1 Thermometry of the magma ocean: Controls on the metal-silicate partitioning of gold

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9 Abstract

10 We have performed experiments to investigate the solubility and metal-silicate partitioning of
11 gold as a function of metal sulphur content (X_s), silicate melt polymerization (NBO/T) and
12 pressure (P). These experiments show that Au becomes less siderophile both with increasing
13 pressure and as the metal phase becomes more sulphur-rich. For the studied range of
14 compositions, melt polymerization has no effect on the solubility of Au. The reduction in the
15 siderophile tendency of gold with increasing metal sulphur content is greater than expected on
16 the basis of activity-composition relationships in the metal phase. This suggests a significant role
17 for complexing between Au and S in the silicate melt. Our new experimental results are
18 combined with literature data to yield a parameterisation for the exchange coefficient of Au
19 ($Kd_{Au}^{Met/Sil}$) as a function of P , T and X_s :

$$\log Kd_{Au}^{Met/Sil} = -1.10 (0.04) + 1.11 (0.01) \frac{10^4}{T(K)} - 67.8 (10.9) \frac{P(\text{GPa})}{T(K)} + 5.81 (0.24) \log(1 - X_s)$$

Using this relationship, alongside similar parameterisations for Ni, Co and V selected from the literature, we performed continuous accretion models to delineate regions of parameter space in which Au and moderately siderophile element (MSE) abundances in the primitive upper mantle (PUM) could be reproduced. These models suggest that for metal-silicate equilibrium at very high pressures, Au will be overabundant in the PUM if equilibrium also occurs at extreme temperatures. Instead, most successful models are found when equilibrium occurs at high pressure but sub-liquidus temperatures. This result is in keeping with the physical conditions expected for a scenario where core-forming metal ponds and equilibrates at the rheological base of a magma ocean (e.g. Wade & Wood 2005).

30

31 **1. Introduction**

Elements with an extreme affinity for iron metal are termed the highly siderophile elements (HSE) and comprise Au, Ir, Os, Pd, Pt, Re, Rh and Ru. During planetary differentiation, liquid iron alloy segregates from molten silicate to form a metallic core composed primarily of iron and nickel. As core segregation proceeds, experiments predict that HSEs will partition into the metal phase, leaving an HSE impoverished mantle with fractionated inter-element ratios (e.g. Borisov & Palme, 1996; Borisov & Palme, 1997; Brenan & McDonough, 2009). Estimates of the primitive upper mantle (PUM) composition however, reveal only a modest depletion relative to chondrite (~2 orders of magnitude) and broadly chondritic element ratios. This discrepancy is termed ‘the highly siderophile element problem’ (Capobianco et al., 1993) and is often

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accounted for by the addition of chondritic material to the PUM subsequent to core-formation. This ‘late-veneer’ of chondritic material does not undergo equilibration with the core, thus raising HSE abundances in the PUM and endowing it with chondritic element ratios.

Gold occupies a unique position among the HSEs by exhibiting several orders of magnitude greater solubility in silicate melt than is typical for the group (Brenan & McDonough, 2009; Bennett & Brenan, 2013). The partitioning of Au into the metal phase during planetary core-formation is therefore expected to be correspondingly weaker than for other HSEs, and chondrite-normalised concentrations of Au in the PUM following core-formation should be elevated relative to elements such as Ir, Os and Re. The distribution of trace elements between liquid metal and silicate can be described by the partition coefficient ($D_i^{Met/Sil}$):

$$D_i^{Met/Sil} = \frac{C_i^{Met}}{C_i^{Sil}} \quad (1)$$

Where C_i is the concentration of element i in the superscript phase. Values of $D_{Au}^{Met/Sil}$ typically decrease with increasing T and are essentially independent of fO_2 at reducing conditions (Brenan & McDonough, 2009; Bennett & Brenan 2013; Righter et al. 2015). This suggests that the Au content of PUM may provide a constraint on the thermal history of core-mantle equilibrium that is not complicated by the effects of progressive oxidation or reduction during accretion. This principle has been used previously to estimate a maximum temperature for metal-silicate equilibration during core segregation of ~3200 K, based on experiments performed at 2 GPa (Bennett & Brenan, 2013). To more confidently use Au partitioning as a thermometer for Earth’s primary differentiation, the effect of other parameters, such as silicate melt composition, metal sulphur content and pressure, must be better understood.

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63 In this study, we have performed series of experiments to systematically determine changes in
64 $D_{Au}^{Met/Sil}$ as a function of pressure, melt composition and the sulphur content of the metal phase.
65 These new results are combined with literature data to parameterise $D_{Au}^{Met/Sil}$ as a function of P , T
66 and metal sulphur content. Continuous core-formation models were performed using this new
67 parameterisation for Au, alongside similar relationships for Ni and Co selected from the
68 literature (Siebert et al. 2012). The results of these models suggest that Au partitioning is a useful
69 constraint on core-mantle equilibration T . Experiments to investigate sulphur, however, suggest
70 further work is required to understand and parameterise the coupled effects of pressure and
71 sulphur content of the system on the metal-silicate partitioning of Au.

72

73 **2. Theoretical Background**

74 **2.1 Calculation of Metal-Silicate Partition Coefficients**

75 Metal-silicate partitioning was determined using two types of experiments: Those that contain
76 Au only as a trace constituent and those which are saturated in Au-metal. Two different
77 approaches are therefore required in order to calculate values of $D_{Au}^{Met/Sil}$. Experiments to
78 determine Au partitioning as a function of sulphur contents of the metal phase contain only
79 minor amounts (<1 wt%) of Au and partition coefficients for a given composition may be
80 calculated simply by means of equation 1. Experiments that explore the effect of silicate melt
81 composition or pressure on Au solubility in silicate melt require a different approach. These
82 experiments are saturated in an Au-rich metallic melt and partition coefficients are calculated

83 from concentrations measured in the silicate phase at the solubility limit (C_{Au}^{SilSat}), by
 84 extrapolating to infinite dilution using the formulation of Borisov & Palme (1994):

$$85 \quad D_i^{Met/Sil} = \frac{1}{A \times C_i^{SilSat} \times \gamma_i^{Fe\infty}} \quad (2)$$

86 where A is a mole to weight conversion factor, and $\gamma_{Au}^{Fe\infty}$ is the activity coefficient of Au at infinite
 87 dilution in liquid iron metal. For a Fe-Au binary composition, A tends toward a value of $2.84 \times$
 88 10^{-7} . A value of 12 was chosen for $\gamma_{Au}^{Fe\infty}$, following Brenan & McDonough (2009) who
 89 determined this parameter from solubility and metal-silicate partitioning experiments done at
 90 2588 K. This is similar to the value of 6 calculated by Liu et al. (2009) for the Fe-Au system at
 91 1623 K.

92

93 **3. Materials & Methods**

94 **3.1 Au Partitioning in Sulphur-Bearing Systems**

95 The effect of adding sulphur to the metal-silicate system was investigated at 0.1 MPa, 1573-1753
 96 K and $\sim IW -1.4$ to -1.1 (where $IW \pm R$ is the deviation in log units from the fO_2 defined by the
 97 iron-wüstite buffer). The sulphur content of liquid Fe-S alloy co-existing with solid Fe decreases
 98 with increasing temperature (e.g. Waldner & Pelton, 2005). Experiments were therefore
 99 performed at different temperatures in order to generate a range of Fe-S alloy compositions.
 100 Temperatures were chosen which correspond to positions on the iron-sulphur binary liquidus
 101 where the system remains saturated in Fe-metal. Target compositions for Fe-S alloy were
 102 typically between $X_s = 0.1-0.3$, as the shallow slope of the liquidus in this compositional range

helps to minimize the T difference between experiments. Starting materials for sulphur-bearing experiments consisted of synthetic basalt, pure Fe and a Fe-S mixture, which were placed as powders into chromite crucibles in a gravitationally stable arrangement. Initially, Au was added to experiments as a pure metal bead, which comprised no more than ~1 wt% of the starting materials in order to ensure Henrian behaviour. In later experiments (AuFeS 9; AuFeNiS 1a, 1b), Au powder was added to the Fe powder portion of experiments to form a 100:1 mixture. The synthetic basalt was prepared by grinding pure oxide and carbonate powders under ethanol in an agate mortar and pestle. The ground mixture was dried at room temperature and calcined overnight at 1373 K before being re-ground then equilibrated at 1673 K in a controlled atmosphere, with a $f\text{O}_2$ close to the iron-wüstite buffer. The equilibrated sample was quenched by immersion into cold water to form a transparent blue-green glass. Fe-S mixtures ($X_{\text{FeS}} = 0.1\text{--}0.35$) were made by grinding Fe and elemental S under ethanol before drying at room temperature. Chromite crucibles were prepared using diamond coring bits to machine cylinders from a slab of adcumulate chromitite donated by the Royal Ontario Museum and sourced from a locality in New Caledonia (ROM reference number M36331). Crucibles were then sonicated in ethanol and annealed overnight in a controlled atmosphere vertical tube furnace at 1673 K and ~IW. Chromite was used as a container material due to its refractory nature, minimal effect on silicate melt composition, and ease of machining by diamond coring tools. All starting materials were stored in either a desiccator or a drying oven maintained at ~348 K prior to use. Experiments were performed in evacuated silica glass ampoules that were contained within alumina crucibles and either suspended in the hot-spot of a vertical tube furnace, or placed into a bottom-loading box furnace (located at The University of Toronto). Experiments were quenched rapidly by immersion into cold water.

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127 **3.2 Ambient Pressure Au Solubility Experiments**

128 Experiments to determine the effect of melt composition on Au solubility and partitioning
129 consisted of synthetic basalt and a pure Au bead contained by a chromite crucible. The synthetic
130 basalt was prepared from pure oxides and carbonates which were ground under ethanol before
131 calcining overnight at 1373 K. Variable quantities of ground San Carlos olivine were then added
132 to the calcined mixture in order to generate a range of final melt compositions. The mixture was
133 then reground and stored in a desiccator. Chromite crucibles were prepared in the same manner
134 as for S-bearing experiments. Experiments were done by placing the assembled chromite
135 crucible into either alumina or silica crucibles, which were then positioned in the hot-spot of a
136 controlled atmosphere vertical tube furnace using a silica glass hook. The $f\text{O}_2$ of experiments
137 was fixed by imposing a CO-CO₂ atmosphere and monitored using an yttrium-doped zirconia
138 oxygen sensor. Experiments were quenched by immersion into cold water. All experiments of
139 this type were performed at The University of Toronto.

