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High pressure partitioning behavior of Mo and W and late sulfur delivery during Earth's core formation

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Abstract

Mo and W in the bulk silicate Earth and their partitioning behavior between molten metal and silicate can be used to constrain the thermochemical conditions during Earth's core-mantle differentiation. In order to improve our understanding of core-forming conditions, we performed a series of superliquidus metal-silicate partitioning experiments on Mo and W at 40-93 GPa and 3000-4700 K in laser-heated diamond anvil cells. Under the extended P-T conditions directly relevant to terrestrial core formation in a deep magma ocean, we find that pressure and temperature have profound yet opposing effects on their partitioning, and a significant amount of O dissolved in the metal. Based on an activity model for liquid Fe-rich metal, it is observed that O enhances the solubility of both Mo and W in the metal, whereas S makes W significantly less siderophile than Mo. Combining our new data with those of the literature, we modeled the effects of pressure, temperature and metal composition on partitioning, and applied them to a multi-stage accretion model. While our model with homogeneous S accretion successfully explains the abundance of Mo, it underestimates that of W and therefore overestimates Mo/W ratio in Earth's mantle, regardless of the oxidation conditions prevailing during core formation. On the other hand, mantle observables (Mo and W abundances, Mo/W ratio) can be reproduced simultaneously if S is supplied to the Earth towards the end of accretion. This corroborates previous work at lower pressures, and agrees with heterogeneous accretion models where the late volatile-rich delivery was envisaged to explain various isotopic signatures of terrestrial bodies. Nonetheless, this conclusion does not discriminate between reducing and oxidizing conditions.

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1. Introduction

Core formation by metal-silicate segregation in a magma ocean is the first significant differentiation event in Earth (Ringwood, 1959; Li and Agee, 1996; Wood et al., 2006). This equilibration process partitions siderophile elements to the core and leaves behind lithophile elements in the magma ocean (i.e., the mantle), establishing the compositions of both reservoirs. The relative depletion of siderophile elements in the mantle is evaluated by comparison between the compositions of the mantle and chondritic meteorites, which are considered to sample the undifferentiated building materials of planets (McDonough and Sun, 1995). Metal-silicate partitioning experiments of siderophile elements under high pressure and high temperature can then be used to match the observed depletions, and further constrain the pressure (P), temperature (T), composition and oxygen fugacity (fO_2) conditions of core formation (Li and Agee, 1996; Righter et al., 1997; Wade and Wood, 2005; Bouhifd and Jephcoat, 2011; Siebert et al., 2013; Badro et al., 2015; Fischer et al., 2015; Huang et al., 2020).

Like other ‘geochemical twins’ (e.g., Zr and Hf, Nb and Ta) vertically adjacent to each other in the periodic table, Mo and W share some important geo/cosmochemical properties. In particular, they are the only two moderately siderophile elements that are at the same time cosmochemically refractory. This makes them a useful monitor of core formation conditions, because they should accrete into the chondritic Earth in the same fashion as other refractory elements and then partition moderately into the core, maintaining their abundances resolvable in both mantle (not easily affected by later additions) and core after core formation. Additionally, the study of W is of broad interest due to the fact that the Hf-W isotope systematics provide important constraints on the timing of core formation (Kleine et al., 2002; Yin et al., 2002).

As two of the most intensively studied elements in terms of partitioning experiments, Mo and W have been found to vary their partitioning behavior dramatically as a function of P, T, silicate and metal compositions and fO_2 , with a spread of measured partition coefficients over several orders of magnitude. Most importantly, they turn out to share many similarities in partitioning. For example, previous experimental studies have generally shown that

