IMPLICATIONS FOR CORE FORMATION OF THE EARTH FROM HIGH PRESSURE-TEMPERATURE AU PARTITIONING EXPERIMENTS.

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Introduction: Siderophile elements in the Earth's mantle are depleted relative to chondrites. This is most pronounced for the highly siderophile elements (HSEs), which are ~400x lower than chondrites [1]. Also remarkable is the relative chondritic abundances of the HSEs. This signature has been interpreted as representing their sequestration into an iron-rich core during the separation of metal from silicate liquids early in the Earth's history, followed by a late addition of chondritic material [2].

Alternative efforts to explain this trace element signature have centered on element partitioning experiments at varying pressures, temperatures, and compositions (P-T-X). However, first results from experiments conducted at 1 bar did not match the observed mantle abundances, which motivated the model described above, a "late veneer" of chondritic material deposited on the earth and mixed into the upper mantle. Alternatively, the mantle trace element signature could be the result of equilibrium partitioning between metal and silicate in the deep mantle, under P-T-X conditions which are not yet completely identified. An earlier model [3] determined that equilibrium between metal and silicate liquids could occur at a depth of ~700 km, 27(±6) GPa and ~2000 (±200) ℃, based on an extrapolation of partitioning data for a variety of moderately siderophile elements obtained at lower pressures and temperatures. Based on Ni-Co partitioning, [4] suggest that the magma ocean may have been as deep as 1450 km. At present, only a small range of possible P-T-X trace element partitioning conditions has been explored, necessitating large extrapolations from experimental to mantle conditions for tests of equilibrium models.

Objective: Our primary objective was to reduce or remove the additional uncertainty introduced by extrapolation by testing the equilibrium core formation hypothesis at P-T-X conditions appropriate to the mantle.

Experiments: A natural chondrite, Richardton H5, was chosen as the starting material to simulate partitioning in the early Earth because: 1) its bulk composition represents a likely component of the Earth, 2) the sulfur content of the metallic fraction is 12%- in the range of modeled S contents of the Earth's core (8-12%; [5,6]), 3) the calculated oxygen fugacity (fO_2) of the starting material [7] is approximately one log unit below the iron-wüstite (Fe-FeO) buffer, and 4) there is abundant material for the experiments. Expecting low levels of Au in the silicate fraction, the starting material was doped with 1.2 wt% Au_2S. Super-liquidus experiments were performed in a Walker-type multi-anvil (at ASU) or piston cylinder apparatus (at ANU), for pressures below 5 GPa. Pressures from 9-13 GPa were obtained using an 8mm truncated edge length (TEL) on the WC cubes. Experiments at 19-23 GPa used a 3mm TEL assembly. Experiment temperatures were 1700-1800 ˚C (3-13 GPa) and 2250-2500 ˚C (19-23 GPa) and were approximately 100 °C above the liquidus. Run durations were 3 to 8 minutes (Table 1). The samples were contained in MgO capsules to contain the silicate and metallic melts while minimizing run product compositional divergence from the bulk Earth.

Analyses: Samples quenched to a polycrystalline mass. Defocused-beam electron probe analyses of the polyphase quench products gave major element chemistry of the two quenched liquids, including Au in sulfide. Reaction between the MgO capsule and the sample resulted in compositions more similar to the bulk silicate earth in FeO and MgO [8,9]. Au contents of the quenched silicate liquid were obtained using secondary ion mass spectrometry in depth profiling mode [10]. The analyses used a Cameca ims 3f and 6f SIMS with a primary beam of K^+ ions and detection of negative secondary ions with 50±20 eV excess kinetic energy, and a primary beam of Cs^+ ions and detection of negative secondary ions at high mass resolving power. A normal incidence electron gun was used for charge compensation and the Au signal was calibrated by comparison with NIST SRM glasses 610, 612, and 614 using the bulk analyses of [11].

Results and Discussion: *The nugget problem:* Nanometer scale blebs of Au-rich material were commonly encountered during these analyses as indicated by temporary increases in the count rate for Au. The Au associated with the blebs could thus be removed from the silicate component for the calculation of partition coefficients (if the blebs were present at high P and T) or included in the silicate (if the blebs represent exsolution from the silicate liquid during the quench). The similarity of the Fe/Ni ratios in the blebs (from analytical TEM) and the larger iron-sulfide quench products suggests that microblebs were present at P and T and so the associated Au signal was removed from the silicate analysis, maximizing the value of D(Au)$_{met/sil}$.