140

141 **3.3 High Pressure Au Solubility Experiments**

142 Experiments to investigate the effect of pressure were performed using split-cylinder type multi-
143 anvil presses at the Carnegie Institution of Washington. Experiments employed ZrO₂ octahedra,
144 in a 14/8 configuration (octahedron edge length/truncated edge length of the WC anvils). The
145 ZrO₂ octahedra were fired in air at 1273 K for ~8 hrs prior to use, and stored in a drying oven
146 maintained at 393 K. Pyrophyllite gaskets and Re foil heaters were used for all experiments. The
147 relationship between oil pressure and sample pressure was calibrated using the garnet-perovskite

transition of CaGeO_3 at 1413 K and 5.99 GPa (Susaki et al. 1995), the coesite-stishovite transition at 1773 K and 10 GPa (Zhang et al. 1996) and the olivine-wadsleyite transition at 1900 K and 14.4 or 15.4 GPa (Fo90 and Fo100 respectively) (Katsura et al. 2004) (Figure S1). Temperature was monitored using a type-C thermocouple, made using a hard-fired 4-bore alumina tube, inserted axially and positioned to monitor T at the top of the sample capsule. The reported temperatures have not been corrected for the effect of pressure on the thermocouple emf. Samples were compressed at a rate of 1.2 GPa/h over the course of ~8-13 h, then heated manually to the desired T in <25 m. For experiments AuIrBas-MA2, 3, the thermocouple failed before the desired T was achieved. In these instances, temperatures were estimated on the basis of power-temperature relationships and are within 35 K of the target T . Samples were held at temperature for 5-7 m then quenched by cutting power to the heater. These durations have previously been shown as sufficient to achieve equilibrium between metallic and silicate liquids in multi-anvil experiments (e.g. Thibault & Walter, 1995; Li & Agee, 2001). To further confirm equilibrium, characteristic lengthscales for diffusion of Au in silicate melt were calculated using the diffusivity estimated by Mungall (2002) for Au in komatiite at ~1800 K, more than 400 K cooler than our lowest experimental T , yielding distances of 1.3-1.6 mm. This is more than double the length of our largest sample chamber, suggesting samples did reach equilibrium. Experiments employed Fe-Ir alloy capsules, that were supported in the hot-spot of the resistance heater with crushable MgO ceramic pieces. MgO ceramics were dried at >1273 K in air using a butane torch immediately before assembling the experiment. Alloy capsules were synthesized by cold-pressing powdered metal mixtures in a silica glass tube by hand, then drilling a sample space in the crucible portion of the capsule before annealing at 0.1 MPa and 1473 K at an $f\text{O}_2$ close to the IW buffer. Starting materials comprised a synthetic basalt mixture with the same

composition used in several previous studies of Au solubility (Brenan & McDonough, 2009; Bennett & Brenan, 2013), and pure Au beads made by briefly melting Au wire in air.

3.4 Run Product Analysis

Run products were prepared for compositional analysis by mounting in epoxy, grinding with silicon carbide to expose a longitudinal section, then polishing with 15, 9 and 1 μm oil-based diamond suspensions. Major element data for experiments performed at 0.1 MPa was acquired with a Cameca SX50 electron microprobe at The University of Toronto. Silicate glasses were analysed with a 15 kV accelerating voltage and 10 nA beam current. A 10 μm diameter defocused beam was used to minimise alkali loss. Analysis of Au alloy, Fe alloy and Fe-S alloy utilised a 20 kV accelerating voltage and 30 nA beam current. A 40 μm defocused beam was used for analyses of Fe-S alloys, to offset the effects of heterogeneity resulting from phase separation during quench. Analyses of the remaining alloy compositions employed a focused beam. Standards for silicate glass analyses were; natural basalt glass (Si, Fe, Al, Mg, Ca), bustamite (Ca), albite (Na) and barite (Ba). Metal-alloy analyses employed high purity metals, pyrite (Fe, S) and pentlandite (Ni) as standards. A ZAF data reduction scheme was used to convert raw count rates to concentrations. For high-pressure experiments, the major element compositions of quenched silicate glass and IrFe alloy capsules were determined with a JEOL JSM-6500F scanning electron microscope, located at the Carnegie Institution of Washington and equipped with a silicon drift detector. All analyses employed a 15kV accelerating voltage and 1 nA beam current. Standards for silicate analyses were pyrope (Si), diopside (Ca), cossyrite (Na, Fe), ENAL20 (Mg, Al), MnO_2 (Mn) and a Ni-bearing olivine (Ni). For alloy analyses, pure

193 element standards (Ir, Fe), pyrope (Si) and Fe_3O_4 (O) were used. EDS spectra were fit using
194 AztecTM software, version 2.4, supplied by Oxford Instruments. EDS analysis of the silicate
195 portion of run products from high-pressure experiments permits straightforward averaging of the
196 coarse quench textures present in the silicate phase. Comparison between the composition
197 determined for the basalt glass standard employed here, using both EDS and wavelength
198 dispersive spectroscopy, reveals no more than a 5% difference between these methods for any of
199 the major and minor elements present in the glass (Armstrong, 2014).

201 The trace element compositions of the silicate glass and Fe-S alloys were determined by laser
202 ablation inductively coupled plasma mass spectrometry (LA-ICPMS) at The University of
203 Toronto. The system is comprised of a frequency quintupled Nd:YAG laser, coupled to a VG
204 PQExcell quadrupole ICP-MS. Laser repetition rates of 4 and 10 hz were used for alloy and
205 silicate analyses respectively. Spot sizes varied from 40 to 100 μm . Analyses consisted of 20 s
206 background acquisition followed by 60 s of ablation. The ablation cell was allowed a minimum
207 of 60 s washout between analyses. Helium was used as the carrier gas in order to enhance
208 sensitivity (Eggins et al., 1998). Analyses were collected sequentially, with the first and last two
209 spectra acquired on standard reference materials. No more than 16 unknown analyses were
210 performed between sets of standard analyses. Data reduction was performed using the GLITTER
211 software package, version 4.4. All data were reduced using the NIST610 trace element doped
212 glass, containing 22.1ppm Au (Sylvester & Eggins, 1997). Calcium and either nickel or copper
213 were used as the reference elements to correct for ablation yields in silicate glass and alloy
214 respectively. The NIST610 standard yields accurate analyses of the Fe-S phase, as previous
215 studies employing the same routine for HSE analysis have found that internal standardization to

correct for ablation yield adequately accounts for matrix differences when using a sulphide standard for silicate glass analyses (Brenan & McDonough 2009; Mungall & Brenan 2014). Brenan & McDonough (2009) also analyzed synthetic glasses containing Ir and Os by LA-ICPMS using an HSE-doped sulphide. The results of these analyses agree within error of the Ir and Os contents of the glasses as measured by isotope dilution (Mann et al. 2012) and a modified NiS fire assay (Brenan & McDonough 2009) respectively, confirming the adequacy of the analytical routine. The isobaric interference of ^{181}Ta oxide on ^{197}Au was assessed by analyzing a sample of rutile containing ~300 ppm Ta but no Au. The average 197/181 counts ratio for this analysis is 1.24×10^{-4} . Using this ratio, analysis of NIST610 (containing 376.6 ppm Ta) yields ~100 counts per second (cps) interference on mass 197. For the same analytical session, the total count rate measured on mass 197 was ~15000 cps, indicating a negligible 0.7% interference of ^{181}Ta on ^{197}Au for the NIST610 standard. Tantalum is absent from the synthetic glasses used in the solubility experiments. The major and trace element concentrations in run-product glasses and alloys are provided in Tables 1-3 for sulphur-bearing, 0.1 MPa solubility and high pressure experiments respectively.

4. Results

4.1 Run Product Textures

Run-products from sulphur bearing experiments consist of silicate glass, a homogeneous Fe-Ni alloy and an Fe-S alloy which has undergone phase separation during quench (Fig 1a,b). In one experiment (AuFeS 5), a portion of the silicate glass was contaminated by a mixture of Fe-S alloy blebs (< 55 μm) and chromite crystals (<30 μm). Despite this, there remained sufficient

‘clean’ silicate for analysis by LA-ICPMS. Ambient pressure experiments that were saturated in Au are comprised of clean silicate glass, a metallic bead and in some cases several small (<250 μm) chromite crystals (Fig 1c). In both sets of experiments, a sharp interface is typically observed between the alloy, silicate glass and chromite phases. Borisov & Palme (1996) demonstrated equilibrium in Au solubility experiments lasting 17 - 61 hrs done at similar T - $f\text{O}_2$ conditions to those used in this study. We therefore employed run durations of 46 to 159 hrs to ensure equilibrium. Analyses of silicate glass run products confirm homogeneity for the major elements and Au.

Run-products from high-pressure experiments done at 2273 K comprise Au metal, quenched silicate melt and in some cases (AuIrBas-MA1, 2, 3) a large (100-300 μm) olivine crystal or crystals present at the base of the sample chamber (Fig 2a). Au is present as small (2-15 μm) blebs that are found at either the interface between quenched silicate melt and the FeIr capsule or filling pores in the FeIr capsule (Fig 2b). Inclusions of quenched silicate melt are commonly observed within the Au blebs. The FeIr capsules possess significant porosity, as evidenced by trapped Au and silicate melt pockets throughout, particularly in the region close to the main sample chamber. This porosity most likely arises from inefficient wetting of the powdered metal interfaces by trapped gas when the capsules were annealed. Permeability associated with this porosity explains the increased MgO content of FeIr encapsulated samples when compared with the nominal starting composition, by allowing interaction between the sample and the surrounding periclase sleeve. The enrichment in MgO of the silicate melt is most likely responsible for the formation of olivine in several experiments. The location of olivine at the base of the sample chamber may be due to a minor temperature gradient across the sample, however, for the axial

length of our samples (<500 μm) we expect such gradients to be negligible (Van Westrenen et al. 2003).

