CORE FORMATION, HSE PARTITIONING AND NON-EQUILIBRIUM PROCESSES.   William F.
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Introduction: The compositional characteristics of the Earth's core-mantle system are best described by a model that recognizes that the present upper mantle is not in equilibrium with the core and that metal-silicate differentiation was in response to secular changes in equilibrium conditions [1-5 and references therein]. That said, however, the silicate Earth has chondritic relative abundances of the HSE (highly siderophile elements, Ru, Rh, Pd, Re, Os, Ir, Pt, and Au) that are ~100-fold depleted relative to chondritic meteorites [6-7]. These HSE characteristics are commonly interpreted as reflecting their late stage (post-core formation) introduction into the silicate Earth, typically invoked as an exogenic contribution (or Late Veneer) [1]. Alternatively, others propose that HSE abundances in the silicate Earth are the result of an equilibrium process [8-10 and references therein] between metal and silicate at P-T-X-fO_2 conditions that satisfy the compositional constraints.

Equilibrium models for core-mantle differentiation require metal-silicate partitioning to be similar for all the HSE, with values of 200-800. Experiments documented partitioning in excess of 10^6 for all the HSE at modest temperatures (circa 1500-1900 K) and higher temperature experiments reveal lower partitioning values for some HSE, although the convergence of partitioning at high temperature for all the HSE has not been confirmed. Results of metal-silicate partitioning experiments for osmium and gold and show that, for conditions approximating core-formation, partitioning of osmium likely exceeds 10^7, and the relative partitioning of osmium to gold is $>10^4$. In the context of equilibrium core formation models, these results are irreconcilable and require the addition of HSE-bearing material to the mantle following core formation.

Methods: Experiments employed samples consisting of synthetic basalt plus a metal mixture, encapsulated in high purity graphite. The added metal mixture contained Au-encapsulated osmium, or in a few cases, Fe powder mixed with 1 to 10 wt% of Au or Au + Os. In the former configuration, preferential wetting of the Os grains by Au texturally isolates the Os from the silicate melt. This configuration inhibits Os nugget formation, which we have found to be a pernicious aspect of experiments containing this element. Experiments were done at temperatures of 2175-2590 K, at a fixed pressure of 2 GPa, using a piston-cylinder apparatus, and employing standard techniques. The amount of Fe dissolved in Au coexisting with FeO-bearing molten silicate was used to calculate the oxygen fugacity, which is expressed here relative to the iron-wustite (IW) buffer. Run products were analyzed for major elements by electron microprobe, and trace elements by laser ablation (LA) ICP-MS. Time-resolved spectra obtained from experiments which were initially metal under-saturated show a uniform distribution of Os and Au, consistent with homogeneous solution of these elements in the silicate melt. The exception is experiments done at the highest temperature investigated (2588 K) which yielded very high concentrations of Au, but a less homogeneous distribution, likely due to metal exsolved on quench, consistent with prograde Au solubility. We assessed equilibrium in our experiments by approaching metal solubilities from both over- and under-saturated conditions. Time-resolved spectra from experiments which were initially oversaturated were generally homogeneous, but showed some high signal intensity glass domains, which are likely to represent residual material from the initial saturation step. These domains were not included in the calculation of metal abundances.

Results: Experiments with Os and Au diluted in the Fe alloy, values of $D^{metal/silicate}$ are calculated directly from the ratio of concentrations in the coexisting metal and silicate phases. Other experiments contained nearly pure solid Os coexisting with Os-free molten Au-Fe alloy. For these experiments metal-silicate partition coefficients are calculated using the silicate melt concentrations of these elements and account for the change in Os or Au activity following dilution in Fe metal [11]. Figure 1 portrays metal-silicate partition coefficients for Os and Au as function of temperature from this and previous studies. Results for experiments done at nearly the same relative oxygen fugacity of ~IW+2 (except for the experiments of Brenan et al., [12] done at IW+4; specific values of relative fO_2 are provided in the figure caption) are shown. Partitioning data show an offset of Os from Au partitioning of ~10^4.