35 temperature, polymerization degree of silicate melt, carbon content in the
36 metal have a positive effect (i.e., more siderophile), whereas pressure, fO_2 ,
37 and sulfur/silicon content in the metal exert a negative influence on both Mo
38 and W partitioning (i.e., more lithophile) (Walter and Thibault, 1995; Jana
39 and Walker, 1997b,c; Righter et al., 2010; Siebert et al., 2011; Tuff et al.,
40 2011; Wade et al., 2012; Shofner et al., 2014; Wood et al., 2014; Righter
41 et al., 2016). A few studies have shown varying properties between Mo and
42 W: Righter et al. (2010) and Siebert et al. (2011) reported opposite tempera-
43 ture dependence for Mo, Cottrell et al. (2009) found negative dependence on
44 temperature and non-monotonic effect of pressure for W, and Jennings et al.
45 (2021) observed negligible pressure influence on W partitioning. Apart from
46 these disagreements as regards pressure and temperature, the partitioning
47 of Mo and W further raises the question of delivery (especially the timing)
48 of volatiles during Earth’s accretion, such as sulfur and carbon. Stronger
49 partitioning of W relative to Mo into the core, which contradicts the mantle
50 abundances of Mo and W, requires S delivery to the Earth only during late
51 stages of core formation (Wade et al., 2012; Wood et al., 2014). Recently,
52 Jennings et al. (2021) found that the interactions between C and Mo (and
53 W) would make both more siderophile, based on which their N-body accre-
54 tion models favored a C-rich scenario in early accreting Earth, in order to
55 reduce the mantle abundances of Mo and W to the observed values. Previous
56 work on Mo and W has in general reached a reasonable level of agreement
57 on the complex effect of P-T-composition- fO_2 , yet the extrapolation to the
58 P-T conditions relevant to a deep magma ocean is somewhat problematic.
59 The aforementioned discrepancies on the effects and magnitudes of different
60 variables on W and Mo partitioning, may be resolved by a much larger P-T
61 range accessible with laser-heated diamond anvil cell (LHDAC) experiments.

62 The study of metal-silicate partitioning under extreme P-T conditions has
63 been shown necessary to improve our understandings towards core formation.
64 The so-called ‘excess siderophile element problem’ arises when one predicts
65 their mantle concentrations based on partitioning experiments conducted at
66 1 bar (Ringwood, 1966). This apparent discrepancy between observation and
67 prediction begins to converge at high pressures and temperatures, remarkably
68 for Ni and Co (Li and Agee, 1996; Siebert et al., 2012), another two important
69 moderately siderophile elements. In the case of both Mo and W, to date
70 most metal-silicate partitioning experiments have a pressure limit of ~ 25
71 GPa using piston-cylinder or multi-anvil press, even though much higher
72 P–T conditions up to 75 GPa / 4350 K for core-mantle equilibration have

73 been recently modeled (Badro et al., 2014). Furthermore, the necessity of
74 DAC experiments also resides in the possibility to probe the interactions of
75 trace elements with oxygen in liquid metal. Unlike Si, S and C which have
76 been widely studied under lower pressures, oxygen solubility in the metal is
77 rather limited in large-volume press compared to LHDAC, because of the
78 limited P-T conditions (Rubie et al., 2004; Asahara et al., 2007; Ricolleau
79 et al., 2011; Siebert et al., 2012). The newly quantified influences of oxygen
80 on siderophile (Siebert et al., 2013) and even lithophile (Badro et al., 2016;
81 Blanchard et al., 2017; Chidester et al., 2017; Badro et al., 2018; Huang et al.,
82 2020) elements have been shown to be dramatic, which warrants the study
83 of Mo and W partitioning under higher P-T conditions in LHDAC. To the
84 best of our knowledge, partitioning data under extreme P-T (> 25 GPa)
85 conditions is unavailable for Mo, and rare for W (Shofner et al., 2014). In
86 this study, we aim to provide constraints on core formation by extending the
87 P-T range of metal-silicate equilibration for Mo and W to 93 GPa and 4700
88 K, and by quantifying the effect of dissolved oxygen along with other light
89 elements, under conditions comparable to a deep magma ocean.

90 **2. Methods**

91 *2.1. Starting materials*

92 The starting silicate glasses were synthesized using an aerodynamic lev-
93 itation furnace at IPGP. High purity oxides (FeO, MgO, Al₂O₃, and SiO₂)
94 and carbonate (CaCO₃) were ground and mixed in ethanol in an agate mor-
95 tar, to produce a pyrolitic composition (McDonough and Sun, 1995) with
96 low FeO content (4 wt%). The pyrolitic composition (Table S1) was used
97 throughout to limit the effect of silicate melt composition on partitioning. W
98 was added as ICP standard solution (in nitric acid) in one of the three differ-
99 ent mixtures. The mixtures were then decarbonated at 950°C, and further
100 transformed into glass beads in an Argon flux using the levitation furnace
101 coupled with a 75 W CO₂ laser ($\lambda = 10.6 \mu\text{m}$). They were subsequently hand
102 polished to $\sim 20 \mu\text{m}$ thick and machined into small disks suitable for DAC
103 loading using a picosecond laser machining system at IPGP.