4.2 Calculation of Oxygen Fugacity

The oxygen fugacity in Au solubility experiments done at 0.1 MPa was maintained by imposing a CO-CO₂ atmosphere of fixed composition for the duration of the experiment. For these experiments, $f\text{O}_2$ was monitored by measuring the electromotive force generated by an yttrium-doped zirconia oxygen sensor. Experiments performed in evacuated silica tubes or at high pressure were not done at a controlled oxygen fugacity. For experiments to investigate sulphur, similar $f\text{O}_2$ between experiments was sought by ensuring solid Fe-metal remained present in the experiments and by using a silicate starting composition that had been pre-equilibrated at a $f\text{O}_2$ close to the iron-wüstite buffer. For sulphur-bearing and high-pressure experiments, $f\text{O}_2$ relative to the iron-wüstite buffer was calculated from the composition of quenched silicate melt and either Fe (low pressure experiments), or IrFe (high pressure experiments) alloy using the relationship:

$$\Delta IW = 2 \log \left(\frac{a_{\text{FeO}}^{\text{Sil}}}{a_{\text{Fe}}^{\text{Met}}} \right) = 2 \log \left(\frac{X_{\text{FeO}}^{\text{Sil}} \gamma_{\text{FeO}}^{\text{Sil}}}{X_{\text{Fe}}^{\text{Met}} \gamma_{\text{Fe}}^{\text{Met}}} \right) \quad (3)$$

Use of equation 3 requires knowledge of the activity coefficients for FeO in silicate melt and Fe in the alloy phases. A value of 1.3 was used for $\gamma_{\text{FeO}}^{\text{Sil}}$ (O'Neill & Eggins, 2002). For iron-rich solutions of solid Fe-Ni alloy, such as those present in the run products of our sulphur-bearing experiments (Ni < 5.23 wt%), Fe behaviour is close to ideal (Hultgren, 1973) and a value of 1 was adopted for $\gamma_{\text{Fe}}^{\text{Met}}$ in calculating the $f\text{O}_2$ of most experiments. For experiment AuFeS 9, solid

Fe-rich alloy was not observed. In this case, the activity of Fe in Fe-S alloy was instead calculated using a 3-species activity-composition model for iron-sulphur liquids from Sharma & Chang (1979) with interaction parameters determined by Chuang et al. (1985). For high-pressure experiments, f_{O_2} was calculated using the activity of Fe in IrFe alloys, which was determined using an asymmetric solution model and the data summarized by Borisov & Palme (2000).

4.3 The Effect of S on the Metal-Silicate Partitioning of Au

Partition coefficients were determined using equation 1 and then recalculated to a common T of 1673 K using the results of Bennett & Brenan (2013). Details of the experiments used by Bennett & Brenan (2013) to determine the temperature dependence of partitioning are provided in Table S1. Recalculated data show that values of $D_{Au}^{Met/Sil}$ decrease with increasing sulphur in the metal phase (Fig 3a). These data, combined with the result of a sulphur-free experiment (AuReBas21) from Bennett & Brenan (2013) performed at otherwise similar conditions, define the following relationship:

$$\log D_{Au}^{Met/Sil} = 5.81(\pm 0.24) \log(1 - X_s) + 5.36(\pm 0.03) \quad (4)$$

where X_s is the mole fraction of sulphur in the metal phase. Jones and Malvin (1990) showed that solid metal-liquid Fe-S partitioning of Au in the Fe-Ni-S system $D_{Au}^{Fe/Fe-S}$ can be described solely by the concentration of non-metal in the liquid alloy (Fe-S) phase:

$$\ln D_{Au}^{Fe/Fe-S} = \ln D_{Au}^0 + \beta \ln(1 - \alpha \omega X_s) \quad (5)$$

301 where D_{Au}^0 is the solid metal-liquid metal partition coefficient for Au in the sulphur free system,
 302 β describes the strength of the interaction between Au and the non-metal of interest, α is a
 303 system-specific constant and ω is a stoichiometry factor which depends upon the speciation of
 304 the non-metal in the system. For the Fe-Ni-S system, the speciation of S is assumed to be FeS
 305 and ω is taken to be 2, as the FeS component occupies both a volume component in the alloy and
 306 removes a Fe from reaction with trace elements (Jones & Malvin, 1990). If the reduction in
 307 $D_{Au}^{Met/Sil}$ displayed by our data results entirely from non-metal avoidance behaviour, it should be
 308 adequately described as a function of the α and β parameters used in equation 5. Chabot and
 309 Jones (2003) re-write equation 5 in terms of $1/D_{Au}^{Fe/Fe-S}$ and $-\beta$ to yield:

$$\frac{1}{D_{Au}^{Fe/Fe-S}} = \frac{(1 - \alpha\omega X_s)^{-\beta}}{D^0} \quad (6)$$

311 Remembering that $D_{Au}^{Fe-S/Fe}$ is the reciprocal of $D_{Au}^{Fe/Fe-S}$ and for the Fe-Ni-S system $\omega = 2$,
 312 equation 6 can be re-written as:

$$D_{Au}^{Fe-S/Fe} = \frac{(1 - 2\alpha X_s)^{-\beta}}{D^0} \quad (7)$$

314 The partition coefficients $D_{Au}^{Fe-S/Fe}$, and $D_{Au}^{Fe/Sil}$ are defined by the following concentration ratios:

$$D_{Au}^{Fe-S/Fe} = C_{Au}^{Fe-S} / C_{Au}^{Fe} \quad (8)$$

$$D_{Au}^{Fe/Sil} = C_{Au}^{Fe} / C_{Au}^{Sil} \quad (9)$$

317 Multiplication of equations 8 and 9 provides the liquid Fe-S-liquid silicate partition coefficient,

318 which after substitution of equation 7 for $C_{Au}^{Fe-S/Fe} / C_{Au}^{Fe}$ yields:

$$D_{Au}^{Fe-S/Sil} = \frac{C_{Au}^{Fe-S}}{C_{Au}^{Fe}} \times \frac{C_{Au}^{Fe}}{C_{Au}^{Sil}} = \frac{(1-2\alpha X_s)^{-\beta}}{D^0} \times \frac{C_{Au}^{Fe}}{C_{Au}^{Sil}} \quad (10)$$

Substituting $C_{Au}^{Fe}/C_{Au}^{FeLiq}$ for D^0 , where the superscript FeLiq denotes sulphur-free liquid metal, provides the following relationship:

$$D_{Au}^{Fe-S/Sil} = \frac{(1-2\alpha X_s)^{-\beta}}{\left(\frac{C_{Au}^{Fe}}{C_{Au}^{FeLiq}} \right)} \times \frac{C_{Au}^{Fe}}{C_{Au}^{Sil}} \quad (11)$$

Simplifying equation 11 yields a relationship between the metal-silicate partition coefficient for Au in a sulphur bearing system, α , β and $D_{Au}^{FeLiq/Sil}$:

$$D_{Au}^{Fe-S/Sil} = (1-2\alpha X_s)^{-\beta} \times D_{Au}^{FeLiq/Sil} \quad (12)$$

Taking the natural logarithm of equation 12 and replacing $D_{Au}^{Fe-S/Sil}$ with the equivalent $D_{Au}^{Met/Sil}$ term, leads to a relationship analogous to equation 5, but for the metal-silicate system relevant to our experiments:

$$\ln D_{Au}^{Met/Sil} = \ln D_{Au}^{FeLiq/Sil} - \beta \ln(1-2\alpha X_s) \quad (13)$$

Equation 13 predicts a linear relationship between $\ln D_{Au}^{Met/Sil}$ and the $\ln(1-2\alpha X_s)$ term, with a slope equal to $-\beta$ and an intercept of $\ln D_{Au}^{FeLiq/Sil}$. Jones and Malvin (1990) determine a value of 1.09 for α from their experiments in the Fe-Ni-S system. A value of 1.082 was adopted for $-\beta$ following the regression of Jones & Malvin (1990) for a compilation of results from solid metal-liquid metal partitioning experiments. Plotting the partition coefficients for Au determined in our sulphur-bearing experiments as a function of $\ln(1-2\alpha X_s)$ shows a linear trend is not obtained

(Fig 3b). Values of $D_{Au}^{Met/Sil}$ determined from experiments which contain ~4–23 wt% sulphur in the metal phase are instead lower than those expected from considerations of non-metal avoidance. Lower values of $-\beta$ (0.59 – 0.82), as determined for Au in Fe-Ni-S melts from Soret experiments (Brenan & Bennett, 2010), only increase the discrepancy between measured $D_{Au}^{Met/Sil}$ values and those predicted by equation 13. Our results therefore suggest that accounting for changes to the activity-composition relationships in the metal phase is not sufficient to predict changes to $D_{Au}^{Met/Sil}$ that arise from the addition of sulphur to core-forming metal. A similar result was found by Wood & Kiseeva (2015) for the partitioning of certain elements between sulphide and silicate melts. These authors suggest that the significant replacement of O^{2-} by S^{2-} in silicate melts at very reducing conditions may act to reduce the chalcophile tendencies of elements such as Cu. In this scenario, it is reasonable to expect that Au may dissolve in silicate melt by complexing with S.

Previous Au solubility experiments done in basaltic and andesitic melt compositions at 1323 K, sulphide saturation and a range of fO_2 , reveal a prominent increase in dissolved Au contents at ~0–1.5 log units above the fayalite-magnetite-quartz (FMQ) buffer (Botcharnikov et al. 2010). The increase in Au solubility over this fO_2 range correlates strongly with the region of maximum S^{2-} solubility in the melt, and the authors suggest the formation of Au-S-O or Au-Fe-S-O species. Calculation of fS_2 for our experiments requires knowledge of a_{FeS}^{Sulph} and ΔG_r^o for the reaction: Fe (met) + $\frac{1}{2}S_2$ (g) $\leftrightarrow$ FeS (sulph). For the Fe-S binary system relevant to our experiments, a_{FeS}^{Sulph} was calculated using the 3-species activity-composition model of Sharma & Chang (1979), with interaction parameters determined by Chuang et al. (1985). Values of ΔG_r^o at the temperatures relevant to our experiments were taken from the NIST-JANAF thermochemical tables. The

dissolution of Au into silicate melt as purely sulphide species can be represented by the following heterogenous reaction:

where n is the oxidation state of Au dissolved in silicate melt. Taking the equilibrium constant for this reaction and rearranging:

$$\log\left(\frac{X_{\text{Au}}}{X_{\text{AuS}_{n/2}}}\right) + \log\left(\frac{\gamma_{\text{Au}}}{\gamma_{\text{AuS}_{n/2}}}\right) = -\frac{n}{4}\log f\text{S}_2 + \text{constant} \quad (15)$$

