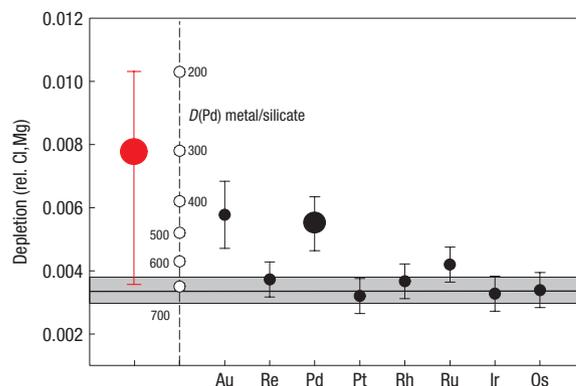


Figure 2 Mantle depletions of highly siderophile elements. Terrestrial mantle depletions of all the HSEs (values and uncertainty for each element are from ref. 6) in the terrestrial mantle normalized to CI chondrites and Mg (values from ref. 25; see also the Supplementary Information). The heavy horizontal line with the shaded box is the value for $0.0030 \times \text{CI chondrites}$ with uncertainty⁶; clearly five of these elements fall within the CI chondritic shaded box. However, the non-chondritic Au, Pd and Ru values (relative to other HSEs) suggest that simple late chondritic additions cannot explain all the HSEs. Shown at the left edge are calculated HSE depletions expected if $D(\text{HSE})$ metal/silicate were 200, 300, 400, 500, 600 and 700. For comparison, the calculated $D(\text{Pd})$ value from our new results and regression 2 (in Supplementary Information) is $300(+400/-100)$. Also, partition coefficients from two of our experiments are $500(\pm 60)$ and $570(\pm 90)$, and would be capable of producing the Pd depletions (see Supplementary Information, Table S1).

on results from this study and ref. 14 and finally the effect of pressure is based on this study and ref. 9. The form of the predictive equation is

$$\ln D(\text{Pd}) = a \ln f\text{O}_2 + b/T + cP/T + d \ln(1 - X_S) + e \ln(1 - X_C) + f(\text{nbo}/t) + g \quad (1)$$

where the coefficients a – g are derived by multiple linear regression of 118 experiments (see the Supplementary Information) from these systematic datasets (a similar approach is used, for example, in refs 19–21). Compositional terms X_S and X_C are the mole fractions of sulphur and carbon, respectively, in the metal phase, and nbo/t is the ratio of non-bridging oxygens to tetrahedrally coordinated cations in the silicate melt. Coefficients derived using this approach (see Supplementary Information, Table S3) can be used to calculate $D(\text{Pd})$ as a function of the controlling variables, and thus to evaluate different models for conditions on the early Earth. For example, use of equation (1) (and regression 2) to calculate a $D(\text{Pd})$ M/S at the P – T – $f\text{O}_2$ – X conditions of $230(\pm 50)$ kb, $2,000(\pm 200)$ °C, $\Delta \text{IW} = -2$, $X_S = X_C = 0$ and $\text{nbo}/t = 2.7$ (similar to those suggested in ref. 21 for the early Earth and where ΔIW is the oxygen fugacity relative to the iron wüstite oxygen buffer) results in a value of $300 (+400/-100)$, very similar to the value required for core–mantle equilibrium ($D(\text{Pd}) = 480$; Fig. 2). Similar values (albeit with slightly larger error) are calculated using the other two regression analyses (as explained in the Supplementary Information). The uncertainty in the calculated PT conditions is based on how much variation in pressure or temperature is tolerable before $D(\text{Pd})$ becomes too small or large for a fit. Uncertainties in relative oxygen fugacity are difficult to constrain, but they are set at $\text{IW} - 2$ to be consistent with the Fe and FeO contents of the Earth's PUM and core. Finally, it is also worth noting that partition coefficients from two of our

experiments are $500(\pm 60)$ and $570(\pm 90)$, and would be capable of reproducing the Pd depletions (see Supplementary Information, Table S1), even at these modest PT conditions.

Furthermore, calculated $D(\text{Pd})/M/S$ values at even higher-PT conditions (for example, ~ 40 GPa, $\sim 3,000$ K, suggested by refs 22,23) are much lower, between 5 and 20, resulting in Pd concentrations far higher than observed in the PUM (Fig. 2). Prediction of $D(\text{Pd})$ at these much-higher-PT conditions involves extrapolation outside the datasets used to calibrate equation (1), and should thus be interpreted with caution until additional high-PT data are acquired to confirm. Nonetheless, it seems that $D(\text{Pd})/M/S$ becomes too low at very high-PT conditions.

In summary, metal–silicate equilibrium at PT conditions of an intermediate-depth magma ocean may thus be an explanation for suprachondritic Pd/Ir of the PUM⁶. Along with these new results for Pd, recent work on Au (ref. 11) and Pt (ref. 12) has demonstrated that the concentration of these elements can be explained by high-PT metal–silicate equilibrium. This raises the possibility that the late veneer might not be sufficient for explaining the HSE concentrations in the primitive terrestrial mantle. Given the current state of understanding of experimental systems, it seems there are two possibilities for the HSE. One is that the late veneer is not required for any of the HSE concentrations in the primitive terrestrial mantle, but this conclusion may be premature owing to the paucity of reliable high-PT partitioning data for several of the HSEs, such as Os, Ir, Rh and Ru. A second scenario is that several of the HSEs (Pd, Au and Pt) can be explained by high-PT metal–silicate equilibrium, whereas the late veneer is required only for a subset of the HSEs (Os, Ir, Ru and Rh). This ‘hybrid’ model would involve a combined high-PT and late-veneer origin for the HSEs, and could even produce superchondritic Pd, Au and Pt observed in some peridotite suites (see, for example, ref. 6 and references therein). A resolution to these two scenarios is possible because they are testable. Guided by the results of calculations such as those here, additional studies of other HSEs (Re, Rh, Ru, Os and Ir) and volatile elements (Te, Cd and so on; ref. 24) at targeted high-PT conditions and on compositions relevant to the early Earth (for example, FeNi metallic liquid and peridotite melt) are required to evaluate whether the late-veneer hypothesis is necessary for any of the HSEs in light of these new results.

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Author contributions

K.R. conceived the project, carried out low-pressure experiments and analysed run products, M.H. analysed trace elements in metals and glasses using laser-ablation inductively-coupled-plasma mass spectrometry, L.D. carried out pressure calibrations and higher-pressure experiments and all authors contributed to interpretation of the data.

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