104 The metallic starting materials were either commercial reagent Fe-rich
105 metal balls (91% Fe + 9% Si, or 96% Fe + 4% S) or synthetic Fe-Mo(-S). The
106 latter alloy was synthesized in a piston-cylinder apparatus by equilibrating
107 natural MORB (doped with Mo +/- S) with the commercial silicon-bearing
108 iron alloy at 2 GPa and 1800°C for 2 minutes. Synthesized metal was then

109 crushed and finely ground to serve as starting metal for DAC experiments.
110 The chemical homogeneity of both silicate glasses and metal was confirmed
111 by microprobe (or EDS) results listed in Table S1.

112 *2.2. Diamond anvil cell experiments*

113 High pressure was generated using symmetric DACs. Re gaskets were
114 pre-indented to 40-50 μm thick by diamond anvils with flat culet diameters
115 of 200 μm or 300 μm . A hole of ~ 100 μm or 150 μm in diameter was drilled
116 in the gasket by a picosecond laser to form a sample chamber. Starting met-
117 als were loaded in between two layers of silicate disks which also served as
118 thermal and chemical insulators during heating. Sample assembly was com-
119 pressed to a pressure of interest and subsequently laser-heated from both
120 sides using a fiber laser ($\lambda = 1070$ nm, 200 W) with a focused beam size of
121 ~ 20 μm in diameter. The laser power was ramped at first and then held for
122 30 to 60 seconds once reaching the target temperature, which was set well
123 above the pyrolitic liquidus (e.g. 4700 K at 93 GPa) (Fiquet et al., 2010;
124 Andrault et al., 2011), before quenching. Previous time series experiments
125 under similar high P-T conditions have shown that the metal-silicate equilib-
126 rium can be attained in less than a few seconds (Walter and Thibault, 1995;
127 Corgne et al., 2008) (details in Section 3.1). Temperature was measured con-
128 tinuously by fitting the visible portion of the black-body radiation (500–750
129 nm) from both sides of the heating spot to the Planck black-body function
130 with an estimated uncertainty of ± 250 K (Benedetti and Loubeyre, 2004).
131 Pressure was determined by diamond Raman spectroscopy before and after
132 each experiment (Akahama and Kawamura, 2004), and corrected for thermal
133 pressure ($\Delta P = 2.7$ MPa/K) estimated from previous experiments following
134 the same protocol with in situ X-ray diffraction measurements (Siebert et al.,
135 2012).

136 *2.3. Sample recovery and analysis*

137 After quenching to ambient conditions, thin sections were extracted from
138 the center of the laser-heated area using a Ga⁺ focused ion beam (FIB)
139 instrument equipped with a field emission gun (Zeiss Auriga 40) at IPGP.
140 Thin sections were removed from the gaskets by an in situ micromanipulator,
141 and welded to TEM copper grids. A thin conductive layer of graphite (~ 10
142 nm thick) was deposited on the surface of the thin section for quantitative
143 analysis. A backscattered electron image of the sample recovered from high
144 pressure and temperature is shown in Fig. 1 as an example.