Assuming the activity coefficient of $\text{AuS}_{n/2}$ in the silicate melt is constant over the composition range of interest, and replacing the ratio $X_{\text{Au}}/X_{\text{AuS}_{n/2}}$ with the partition coefficient, equation 15 can be simplified to yield:

$$\log D_{\text{Au}}^{\text{Met/Sil}} + \log \gamma_{\text{Au}} = -\frac{n}{4}\log f\text{S}_2 + \text{constant} \quad (16)$$

The slope defined by a plot of $\log D_{\text{Met/Sil}} + \log \gamma_{\text{Au}}$ versus $\log f\text{S}_2$ should therefore be proportional to the oxidation state of Au in the silicate melt. To account for the minor differences in T between samples, $\log f\text{S}_2$ can be replaced with $\Delta\text{Fe-FeS}$, the deviation in $\log f\text{S}_2$ from the Fe-FeS buffer. Activity coefficients of Au in the metal phase were determined using the formalism of Jones & Malvin (1990) described above. A plot of $\log D_{\text{Met/Sil}} + \log \gamma_{\text{Au}}$ versus $\Delta\text{Fe-FeS}$ for our experiments defines a weak negative correlation ($R^2 = 0.48$), that trends more steeply than the slope of 0.25 expected for Au^{1+} . On the basis of previous Au solubility experiments in a sulphur-free system, more oxidized species of Au are not plausible at the reducing conditions of our experiments (Borisov & Palme 1996). The observed trend therefore indicates either a significant

change in $\gamma_{\text{AuS}_{n/2}}$ over the composition range of our experiments, or the formation of more complex S-bearing species, such as those suggested by Botcharnikov et al. (2010). In summary, changes to the activity coefficient of Au in Fe-S alloy, in concert with complexing between sulphur and gold in silicate melt provides a likely explanation for our results, however, the formation of simple $\text{AuS}_{1/2}$ species in the silicate melt are not adequate to describe the data, consistent with previous studies.

It should be noted that sample AuFeS 5, which contains the highest S contents of our experiments (~30 wt% in the alloy; confirmed by repeat analysis in a separate analytical session), displays moderate agreement with the non-metal avoidance model (Fig 3b). Rather than signalling a change in the partitioning behaviour of Au, we suspect that microprobe analyses of the Fe-S phase in this experiment do not accurately reflect the true S concentrations. We calculate $X_s = 0.45$ for the Fe-S phase in this experiment which, if correct, would indicate an alloy composition too sulphur rich to co-exist with solid Fe at the run temperature of this experiment ($X_s \approx 0.33$ at 1573 K). Solid Fe is observed in the run-product of AuFeS 5, supporting our assertion that the measured S contents in Fe-S alloy are overestimated. This datapoint was therefore omitted from the regression used to define equation 4.

4.4 The Effect of Melt Polymerisation on the Solubility and Partitioning of Au

Experiments at 1723 K, 0.1 MPa, IW +1 and a range of melt compositions were performed to investigate the effects of changing melt polymerisation on Au solubility. Melt composition was varied by adding different quantities of San Carlos Olivine to silicate starting materials, yielding

NBO/T (non-bridging oxygens over tetrahedrally co-ordinated cations) values of 0.77 to 1.45 (calculated using the equations summarized by Mills, 1993). Due to minor (<5 wt%) amounts of Fe dissolved in the Au-phase, solubilities measured in the silicate glass were recalculated to unit activity of Au in the metal (C_{Au}^{SilSat}):

$$C_{Au}^{SilSat} = \frac{C_{Au}^{Sil}}{X_{Au}^{Met} \gamma_{Au}^{Met}} \quad (17)$$

The activity coefficient for Au in binary solution with Fe (γ_{Au}^{Met}) was calculated using the Margules interaction parameters summarised by Borisov & Palme (2000), from the primary data of Hultgren (1973). Figure 4a displays the solubility of Au as a function of NBO/T at reducing conditions (IW +0.92). The dependence of solubility on melt composition is weak, in agreement with previous experiments to determine Au solubility in S-free melts at more oxidizing conditions (Zajacz et al., 2013). We observe less than a 2-fold difference in Au solubility between experiments at the extremes of the studied compositional range (i.e. NBO/T = 0.77 vs 1.45). Linear regression of the measured solubilities versus NBO/T provides a similar quality of fit to a zero-slope (sum of squares = 0.17 in both cases), indicating Au solubility is not sensitive to melt polymerization across the range of experimental melt compositions. We restricted our investigation to melt compositions that quench easily to a glass, as the formation of a quench matte complicates interpretation of the run-products with regard to nugget formation (see Ertel et al. 2008; Brenan et al. 2016 for in-depth reviews of HSE nugget formation). Our experiments therefore do not extend to the peridotitic melt compositions most relevant to core formation. Righter et al. (2015), however, also find a weak dependence of partitioning on silicate melt composition from multiple linear regression of a large experimental database (n = 85) that includes samples with ultramafic liquids. The expression of Righter et al. (2015) predicts <0.8

log units change in $D_{Met/Sil}$ as NBO/T varies from 1.45 (our most depolymerised experiment) to 2.7 (molten peridotite), suggesting the trend defined by our systematic experimental series can be reliably extrapolated to more basic liquids.

Partition coefficients were calculated from experiments containing Au-rich alloys using equation 2 and are listed in Table 2. It has previously been noted that under certain conditions, Fe-bearing silicate melt may display enhanced HSE solubility (and thus lower partition coefficients) relative to Fe-free compositions, independent from the effect of melt polymerization (Capobianco & Hervig 1996; Laurenz et al. 2010; Laurenz et al. 2012). To assess if Au partitioning is similarly affected in Fe-bearing melts, partition-coefficients were calculated from the highest T experiments (≥ 1672 K) of Borisov & Palme (1996), for Au solubility in melts with an anorthite-diopside eutectic composition (NBO/T = 0.93). These $D_{Au}^{Met/Sil}$ values were recalculated to 1723 K using the temperature dependence found by Bennett & Brenan (2013) and compared with those calculated from our experiments that used Fe-bearing melts. Figure 4b displays these results alongside the mean $D_{Au}^{Met/Sil}$ value for the Fe-bearing experiments, indicated by the dashed grey line. Partition coefficients for the Fe-free experiments are within ~ 0.5 log units of the mean value defined by our Fe-bearing results, suggesting that Au partitioning is not significantly affected by the presence of Fe in reduced silicate melt ($<IW+1$). This is similar to the results of Capobianco & Hervig (1996) for Pd, who observed no change in solubility at reducing conditions ($-\log fO_2 = 5.0$) following partial substitution of MgO for FeO in the silicate melt.

4.5 The Effect of Pressure on $D^{Met/Sil}$

444 Values of $D_{Au}^{Met/Sil}$ for samples from multi-anvil experiments were calculated using equation 2,
 445 following correction of measured Au concentrations in the silicate melt to those corresponding to
 446 unit Au activity with equation 14. Blebs of Au alloy were typically too small to permit accurate
 447 analyses of their dissolved Fe content. Fe activity in the Au alloy was therefore estimated by
 448 equating the chemical potentials of Fe in both the AuFe and IrFe alloys:

$$449 \quad \mu_{Fe}^{AuFe} = \mu_{Fe}^{IrFe} \quad (18)$$

450 Where:

$$451 \quad \begin{aligned} \mu_{Fe}^{AuFe} &= \mu_{Fe}^{\circ} + RT \ln a_{Fe}^{AuFe} \\ \mu_{Fe}^{IrFe} &= \mu_{Fe}^{\circ} + RT \ln a_{Fe}^{IrFe} \end{aligned} \quad (19)$$

452 Taking the standard state to be pure Fe at the P and T of interest, the μ_{Fe}° terms cancel and the
 453 activity of Fe in AuFe alloy is equal to its activity in IrFe alloy:

$$454 \quad a_{Fe}^{AuFe} = a_{Fe}^{IrFe} \quad (20)$$

455 Remembering that $a_i = X_i \times \gamma_i$, the activity of Fe in IrFe alloy is determined from analyses of
 456 the IrFe capsule, with values for γ_{Fe}^{IrFe} calculated as a function of composition using the
 457 asymmetric solution model and interaction parameters summarized by Borisov & Palme (2000).
 458 For the assumed binary solution of Au and Fe in equilibrium with the IrFe capsule, a_{Fe}^{AuFe} is
 459 therefore known and the corresponding activity of Au (a_{Au}^{AuFe}) for use in equation 14 was
 460 determined from the activity-composition relations listed by Borisov & Palme (2000).

461

Experiments at 2273 K and IW 0.96 to 1.72 display a decrease in $D_{Au}^{Met/Sil}$ with increasing P between 10 and 15 GPa. Data from this study were combined with results from previous experiments at 2 GPa, 2273 K and covering the same range of fO_2 (Brenan & McDonough 2009; Bennett & Brenan 2013). Linear regression of this data yields the following dependence of $D_{Au}^{Met/Sil}$ on P (Fig 5):

$$\log D_{Au}^{Met/Sil} = 3.83 (\pm 0.05) - 67.8 (\pm 10.9) \frac{P(\text{GPa})}{T(\text{K})} \quad (21)$$

Also plotted on Figure 5 is the average $D_{Au}^{Met/Sil}$ for 0.1 MPa experiments at ~IW 0.9 to 1.6, obtained by combining data from Borisov & Palme (1996) with the mean partition coefficient for our AuMg-series experiments (see gray line in Fig 4). Following recalculation to account for differences in T using the dependence found by Bennett & Brenan (2013), good agreement is observed between the trend defined by high-pressure data and the ambient pressure results (Fig 5). The metal-silicate partitioning of Au has been investigated at pressures >2 GPa in several previous studies (Jana & Walker, 1997; Richter et al., 2015). Unlike the present experiments, that were done close to saturation in pure Au metal, these earlier partitioning experiments were performed at relatively dilute concentrations of Au. Direct comparison between datasets is complicated by the fact that run-products in the Jana & Walker (1997) study contain sulphur and are graphite saturated, while the Richter et al. (2015) experiments contain sulphur and were performed over a wide range of temperature. Data at >2 GPa from both studies, however, is well reproduced by the predictive equation for Au partitioning described in section 5.2, that uses the pressure dependence defined by equation 21. Predicted partition coefficients for the 1 GPa experiments of Jana & Walker (1997) are systematically higher than those measured, although these authors note that values of $D_{Au}^{Met/Sil}$ they determine for these experiments are likely minima,

due to concentrations of Au in the silicate melt being close to the detection limit of their analytical protocol.