Figure 2 shows Os D-values increase in partitioning with decreasing fO_2, consistent with solution of Os as an oxide species in the silicate melt. Results for Au show a slight drop in partitioning with decreasing fO_2. At 2588 K and IW-1.5, which is the lowest fO_2 of our study, and only ~1 log unit more oxidized than likely core-forming conditions, the metal-silicate partition coefficient for Au is ~330, whereas the minimum value for Os measured in the same experiment is ~10^7, indicating a minimum difference in partitioning of ~10^4. Predicted equilibrium core separation leaves

behind a mantle with depleted Au abundances, highly impoverished in osmium and non-chondritic Os/Au, which is not observed and is also inconsistent with osmium isotopic evolution of the mantle. Thus, the silicate Earth's HSE composition is irreconcilable in the context of metal-silicate equilibrium models, as neither the effects of temperature or fO_2 on metal-silicate partitioning can account for the "excess" of osmium in mantle rocks.

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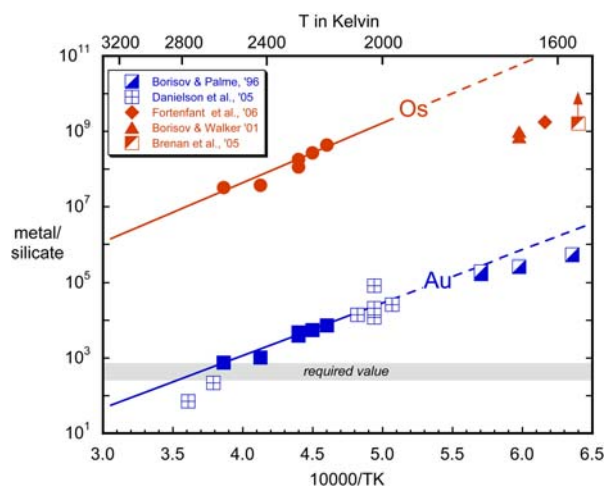
Fig. 1. Metal-silicate partition coefficients for osmium and gold as a function of inverse absolute temperature. Data from this study (filled circles and squares) are calculated from solubility experiments done at 2 GPa and a nearly constant relative oxygen fugacity of ~IW + 2. Solid and dashed lines were calculated by weighted least squares linear regression of the data, and the fit equations are: $\log D_{Os} = 1.32(0.41) + [1.58(0.09) \times 10^4]/TK$ and $\log D_{Au} = -2.53(1.09) + [1.40(0.24) \times 10^4]/TK$. Additional Au partitioning values are from a) Danielson et al. [13] done at pressures of 3-23 GPa and fO_2 of IW-1.2 to -2.45 and b) calculated from the gold solubility measurements of Borisov and Palme [14] done at a pressure of 0.1 MPa and ~IW+2. Other values for osmium are calculated from the 0.1 MPa metal solubility data of Borisov and Walker ([15]; IW+2.1), Brenan et al. ([12]; IW+4), and Fortenfant et al. ([16]; IW+2). Data points with upward-pointing arrows are minimum values corresponding to experiments in which the osmium concentration in the glass phase is below detection. The field denoted as "required value" corresponds to the metal-silicate partition coefficient necessary to account for the abundances of these elements in the primitive mantle. See the text for details of converting solubility measurements to metal-silicate partition coefficients.
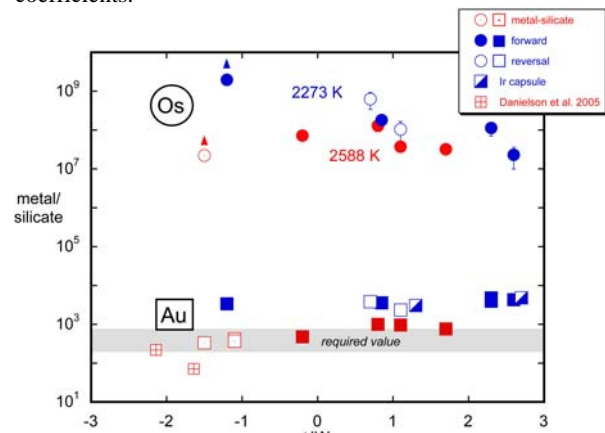

Fig. 2. Metal-silicate partition coefficient for osmium and gold as a function of the oxygen fugacity relative to the iron-wustite buffer. The oxygen fugacity estimated for core-forming conditions is approximately IW-2. Most partition coefficients are calculated from the solubility of the pure metal, but data denoted as "metal-silicate" are direct determinations from experiments employing an iron-rich metal phase (including the experiments of Danielson et al., [13]). In forward experiments, silicate melts were initially under-saturated in the metal of interest, and achieve saturation by dissolution of an added metal source. Reversal experiments were done by first saturating the silicate melt at 2588 K, then re-equilibrating the experiment at a 2273 K, in which the metal solubility is lower.