145 Chemical compositions of both metal and silicate phases were obtained
146 by wavelength dispersive X-ray spectroscopy (WDS) using electron probe
147 micro-analysis (EPMA) on a Cameca SX-five at Camparis, and reported in
148 Table S2. An accelerating voltage of 25 kV and a beam current of 40 nA
149 were used in all cases. Peak and background counting times were 15 s for
150 major elements (Mg, Al, Ca, Fe and Si) in the silicate melts and for Fe in
151 the quenched metals, and 60 s for minor and trace elements in both phases,
152 including Si, O, Mg, Al and S in the metal. The detection limits were 100-
153 400 ppm for most elements. Diopside (Ca and Mg), orthoclase (Al and Si),
154 hematite (Fe and O), BaSO₄ (S) and pure Mo and W metals were employed as
155 internal standards. Mo and W were analyzed using $L_{\alpha 1}$ line, whereas all the
156 other elements using $K_{\alpha 1}$ line. For each metal and silicate phase, at least 5
157 spots were measured by microprobe to obtain the mean. To avoid secondary
158 fluorescence from adjacent phases during analysis, samples were sectioned
159 down to 3-4 μm thick with the same proportions of metal-to-silicate on both
160 sides, and electron beam size less than $1\mu\text{m}$ was used to analyze the areas
161 far enough (given the Z- and voltage-dependent interaction volume activated
162 by the electron probe) from the metal-silicate phase boundary. Because
163 quantitative chemical analysis using energy dispersive X-ray spectroscopy
164 (EDS) coupled with FEG-FIB has shown an excellent agreement with EPMA
165 results (Huang and Badro, 2018), we opted for EDS data for four of the
166 samples (X5, X1, X4-1, X6-1, Table S2) whose silicate compositions were
167 biased by the adjacent metal due to the large EPMA beam relative to the
168 silicate. Accuracy of the EDS measurements is expected to be 1% based on
169 the analytical calibrants.

170 Carbon diffusion from diamond anvils during heating was observed in the
171 quenched metallic phase in some DAC experiments e.g., by Fischer et al.
172 (2015). However, our previous superliquidus experiments following the same
173 experimental procedure (Siebert et al., 2012, 2013) found carbon content be-
174 low detection limit. We therefore infer carbon content in our samples to be
175 insignificant, or below the detection limit of EPMA ($\sim 1\text{wt}\%$), based on the
176 following additional observations: i) the molten silicate and metal are chemi-
177 cally isolated from the diamond anvils by a layer of untransformed solid glass
178 (Fig. 1), and ii) quantitative EDS analyses show similar peak intensities of
179 carbon in both metal and silicate melts, indicating that carbon contamina-
180 tion was likely introduced during analysis (e.g., by carbon coating or carbon
181 tape), instead of during high-pressure experiments. However, even if C was
182 below detection limit, its presence in the metal might still exert influence on

183 the partitioning of Mo and W, which needs to be addressed. Assuming the
 184 carbon content in all our metal liquids to be 1 wt%, the maximum amount
 185 estimated based on our previous discussion, we refit Eq. 11 (see Section 3),
 186 and compared the parameters with and without C in the metal (Table S5).
 187 As can be found in Table S5, the temperature (b) and pressure (c) terms in
 188 either case are indistinguishable from each other within uncertainties. This
 189 shows that the maximum 1 wt% C conceived in the metal has negligible effect
 on the partitioning of Mo and W.

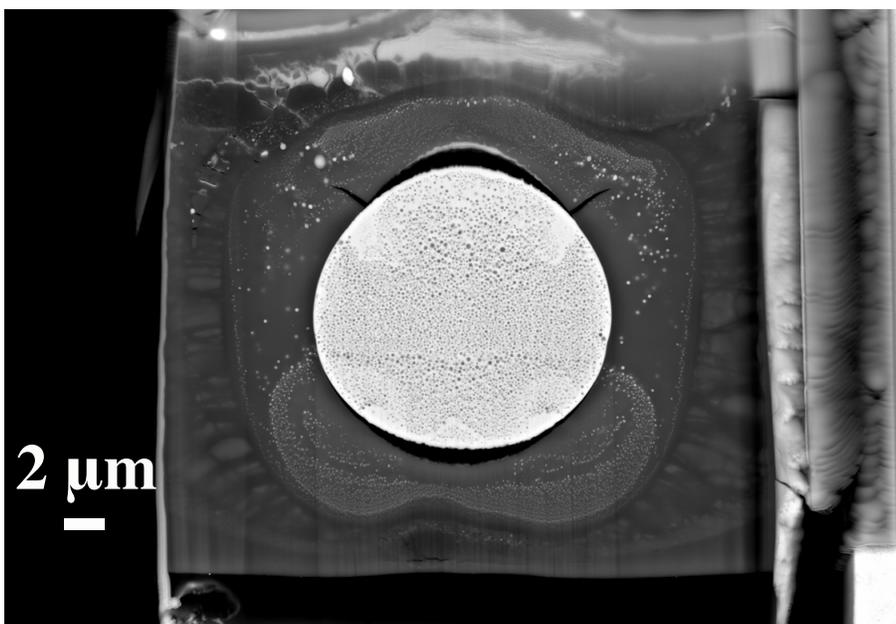


Figure 1: Backscattered electron image of a FIB section recovered from one of our diamond anvil cell experiments containing W at 48 GPa and 3670 K.