5. Discussion

5.1 Single Step Core Formation and the Role of Sulphur

A potentially important control on the distribution of siderophile elements between metal and silicate phases during core-segregation is the light element content of the metallic phase (e.g. Jana & Walker, 1997; Corgne et al., 2009; Siebert et al., 2013). Highly siderophile element atoms typically avoid non-metal solutes in Fe-rich alloys (e.g. Jones & Malvin, 1990; Chabot & Jones, 2003; Brenan & Bennett, 2010) and the results of this study are consistent with this observation. The change in $D_{Au}^{Met/Sil}$ values with fS_2 determined here also suggests the formation of S-bearing Au complexes in silicate melt, thus further reducing the siderophile behaviour of Au. The core is thought to contain ~5-10 wt% of a light element, the precise identity of which is unknown (Birch 1952). Sulphur, however, is likely to account for at least some of this light element contents, on the basis of iron meteorite compositions; a low-pressure analogue for the terrestrial core (McDonough, 2003). Furthermore, it has been suggested that the core may have acquired part of its sulphur budget *via* segregation of a sulphide melt, likely during the later stages of accretion (O'Neill, 1991; Wood & Halliday, 2005; Wolthers & Wood, 2015). If sulphur is present during the metal-silicate equilibrium which accompanies core-formation, Au should partition less strongly into the metal phase. To assess the significance of sulphur on the distribution of Au between core and mantle, we consider a simple model in which core segregation occurs as a single metal-silicate equilibration event. Figure 6 portrays the Au

contents of a model PUM following equilibration with sulphur-bearing metal and the addition of 0.5% chondritic late veneer. Even if the entire light element content of the core is assigned to S, the predicted Au content of PUM changes approximately within uncertainty of the observed PUM value. A more conservative estimate for the core S content of ~2 wt% (McDonough, 2003) therefore affects little change on the concentration of Au in PUM, particularly if equilibrium is at moderate T and the Au budget of PUM is dominated by the addition of late accreted material. The effects of S on conditions of metal-silicate equilibrium inferred from Au partitioning are discussed further in the following section.

5.2 Continuous Accretion Models and Constraints on Magma Ocean Depth

To better understand how the Au content of Earth's mantle might constrain the depth of metal-silicate equilibrium in the magma ocean, we have constructed several continuous accretion and core-formation models (e.g. Wade & Wood 2005, Siebert et al. 2011). Our primary goal for these models is to gauge the usefulness of Au as a constraint on the maximum metal-silicate equilibration temperature during core-formation. Alongside Au, we have also considered Ni and Co partitioning. These elements were chosen as they have been extensively studied and shown to require metal-silicate equilibrium at the high pressures associated with a deep magma ocean to generate the estimated Ni/Co of PUM (e.g. Li & Agee 1996; Wade & Wood 2005; Siebert et al. 2011, 2012; Bouhifd & Jephcoat 2011). To simplify the parameterisation (by removing the fO_2 term), siderophile element partitioning data is often cast in the form of an exchange coefficient ($Kd_M^{Met/Sil}$) that describes the distribution of an element M with respect to the complementary distribution of Fe:

$$\log Kd_M^{Met/Sil} = \log \left(\frac{D_M^{*Met/Sil}}{(D_{Fe}^{*Met/Sil})^{n/2}} \right) = \log \left(\frac{(X_M^{Met} / X_{MO_{n/2}}^{Sil})}{(X_{Fe}^{Met} / X_{FeO}^{Sil})^{n/2}} \right) \quad (22)$$

where $D_M^{*Met/Sil}$ and $D_{Fe}^{*Met/Sil}$ are the molar partition coefficients of M and Fe respectively and n is the valence of M. Assuming that Au behaves as a neutral species (i.e. $n=0$) when dissolved in silicate melt at the reducing conditions relevant to core-formation (Fig S2a; Brenan & McDonough 2009, Bennett & Brenan 2013) equation 22 is simply:

$$\log Kd_{Au}^{Met/Sil} = \log D_{Au}^{*Met/Sil} \quad (23)$$

Values of $D_{Au}^{*Met/Sil}$ are related to the weight-based partition coefficients via mole to weight conversion factors:

$$X_{Au}^{Met} = A \times C_{Au}^{Met} \quad (24)$$

$$X_{Au}^{Sil} = B \times C_{Au}^{Sil} \quad (25)$$

Substituting 24 and 25 into 23, values of $Kd_M^{Met/Sil}$ at infinite dilution are calculated from our results using the relation:

$$\log Kd_{Au}^{Met/Sil} = \log \left(\frac{A}{B} \times D_{Au}^{Met/Sil} \right) \quad (26)$$

where A is equal to 2.84×10^{-7} and B is calculated from the composition of our experimental run-products. Values of $\log Kd$ are then parameterized in terms of P , T and X_s :

$$\log Kd_{Au}^{Met/Sil} = a + b \frac{10^4}{T} + c \frac{P}{T} + d \log(1 - X_s) \quad (27)$$

The coefficients a - d are determined by regression of the experimental data. Although the independence of Au partitioning on fO_2 may make the exchange coefficient approach seem somewhat unnecessary, it provides a parameterisation in the same framework as used for Ni and Co taken from previous studies. Values and references for n and the coefficients a - d used in the models are provided in Table 4. Before outlining the data used to determine coefficients a - d , it is useful to discuss the limitations of Equation 27 in parameterising the available data on Au partitioning, with regard to the treatment of sulphur. Our data for the effect of S on $D_{Au}^{Met/Sil}$ suggest changes to both the metallic and silicate melts upon S-addition are important. One implication of this result is that changes in the metal-silicate partitioning of S will also affect the behaviour of Au. $D_S^{Met/Sil}$ is sensitive to changes in P and T (becoming more siderophile with increasing P and T e.g. Rose-Weston et al. 2009; Boujibar et al. 2014) as well as phase composition, thus rendering values of d determined by regression of experiments performed at different P - T - X quite uncertain. Similarly, values of c determined from experiments that contain sulphur may also be compromised due to the pressure dependence of $D_S^{Met/Sil}$. We are not aware of any existing data that will allow the independent effects of S on both the metal and silicate phases to be determined for the P range pertinent to modeling core-formation. In light of this, we have performed two sets of models, with and without sulphur addition. Despite the tentative nature of our sulphur-bearing models, they yield a similar result to sulphur-free model scenarios, providing X_S^{Metal} remains relatively low (see also section 5.1). A goal of future work will be to better understand the coupled effects of pressure and light element content, permitting more realistic parameterisation of the experimental data than allowed for by relationships with the form of equation 27.

For Au, we have determined the coefficients b - d from individual suites of experiments that aimed to vary only a single intensive variable. Values for c and d are taken directly from equations 21 and 4 respectively, that result from regression of the experimental data collected in this study. The coefficient b is determined from the results of Brenan & McDonough (2009) and Bennett & Brenan (2013), using only experiments performed at 2 GPa, IW 1.7-2.3 and employing the same silicate starting material (Fig S2b). This regression yields a value for b of 1.11 ± 0.01 . The value of a is determined by least squares fitting of our parameterized $Kd^{Met/Sil}$ values to those measured experimentally for the same database of experiments as used to define coefficients b - d . Further details of the experiments used to determine each of these coefficients is provided in Table S1. We recognize that the approach taken to data regression when parameterising $Kd^{Met/Sil}$ can have a significant effect on the outcome of subsequent modeling (Walter & Cottrell 2013). To test the robustness of our parameterisation, we have determined $Kd_{Au}^{Met/Sil}$ values using equation 27 for a large database of literature experiments (see Table S1). Comparison between the model and measured values for this data is displayed in Fig S3a, and reveals that the parameterisation successfully reproduces data from 0.1MPa–23 GPa, 1573–2770 K and $X_s < 0.36$. We have included only experiments that concern metal-silicate and not sulphide-silicate partitioning in this comparison. Data from Jana & Walker (1997) are excluded from the comparison in Fig S3a, because the alloys in those experiments are graphite saturated. Solid metal-liquid metal partition coefficients for Au increase with the addition of carbon to Fe-Ni liquid (Chabot et al. 2006), suggesting values of $D_{Au}^{Met/Sil}$ may decrease if the metal is carbon bearing. Nevertheless, experiments at 5 GPa, 2073-2473 K and $X_s = 0$ -0.46 from the Jana and Walker (1997) study are plotted in Fig S3b and show reasonable agreement with the model predictions despite the presence of carbon.

590

591 It should be noted that our parameterisation for $Kd_{Au}^{Met/Sil}$ differs from that presented by Righter et
592 al. (2015). Importantly, these authors suggest a different effect of pressure on Au partitioning,
593 finding a positive value for c rather than the negative value determined in this study. There may
594 be several reasons for this difference. Firstly, Righter et al. (2015) included sulphide-silicate
595 partitioning data in their regression, which we have excluded due to potentially important
596 differences in structure between Fe-rich metallic and sulphide melts, especially at low P (Morard
597 et al. 2008). Secondly, they take a different approach to regressing their data; using a relationship
598 for $D_{Au}^{Met/Sil}$ that also depends upon fO_2 , X_C and melt polymerization, and performing multiple
599 linear regression for all coefficients simultaneously. The effect of carbon (and sulphur) is
600 parameterised by Righter et al. (2015) in the same manner as we incorporate sulphur in equation
601 27. Borisov & Palme (1996) suggest that the formation of Au-C species may be responsible for
602 the dependence of Au solubility on fO_2 observed at reducing conditions in silicate melt. Although
603 Au solubility measured in experiments done at 2 GPa and both C-free and C-saturated conditions
604 suggest carbon has a negligible effect on Au solubility, it remains uncertain if carbon may play a
605 role at other conditions (Brenan & McDonough 2009; Bennett & Brenan 2013). Accordingly,
606 this parameterisation of carbon may be subject to the same limitations as we discuss above for
607 sulphur. In order to explore the effect of differences in parameterising the data we have also
608 performed models that employ the relationship given by Righter et al. (2015).