Au partitioning: Partition coefficients for Au are displayed in Table 1. Values of D(Au)$_{met/sil}$ range from ~ 3×10^4 to 100 as pressures increase from 3 to 23 GPa. D(Au)$_{met/sil}$ decreases with increasing P and T, while showing no obvi-

ous trend with changes in fO_2. In the table below, fO_2 is reported in log units relative to iron-wustite (IW), assuming ideal behavior of Fe in metal and FeO in silicate. If activity coefficients for FeO are used after Holzheid, ΔIW increases by less than one log unit.

Table 1.	t	T	Δ IW	Au_{sil}	P	$D(Au)_{met/sil}$
Label	min	dec C	ideal	ppm	GPa	
C2043	5	1750	-1.2	1.0	3	1.2×10^4
H162	5	1750	-1.2	0.6	5	2.1×10^4
BB176	6	1800	-2.22	3.27	9	1.4×10^4
BB172	4.3	1700	-2.27	3.71	11	2.6×10^4
BB175	8.5	1750	-2.45	3.40	13	8.3×10^3
BB209	5.5	2494	-1.64	443	21	71
BB206	8	2368	-2.14	140	23	219

Although it is expected that sulfur will have a profound effect on changing HSE partitioning P, T and fO_2 may also be strong contributors to changes in partitioning behavior. Holzheid et al. [12] suggest pressure has no effect on partitioning behavior, while increasing temperature decreases $D(HSE)_{met/sil}$. Borisov and Palme [13] show decreasing HSE solubility with decreasing fO_2 and suggest that Au solubility in silicate liquids may be independent of fO_2 below IW (if Au-metal mixing behavior is ideal). At relatively low pressures, [13] measured D(Au) of $\sim 10^7$ in sulfur-free systems while Fleet et al. [14] found $D(Au)_{met/sil}$ to be $\sim 10^3$ when 35 wt% sulfur was added to the metallic fraction. Li and Agee [4] show increasing $D(S)_{met/sil}$ with increasing pressure. When these observations are combined, they suggest decreasing $D(Au)_{met/sil}$ is largely the result of changes in $D(S)_{met/sil}$ with increasing P and T.

In order to more fully gauge the relative effects of intensive variables affecting partitioning behavior, a multiple linear regression was performed similar to [3], using the empirical expression: $\ln D(Au)_{met/sil} = a \Delta IW + b\, 1/T + c\, P/T + d\, nbo/t + e \ln(1-X_S) + f$ where the coefficients $a, b, c, d, e,$ and f are constants related to the metal valence (a), the expansion of the free energy equation (b, c, f), the composition of the silicate liquid (d), and the amount of sulfur in the metallic liquid (e). Coefficients determined in this study are given below in Table 2.

Table 2.

a	0.12
b	40156.52
c	8.91
d	-0.08
e	1.13
f	-9.98

We evaluated this model by substituting the resultant best fit equilibrium condition variables from the

Righter and Drake model into the empirical expression above, using our coefficients from Table 2. Results from this calculation give a $D(Au)_{met/sil}$ of 5×10^3, close to the D required to match the abundance of Au observed in the Earth's upper mantle, $\sim 10^3$.

Table 3.	Righter and Drake (1999)	this study
ΔIW	-0.4	-2.3
T (°C)	1977	2127
P GPa	27	27
nbo/t	2.65	2.65
X_S	0.9	0.9
$D(Au)_{met/sil}$	5×10^3	1×10^3

We tested the sensitivity of the model by changing equilibrium condition variables with a range of values that are relevant to the bulk silicate Earth and the primordial accreting Earth. We assumed a lower fO_2 [8,12]. Silicate composition (nbo/t ≈ 2.5 for BSE) and sulfur content of the core for the Righter and Drake model are already close to proposed values for the accreting Earth [5,6,8,9]. In general, the model is relatively insensitive to independent changes in nbo/t or X_S, and is most sensitive to changes in fO_2, T, and P. Changes in P and T are coupled; both must increase to manintain $D(Au)_{met/sil}$ at 10^3.

Conclusions: The results of the parameterization model are consistent with the equilibrium core formation hypothesis. They further suggest that metal-silicate equilibrium may have taken place at a higher T than previous suggested. However, this strengthens the support for a magma ocean scenario because at 27 GPa, this temperature is above the liquidus for Allende [15].

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