190

191 3. Results

192 Twelve superliquidus metal-silicate partitioning experiments in diamond
 193 anvil cells were performed at various P-T conditions and summarized in Table
 194 1. Oxygen fugacity is evaluated relative to the iron-wüstite (IW) buffer:

$$fO_2(\Delta IW) = 2 \log \left(\frac{a_{FeO}^{sil}}{a_{Fe}^{met}} \right), \quad (1)$$

195 where a_{FeO}^{sil} and a_{Fe}^{met} are the activities of FeO and Fe in the silicate and
 196 metal, respectively, which are approximated as their mole fractions by as-
 197 suming ideal behavior. Most of our experiments result in similar oxidized
 198 conditions (1 to 2 log units below the IW buffer) regardless of the reduced
 199 starting compositions with low-FeO silicates (Table S1), which is similar to
 200 previous studies using DACs (Siebert et al., 2012; Fischer et al., 2015; Badro
 201 et al., 2016; Huang and Badro, 2018). This may be explained by the in-
 202 creased partitioning of Si into the metal with increasing P-T resulting in
 203 metallic Fe being oxidized, and of FeO from solid to liquid silicate due to its
 204 incompatibility (cf. Siebert et al. (2012)).

205 The typical morphology of a recovered sample consists of a spherical
 206 metallic blob embedded in a silicate melt, as shown in Fig. 1. Quench
 207 textures were formed by rapid exsolutions of Si-O-rich (in the metal) and Fe-
 208 rich blobs (in the silicate) (both < 200 nm) during the quench. These features
 209 were observed in all our experiments, and shared by previous partitioning
 210 studies using LHDAC (Siebert et al., 2012; Fischer et al., 2015; Badro et al.,
 211 2016; Huang and Badro, 2018). Although it seemingly exhibits zonation in
 212 both phases, point analysis at the length scale of 1-2 μm (estimated from the
 213 X-ray excitation volume for metal and silicate phases) and larger window
 214 analysis (raster-scanned electron beam, whenever possible) show chemical
 215 homogeneity within each phase over the entire thin section (Table S2).

Table 1: Runs summary for the diamond anvil cell experiments.

Exp. No.	X5	X1	X4-1	X6-1	X4-J	X6-J	X4-2	X17	X7	X6-2	X9	X3
Pressure (GPa)	57(6)	39(4)	70(7)	93(9)	54(5)	41(4)	48(5)	60(6)	71(7)	48(5)	58(6)	71(7)
Temperature (K)	3950(200)	3020(150)	4190(210)	4670(250)	3600(180)	3100(160)	3670(180)	4070(200)	4250(220)	3700(190)	4050(200)	4290(220)
f_{O_2} (ΔIW) ^a	-2.6	-1.4	-1.7	-3.5	-1.4	-1.7	-1.3	-1.3	-1.3	-1.3	-1.5	-1.2
Starting Metal	Fe-Mo alloy	Fe-Mo alloy	Fe-Mo alloy	Fe-Mo alloy	Fe-Mo-S alloy	Fe-Mo-S alloy	Fe-Si alloy	Fe-Si alloy	Fe-Si alloy	Fe-Si alloy	Fe-S alloy	Fe-S alloy
Starting Silicate ^b	PYR4-1	PYR4-1	PYR4-1	PYR4-1	PYR-J	PYR-J	PYR-W	PYR-W	PYR-W	PYR-W	PYR-W	PYR-W
D_{Mo}	22(10)	25(5)	25(7)	58(14)	20(6)	31(9)						
D_W							26(5)	16(4)	32(8)	29(5)	12(2)	9(1)

Note: (a) Oxygen fugacity relative to the iron-wüstite buffer is approximated as $f_{O_2}(\Delta IW) = 2log_{10}(x_{FeO}/x_{Fe})$, assuming ideal mixing. (b) PYR denotes pyrolytic, which were synthesized with 4wt% FeO, see Table S1.