609

610 Finally, we note that our parameterisation for Au does not include the effect of other potential
611 light-elements in the core, such as Si, C and O. Although we are unaware of experiments to

determine the effect of O in metallic melt on Au partitioning, both Si (0.1 MPa experiments) and C (0.1-5 GPa experiments) have been shown to have an effect on the solid metal-liquid metal partitioning of Au (Chabot et al. 2006; 2008; 2010). In both cases, Au displays non-metal avoidance behaviour, suggesting $D_{Au}^{Met/Sil}$ will decrease with increasing concentrations of these elements in the metal phase due to changes in γ_{Au}^{Met} . On the basis of activity-composition relations for the metal found by Chabot et al. (2006; 2010), addition of Si or C to core-forming metal will result in a greater reduction in $D_{Au}^{Met/Sil}$ than S, for the same quantity of light-element addition and neglecting effects on Au in the silicate melt. Both C and Si have also been proposed as possible complexing agents with Au in silicate melt at 0.1 MPa and reducing conditions (Borisov & Palme 1996), although it is unclear what the magnitude of their effect may be or how it will change with increased pressure. Clearly, the current database of experimental results does not provide a satisfying understanding of the behaviour of light elements on the partitioning of Au, particularly at the high pressures accompanying core-formation. We therefore focus our attention on S as a representative light-element in the core, as it is the subject of experiments in this study and likely exerts the smallest reduction in $D_{Au}^{Met/Sil}$, thus providing the most conservative constraint on maximum metal-silicate equilibration temperature.

Uncertainties in the coefficients a - d are incorporated into the model calculations with a Monte-Carlo method. Element distribution in each model step is calculated 1000 times, with exchange coefficients calculated using values of a - d selected at random within their error bounds (see Table 4). We performed models in which the Earth accretes its mass in 1% increments and therefore incorporates 100,000 calculations of $Kd_M^{Met/Sil}$ for each element. Accreting planetesimals are pre-differentiated into metal and silicate reservoirs. Concentrations in each of

these reservoirs are determined by partition coefficients corresponding to the P - T conditions at
 the core-mantle boundary of a body with a radius of ~ 1300 km (0.01 Earth masses), where T is
 fixed at the peridotite solidus. Terrestrial core formation is modeled assuming that incoming
 metal equilibrates with a global magma ocean and is then isolated from re-equilibration once
 segregated to the proto-core. Potential for disequilibrium between metal and silicate is
 incorporated into the model by allowing a fraction of the incoming metal (ϕ) to segregate
 directly to the growing core. In order to find the most conservative limit on metal-silicate
 equilibration temperature, we have considered several scenarios for the Earth's redox evolution
 during accretion: constant $f\text{O}_2$, progressive oxidation during accretion (Wade & Wood 2005;
 Siebert et al. 2011; Rubie et al. 2011), and progressive reduction during accretion (Siebert et al.
 2013; Blanchard et al. 2015). In the first of these models, $X_{\text{FeO}}/X_{\text{Fe}}$ is fixed at 0.09 ± 0.01
 throughout core formation. In the second, $X_{\text{FeO}}/X_{\text{Fe}}$ increases from 0.009 to 0.09 ± 0.01 and in the
 third scenario it decreases from 0.21 to 0.09 ± 0.01 . For models that undergo oxidation or
 reduction during accretion, $\log f\text{O}_2$ is initially constant, then evolves linearly, starting at 10-90%
 of accretion. The final $f\text{O}_2$ in all models corresponds to IW-2 ± 0.1 (calculated as $2\log[X_{\text{FeO}}/X_{\text{Fe}}]$).
 We have also considered both S-bearing and S-free models, but note that the results of S-bearing
 models should be regarded with caution, due to our incomplete understanding of the effects of S
 on $D_{\text{Au}}^{\text{Met/Sil}}$ at high P .

Representative temperatures of metal-silicate equilibrium in the magma ocean may plausibly fall
 between the liquidus and solidus of a primitive mantle composition. We have therefore
 performed models that consider this range of temperatures, by setting the imposed equilibrium
 temperature (T_λ) as a fraction of the temperature difference between liquidus and solidus

658 $(T_{\lambda} = \lambda \times T_{Liquidus} + (1 - \lambda) \times T_{Solidus}; \text{ where } 0 \leq \lambda \leq 1)$. There is significant uncertainty, however, in
659 the melting relations of likely mantle compositions at high pressure (>20 GPa), which is
660 important to our constraining the metal-silicate equilibration temperature. In order to assess the
661 effect of this uncertainty, we have performed models that employ two different sets of phase
662 relations. The first using “cold” solidus and liquidus curves taken from Andraut et al. (2011) and
663 the latter using “hot” solidus and liquidus curves from Fiquet et al. (2010).

664

665 To find the range of conditions most likely to yield the correct core-mantle distribution of Au, Ni
666 and Co, we have performed a total of 6×10^6 simulations that explore the parameters described
667 above. Namely: the effect of magma ocean depth as a percentage of the core-mantle boundary
668 depth (%CMB depth; 1-100%), metal-silicate disequilibrium (ϕ ; 0-1), sulphur content of the
669 metal phase (as a representative light-element) (X_s ; 0.01-0.16), temperature relative to the magma
670 ocean liquidus (T_{λ} ; 0-1), and redox evolution during core segregation ($X_{FeO}^{initial}$; 0.009, 0.09±0.01,
671 0.21, oxidation step; 10-90% accretion). For each simulation, new values for each of the above
672 parameters are selected at random from the stated ranges. A summary of the model conditions,
673 partitioning parameterisations and number of simulations is provided in Table 4. An individual
674 set of model conditions is considered successful if it produces a core-mantle distribution for all
675 elements that is within error of the apparent partition coefficients estimated for Earth. Values for
676 the apparent partition coefficients (as $D^{Met/Sil}$) of Ni and Co between core and mantle are those
677 summarized by Siebert et al. (2011). For Au, the apparent value of $D^{Met/Sil}$ is calculated using the
678 CI and PUM concentrations of Au from Palme & O'Neill (2003) and Fischer-Gödde et al. (2011)

679 respectively. This yields a value of 2.65 ± 0.60 (2σ) for $\log D_{Au}^{Met/Sil}$. Models were performed using
680 the Mathematica programming language and the script provided as supplement S4.

681
682 Figure 7 displays the “hot” (Fig 7a) and “cold” (Fig 7b) solidus and liquidus curves used in the
683 models, alongside the final P - T conditions of successful model scenarios. Apparent from this
684 figure is that models employing the Righter et al. (2015) parameterisation yield successful results
685 at generally higher pressures and temperatures than models using the parameterisation found in
686 this study. Maximum equilibration temperatures determined using either parameterisation,
687 however, display a modest change over the range of respective maximum equilibration pressures
688 (<200 K). This result can be observed graphically in Fig 7 as a shift in temperatures toward the
689 solidus with increasing magma ocean depth. Figure 7 also reveals that models employing the
690 “hot” solidus and liquidus curves of Fiquet et al. (2010) yield a much smaller range of conditions
691 at which core-mantle distributions of Au, Ni and Co are successfully reproduced. This restriction
692 is particularly severe when using the parameterisation for Au partitioning determined in this
693 study. Conversely, for models that use the melting relations of Andraut et al. (2011), a wide
694 range of successful conditions are found, in which permissible temperatures extend from the
695 solidus to the liquidus over a broad pressure range (~ 30 -70 GPa).

696
697 It has been suggested that equilibrium between metal and silicate melts during core-segregation
698 may be incomplete (e.g. Allegre et al. 2008; Dahl & Stevenson, 2010; Rudge et al., 2010).
699 Figures 8a and b display the effect of disequilibrium on metal-silicate equilibration depth and
700 redox evolution for “hot” and “cold” melting models respectively. Regardless of the melting

relations used, magma ocean depths recorded by successful models using the Righter et al. (2015) parameterisation generally increase as metal-silicate equilibrium becomes less efficient. For models employing the parameterisation determined in this study, however, disequilibrium shows little correlation with magma ocean depth. It is also noteworthy that models in which the proto-earth is initially oxidized, and undergoes reduction during accretion, generally yield a larger number of successful models that span a broader range of P - T - ϕ conditions, regardless of the parameterisation used for Au. This is due to the effect of redox evolution on the partitioning of Ni and Co however, as the distribution of Au is only weakly dependant (Righter et al. 2015) or independent (this study) of fO_2 under reducing conditions. No successful models are found for values of ϕ less than ~ 0.1 .

Models which include the effect of adding 0.1-10 wt% S to core-forming metal are shown as the green squares and crosses in Figure 7 for models using the parameterisation from this study and Righter et al. (2015) respectively. As expected, the addition of S decreases the maximum P - T conditions of metal-silicate equilibration. Using the parameterisation determined in this study, no successful models are found for $X_s > 0.07$ when using the “cold” melting relations and no successful results were found when using the “hot” melting relations after 10^6 simulations. The difficulty in simultaneously matching Ni, Co and Au abundances in models that include a significant abundance of S suggests more work is required to properly understand the effect of this and other light elements on the metal-silicate partitioning of Au at high pressure.

A much greater number of successful model results are found when using the parameterisation found by Richter et al. (2015), due to the weaker dependency of partitioning on T and inverse dependence on P they find relative to this study. As discussed above, the existing database of experiments does not fully illuminate the coupled effects of P and light-element content, which lends uncertainty to the c term determined by Richter et al. (2015) and in this study. We are more confident, however, in the higher value for b used in our parameterisation, as it was determined from a series of experiments ($n = 15$), performed at the same laboratory, in which silicate melt composition, oxygen fugacity and pressure were carefully controlled to ensure T was the only variable. In the absence of thermodynamic data from which the T dependence of $Kd_{Au}^{Met/Sil}$ can be independently constrained (c.f. Wade & Wood 2005), we consider experimental series of this type the safest way to determine the effect of individual variables. Despite differences between these alternative parameterisations, and thus the breadth of conditions under which successful model results are found, the observation that maximum equilibration T depends only weakly on redox evolution, equilibration P and the efficiency of metal-silicate equilibration confirms the usefulness of Au as a magma ocean thermometer.

Despite the limitations discussed above, several broad implications can be drawn from the model results. The first is that metal-silicate equilibration is unlikely to have occurred at extreme temperatures (i.e. final equilibration above ~ 3600 K), and the highest density of successful models is associated with much lower temperatures (final equilibration ≤ 3200 K). Many successful results are found for sub-liquidus equilibration temperatures, and for models 1-6, there is a noteworthy increase in the density of successful results when $T_{\lambda} \leq 0.5$. This is consistent with metal ponding, equilibrating and then segregating from the rheological base of a magma

ocean as suggested by numerous previous studies (e.g. Solomatov 2000; Wade & Wood 2005; Wood et al. 2006; Rubie et al. 2007). This raises the possibility of element fractionation arising from partitioning between metal and crystalline phases during core-formation. For Au, mineral-melt partitioning has only been determined experimentally for olivine and chromite (Richter et al. 2004; Brenan et al. 2005). It is seen to be incompatible in both these phases, however, suggesting silicate melt may remain the primary mantle host for Au during core-segregation if similar incompatibility persists for high pressure crystalline phases. Secondly, the restriction of metal-silicate equilibrium to modest T has implications for the partitioning of light elements into the core. Metal-silicate partitioning experiments for oxygen, silicon and sulphur reveal a significant dependence upon temperature for all these elements (e.g. Ricolleau et al. 2011, Boujibar et al. 2014), which may be further complicated by the effect of T on activity-composition relations for core-forming alloys. As an example, we have calculated the Si and O content of the core following single-step equilibration using the model of Ricolleau et al. (2011), for conditions corresponding to the “hot” solidus and liquidus employed in our earlier models. If the maximum P - T conditions of metal-silicate equilibrium are as low as suggested by the results of models 1-4, Si and O will comprise <2.5 wt% of the core; thus requiring additional light element components (e.g. S, C) to account for the total core density deficit.

6. Summary

We have investigated the solubility and metal-silicate partitioning of Au as a function of changes to the composition of metal and silicate melts at 0.1 MPa and $\sim$ IW -1 to +1. We have also determined the effect of pressure on Au solubility from isothermal experiments performed at 2-

15 GPa. Our results show that Au becomes less siderophile as S is added to the system, both through the avoidance of non-metal in the Fe phase and enhanced solubility in the silicate melt. This is consistent with investigations of Au solubility in sulphur-bearing silicate melt at conditions close to the fayalite-magnetite-quartz buffer (Botcharnikov et al., 2010; Zajacz et al., 2013). Importantly, the change in $D^{Met/Sil}$ with sulphur addition is not adequately described by changes solely to the activity-composition relations of the metal. Melt polymerisation has no discernable effect on Au partitioning over the studied range of compositions (NBO/T ~0.7 – 1.5). Experiments to investigate the effect of P display a slight decrease in values of $D^{Met/Sil}$ as P increases. Using the results of this and previous studies, Au partitioning was parameterized as a function of P , T and metal sulphur content. This parameterisation was used, alongside similar relationships for Ni and Co, to constrain the maximum P - T conditions of metal-silicate equilibrium in the terrestrial magma ocean. Results from continuous accretion models suggest that metal-silicate equilibrium in a deep magma ocean (final $P > 40$ or > 70 GPa for “hot” and “cold” melting relations respectively) would have occurred at temperatures below the peridotite liquidus. This is in keeping with the physical conditions expected for a scenario where core-forming metal ponds and equilibrates at the base of a magma ocean (e.g. Wade & Wood, 2005).

Acknowledgements

Work completed at The University of Toronto was supported by research and facilities funding provided to J.M.B. by the Natural Sciences and Engineering Research Council of Canada (NSERC). Pressure calibration experiments for the 14/8 multi-anvil assembly were performed by Gummi Gudfinnsson. Experiments and analyses done at the Geophysical Lab were supported by

the post-doctoral fellowship program at the Carnegie Institution of Washington and by a NSF Geochemistry grant (awarded to Y.F.). Thanks are extended to Yanan Liu, John Armstrong and Katherine Crispin for assistance with sample analysis by electron beam techniques. Juzer Noman is acknowledged for his involvement with experiments to investigate the effect of sulphur as part a NSERC summer research fellowship. We also thank Angele Ricolleau for sharing details of her calculation for O and Si partitioning during single-step core formation.

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1045 Figure 1: (a) Overview of a typical sulphur-bearing experiment (AuFeS 2). The dark lines and
1046 spots are pits remaining after analysis by LA-ICPMS. (b) Enlarged view of the highlighted area
1047 in (a), displaying the solid Fe alloy (containing LA-ICPMS pits) and the quench textures present
1048 in Fe-S alloy, which was a single liquid phase at the experimental conditions. (c) Overview of a
1049 typical Au solubility experiment (AuMg 3). The crystals forming around the Au bead are
1050 chromite and appear to be nucleating on the surface of the metal phase.

1051

1052 Figure 2: (a) Run product from a multi-anvil experiment done at 2273 K (AuIrBas-MA2). (b)
1053 Example of the Au distribution in experiment AuIrBas-MA1. Au alloy is typically observed
1054 filling pore spaces in the IrFe capsule, or at the interface between silicate melt and the IrFe alloy.
1055 Dispersed inclusions of silicate melt are also often found within the trapped Au pockets.

1056

1057 Figure 3: The effect of sulphur addition on the metal-silicate partitioning of Au. (a) The change
1058 in $\log D^{Met/Sil}$ for Au, as a function of the sulphur content of liquid Fe-S alloy. As sulphur is
1059 added to the system, Au partitions less strongly into the metal phase. (b) Comparison of $\log$
1060 $D^{Met/Sil}$ values for Au measured in these experiments with the values predicted only from non-

metal avoidance in the metal phase (solid black line, see main text for details). Measured $D^{Met/Sil}$ values fall below the predicted line, suggesting S acts to enhance Au solubility in the melt.

Figure 4: The effect of NBO/T on the solubility of Au. (a) Au solubility as a function of NBO/T for experiments at 0.1 MPa, 1723 K and $\sim IW + 1$. No dependence of solubility on melt polymerisation is observed. (b) The metal-silicate partitioning of Au as a function of melt composition: Results from this study for Fe-bearing melts (black diamonds) display no dependence on melt polymerisation. Results from the Fe-free melts of Borisov & Palme (1996) (white circles) were recalculated to 1723 K and agree well with the partition coefficients determined in this study. The mean partition coefficient for iron-bearing experiments is shown as the grey dashed line.

Figure 5: $D_{Au}^{Met/Sil}$ as a function of pressure. The displayed trend is defined by data at 2-15 GPa. The ambient pressure datapoint and error bar are the mean and standard deviation of experiments done at IW 0.9-1.6 from this study and Borisov & Palme (1996) as described in the main text.

Figure 6: The effect of sulphur on the PUM abundance of Au. Gold concentrations in the PUM subsequent to metal-silicate equilibrium and addition of a chondritic late-veneer. X_s is the mole fraction of sulphur in the equilibrating metal phase. The shaded horizontal region indicates the estimated Au contents of PUM and the associated 1σ error on this value (Fisher-Gödde et al. 2011). The stippled region corresponds to the metal sulphur contents if close to the entire density

deficit of the core is attributed to S. The dashed vertical line is the preferred core S contents following McDonough (2003).

Figure 7: Final P - T conditions of metal-silicate equilibrium for models 1, 2, 5, 6 (Fig 7a) and 3, 4, 7, 8 (Fig 7b), projected onto the mantle melting relations used in each case. Red and blue curves correspond to the liquidus and solidus respectively. Grey lines define 10% intervals between the solidus and liquidus, i.e. equilibration T where $\lambda = 0.1$ - 0.9 . Circles and triangles refer to sulphur-free models using the parameterisation for Au partitioning from this study and Righter et al. (2015) respectively. Squares and crosses refer to sulphur-bearing models using the parameterisation for Au partitioning from this study and Righter et al. (2015) respectively. The inset in Fig 7b is an enlargement of the P - T space in which successful models are found when using the parameterisation for Au determined in this study.

Figure 8: Depth of equilibrium (as a percentage of core-mantle boundary depth) versus the efficiency of equilibration (ϕ). Grey circles are the results of models 1 and 3, shown in figures 8a and 8b respectively. The light gray shaded fields represent 2σ confidence intervals for the results of models 5 and 7 (Figs 8a and 8b respectively).

Table 1: Results of sulphur bearing experiments

Table 2: Results of AuMg series experiments

1102 Table 3: Results of multi-anvil experiments

1103 Table 4: Parameters used in models of continuous accretion and core-formation

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1105

Table 1: Sulphur-Bearing Series Phase compositions and Experimental Details

		AuFeS 1	AuFeS 2	AuFeS 5	AuFeS 9	AuFeNiS 1a	AuFeNiS 1b
		wt% (1 s.d.)	wt% (1 s.d.)	wt% (1 s.d.)	wt% (1 s.d.)	wt% (1 s.d.)	wt% (1 s.d.)
Silicate Glass	SiO ₂	45.71 (0.29)	44.81 (0.29)	47.35 (0.29)	46.19 (0.29)	51.21 (0.31)	50.58 (0.31)
	Al ₂ O ₃	10.56 (0.1)	11.38 (0.11)	11.81 (0.11)	08.94 (0.1)	08. (0.14)	09.56 (0.14)
	FeO	22.29 (0.26)	22.03 (0.26)	20.67 (0.25)	19.7 (0.24)	15.37 (0.22)	20.78 (0.22)
	MgO	12.32 (0.12)	13.64 (0.12)	11.42 (0.11)	15.68 (0.13)	19.98 (0.16)	14.7 (0.16)
	CaO	09.06 (0.11)	08.68 (0.11)	08.15 (0.11)	05.37 (0.09)	04.3 (0.14)	02.27 (0.14)
	Na ₂ O	0.2 (0.03)	0.12 (0.03)	0.18 (0.03)	nd	0.16 (0.04)	0.17 (0.04)
	MnO	0.1 (0.05)	0.09 (0.05)	0.09 (0.06)	0.08 (0.04)	0.08 (0.05)	0.13 (0.05)
	SO ₃	0.75 (0.04)	0.72 (0.04)	0.57 (0.05)	0.53 (0.04)	0.34 (0.47)	0.52 (0.47)
	NiO	nd	nd	nd	nd	nd	nd
	Cr ₂ O ₃	nd	nd	0.89 (0.04)	04.92 (0.08)	01.58 (0.05)	02.88 (0.05)
Totals		100.99	101.47	101.11	101.40	101.03	101.59
Sulphide Melt	Fe	74.61 (0.21)	78.01 (0.22)	66.72 (0.2)	94.01 (0.24)	71.43 (0.21)	80.84 (0.22)
	Ni	nd	0.05 (0.04)	0.04 (0.03)	01.51 (0.04)	04.27 (0.06)	05.23 (0.07)
	S	23.35 (0.18)	21.05 (0.17)	31.13 (0.2)	04.28 (0.08)	21.68 (0.17)	11.72 (0.13)
	Si	0.36 (0.05)	nd	0.11 (0.03)	nd	nd	0.04 (0.03)
	Au	0.41 (0.07)	0.33 (0.08)	0.6 (0.08)	0.5 (0.09)	01.21 (0.1)	02.02 (0.12)
	Totals	98.72	99.43	98.61	100.30	98.59	99.87
Solid Iron Alloy	Fe	98.75 (0.36)	100.1 (0.24)	98.41 (0.24)	-	93.56 (0.23)	93.68 (0.23)
	Ni	0.05 (0.03)	0.05 (0.03)	0.06 (0.03)	-	05.23 (0.07)	05.17 (0.07)
	S	0.06 (0.01)	0.06 (0.02)	0.06 (0.02)	-	0.05 (0.04)	0.06 (0.02)
	Si	nd	0.03 (0.03)	0. (0.04)	-	0.1 (0.03)	nd
	Au	0.33 (0.5)	0.28 (0.08)	0.84 (0.09)	-	0.87 (0.09)	0.74 (0.09)
	Totals	99.19	100.52	99.36	-	99.80	99.65
ΔIW		-1.22	-1.24	-1.28	-1.24	-1.54	-1.24
log fS ₂ ¹		-4.38	-4.37	-4.65	-4.04	-4.24	-4.38
T (K)		1623	1621	1573	1753	1650	1609
P (MPa)		0.1	0.1	0.1	0.1	0.1	0.1
log D ^{Met/Sil}		4.20	4.41	4.18	4.73	4.60	4.84
log D ^{Met/Sil} (recalc) ²		4.01 (0.07)	4.21 (0.08)	3.79 (0.09)	5.01 (0.06)	4.52 (0.05)	4.59 (0.03)
Duration (mins)		133	118	88	72	46	91

¹Sulphur fugacity calculated using the 3-species model for Fe-S liquids from Sharma & Chang (1979) with the interaction parameters determined by Chuang et al (1985).

²Partition coefficients following recalculation to a common T of 1673 K.

Table 2: AuMg Series Phase Compositions and Experimental Details

		AuMg1	AuMg2	AuMg3	AuMg6	AuMg12	AuMg13
		wt% (1 s.d.)	wt% (1 s.d.)	wt% (1 s.d.)	wt% (1 s.d.)	wt% (1 s.d.)	wt% (1 s.d.)
Silicate Glass	SiO ₂	52.35 (0.31)	54.56 (0.32)	51.87 (0.31)	57.9 (0.33)	56.11 (0.34)	55.16 (0.33)
	Al ₂ O ₃	10.86 (0.1)	09.5 (0.1)	08.7 (0.09)	08.5 (0.09)	13.1 (0.12)	13.29 (0.12)
	FeO	05.54 (0.13)	06.1 (0.14)	07.13 (0.15)	06.94 (0.15)	12.1 (0.19)	11.85 (0.19)
	MgO	19.74 (0.14)	20.38 (0.15)	23.27 (0.16)	20.57 (0.15)	16.02 (0.14)	17.45 (0.14)
	CaO	10.32 (0.13)	07.63 (0.11)	08.03 (0.11)	05.63 (0.09)	0.36 (0.03)	0.64 (0.04)
	Na ₂ O	nd	0.06 (0.03)	0.03 (0.02)	0.1 (0.03)	nd	nd
	MnO	nd	0.12 (0.04)	0.15 (0.04)	0.17 (0.04)	0.26 (0.04)	0.19 (0.04)
	Cr ₂ O ₃	02.42 (0.06)	02.94 (0.06)	02.21 (0.06)	01.46 (0.05)	01.85 (0.05)	01.62 (0.05)
	Total	101.23	101.29	101.40	101.26	99.79	100.20
Au Alloy	Fe	03.7 (0.05)	03.96 (0.05)	04.58 (0.05)	01.15 (0.03)	02.11 (0.04)	02.09 (0.04)
	Ni	0.14 (0.03)	0.14 (0.03)	0.19 (0.03)	nd	nd	0.13 (0.03)
	Au	96.81 (0.62)	95.78 (0.61)	94.13 (0.61)	99.17 (0.62)	97.34 (0.62)	96.4 (0.61)
	Si	0.1 (0.03)	nd	0.85 (0.05)	nd	nd	0.15 (0.06)
	Total	100.74	99.88	99.76	100.32	99.89	98.76
NBO/t		1.22	1.19	1.45	1.12	0.77	0.83
T (K)		1723	1723	1723	1723	1723	1723
P (MPa)		0.1	0.1	0.1	0.1	0.1	0.1
¹ C Au (ppm)		2.68 (0.52)	4.7 (0.54)	3.14 (0.59)	1.69 (0.08)	2.28 (0.14)	2.26 (0.12)
² log D ^{Met/Sil}		5.04 (0.08)	4.79 (0.05)	4.97 (0.08)	5.24 (0.02)	5.11 (0.00)	5.11 (0.02)
Duration (min)		114	114	114	111	159	159

¹Concentration of Au measured in run product glass following correction to unit activity of Au in the alloy phase.²Metal-silicate partition coefficient for Au, calculated using equation 7 after activity correction.

Table 3: High Pressure Series Phase Compositions and Experimental Details

		AulrBas-MA1	AulrBas-MA2	AulrBas-MA3	AulrBas-MA4
		wt% (1 s.d.)	wt% (1 s.d.)	wt% (1 s.d.)	wt% (1 s.d.)
Quenched Silicate Melt	SiO ₂	37.57 (0.45)	33.74 (0.96)	31.9 (0.69)	33.68 (0.77)
	Al ₂ O ₃	0.53 (0.12)	0.67 (0.07)	0.61 (0.06)	0.58 (0.06)
	FeO	24.85 (02.13)	35.62 (01.99)	40.45 (01.58)	33.4 (01.56)
	MgO	34.71 (02.02)	28.14 (0.92)	23.9 (01.39)	29.52 (0.95)
	CaO	0.7 (0.13)	0.9 (0.1)	0.92 (0.14)	0.71 (0.07)
	MnO	0.03 (0.03)	0.05 (0.04)	0.02 (0.03)	0.02 (0.03)
	Na ₂ O	0.54 (0.1)	0.87 (0.1)	0.38 (0.05)	0.64 (0.08)
	NiO	0.05 (0.04)	0.08 (0.05)	0.08 (0.04)	0.1 (0.06)
	Total	99.55	100.06	98.24	98.64
Ir Fe Alloy Capsule	¹ O	1.49 (0.07)	1.46 (0.1)	1.24 (0.17)	1.32 (0.1)
	Si	0.29 (0.01)	0.33 (0.01)	0.3 (0.02)	0.31 (0.02)
	Fe	6.85 (0.08)	6.95 (0.06)	5.64 (0.07)	7.03 (0.03)
	Ir	91.26 (0.13)	91.7 (0.17)	93.26 (0.22)	90.39 (0.22)
	Total	99.90	100.46	100.45	99.06
		<i>T</i> (K)	² 2238	² 2278	2277
		<i>P</i> (Gpa)	15	13	11
		ΔIW	0.96	1.72	1.29
		<i>C</i> Au (ppm)	102.4 (12.9)	102.5 (12.3)	86.4 (5.5)
		<i>C</i> Au (ppm) corr ³	114.7 (14.4)	111.6 (13.4)	96.3 (6.1)
		log <i>D</i> ^{Met/Sil}	3.41 (0.05)	3.42 (0.05)	3.48 (0.03)
		Duration (m)	7	5	5

¹Oxygen analyses were subject to a background correction of 0.89wt%, determined from analysis of a nominally oxygen-free Re foil.

²Temperature determined from power-temperature relationship.

³Gold concentrations after correction to unit activity of Au as described in the main text.

Table 4: Parameters Used for Continuous Accretion Model

		Au	Ni ¹	Co ¹
Coefficients for use with equation 27	<i>a</i>	-1.10 (0.04)	0.1 (0.16)	0.27 (0.16)
	<i>b</i>	1.11 (0.01)	0.36 (0.03)	0.18 (0.03)
	<i>c</i>	-67.8 (10.9)	-57.0 (5.0)	-37.0 (5.0)
	<i>d</i>	5.81 (0.24)	-	-
	<i>n</i>	0	2	2
² Coefficients for use with Righter et al. (2015) parameterisation for $\ln D^{Met/Sil}$	<i>a</i>	-0.23 (0.77)	-	-
	<i>b</i>	1.5650 (0.15)	-	-
	<i>c</i>	31.4 (9.8)	-	-
	<i>d</i>	9.0 (0.6)	-	-
	<i>e</i>	3.8 (2.3)	-	-
	<i>f</i>	-0.21 (0.18)	-	-
	<i>g</i>	-0.15 (0.02)	-	-
"Hot" melting relations from Fiquet et al. (2010)	Planetesimal $D^{Met/Sil}$	2140	202	463
	Core Fraction	0.325		
	Mantle Fraction	0.675		
	Liquidus T	$1865+49.494P-0.1788P^2$		
	Solidus $T < 20$ GPa	$1358.8+174.29P-10.559P^2+0.2252P^3$		
	Solidus $T > 20$ GPa	$1922.1+23.541P+0.0421P^2-0.0011P^3+3E-6P^4$		
"Cold" melting relations from Andraut et al. (2011)	Liquidus T	$2090.49+23.68P-0.00449P^2-0.00019P^3$		
	Solidus T	$2162.45+10.90P+0.07678P^2-0.00036P^3$		
Model No.	Parameterisation	Melting Relations	No. of Simulations	Sulphur
1	This Study	Hot	$1*10^6$	x
2	This Study	Hot	$1*10^6$	✓
3	This Study	Cold	$1*10^6$	x
4	This Study	Cold	$1*10^6$	✓
5	Righter et al. (2015)	Hot	$5*10^5$	x
6	Righter et al. (2015)	Hot	$5*10^5$	✓
7	Righter et al. (2015)	Cold	$5*10^5$	x
8	Righter et al. (2015)	Cold	$5*10^5$	✓

¹Coefficients for Ni and Co taken from Siebert et al. (2012).² $\ln D^{Met/Sil} (Au) = a + b 10^4/T + cP/T + d \ln(1-X_s) + e \ln(1-X_c) + f(nbo/t) + g \ln fO_2$

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8