216 3.1. Attainment of equilibrium

217 The time needed to reach chemical equilibrium for a given element be-
 218 tween two phases is governed by the diffusion rate of that element. The
 219 characteristic length of diffusion λ is calculated by diffusion coefficient D
 220 and time t using

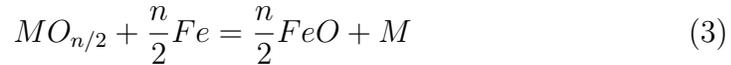
$$\lambda = 2\sqrt{D \cdot t}. \quad (2)$$

221 It has been proposed that diffusion coefficients for principal elements in sil-
 222 icate melt are 10^{-11} to 10^{-9} m^2/s from 1800 to 2800 K, 15 to 25 GPa by

223 Walker and Agee (1989) and 10^{-10} to 10^{-9} m²/s at 4000 K and 136 GPa by
 224 Karki et al. (2010). On the other hand, recent ab initio calculations showed
 225 that self-diffusion coefficients for Fe, Si and O in liquid metal are on the or-
 226 ders of 10^{-7} - 10^{-8} m²/s under core pressures with temperatures higher than
 227 3800 K (Pozzo et al., 2013; Huang et al., 2019). Moreover, time series exper-
 228 iments demonstrated that partitioning equilibrium was achieved within 5 s
 229 at 5 GPa and 2300 K for Ni and less than 20 s at 2273 K and 3.6 GPa for
 230 a series of elements with a typical sample size of a few millimeters (Corgne
 231 et al., 2008; Thibault and Walter, 1995). Given the above range of diffusivity,
 232 the extremely high temperatures (from 3000 to 4700 K) and small samples
 233 (a few micrometers), the equilibrium should be readily attained within the
 234 typical duration of ~ 60 s in our experimental run. The attainment of equi-
 235 librium between molten silicate and liquid metal can also find supports from
 236 (1) the compositional homogeneity, as indicated by the small standard de-
 237 viations, observed in the quenched phases in Table S2, and (2) consistency
 238 within the same thermodynamic model between DAC data and low-P data
 239 obtained from piston-cylinder or multi-anvil press, as will be discussed in the
 240 following text.

241 3.2. Equilibrium constant

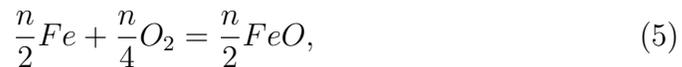
242 The partitioning of an element M between molten metal and silicate takes
 243 place according to an exchange reaction:



244 that combines two redox reactions:



245 and



246 where n is the valence of the cation M in the silicate melt. The partition
 247 coefficient of element M is calculated using molar fractions (x) of M in
 248 the relevant phase by $D_M = \frac{x_M}{x_{MO_{n/2}}}$. D is a function of P, T, composition
 249 and oxygen fugacity. The exchange coefficient, $K_D = D_M/D_{Fe}^{n/2}$, can be
 250 considered partition coefficient D_M corrected for oxygen fugacity which is
 251 conveniently expressed as D_{Fe} . The equilibrium constant K of reaction 3 can

252 then be defined in terms of K_D and activity coefficients (γ) in the silicate
 253 and metallic phases by

$$\log K = \log K_D + \log\left(\frac{\gamma_M}{\gamma_{Fe}^{n/2}}\right)^{metal} + \log\left(\frac{\gamma_{FeO}^{n/2}}{\gamma_{MO_{n/2}}}\right)^{silicate}. \quad (6)$$

254 The valence (n) of Mo and W has been reported to change with redox con-
 255 dition, while being insensitive to pressure and temperature in the previously
 256 investigated P-T range (Wade et al., 2012; Righter et al., 2016). Following
 257 previous studies, where Mo was found in tetravalent state (Righter et al.,
 258 2016) and W in 6+ (Wade et al., 2012) at fO_2 lower than 1 log unit below
 259 the IW buffer, we fixed the valence of Mo and W to 4+ and 6+ respectively,
 260 given reducing conditions (IW-1 to IW-3) observed in our experiments. The
 261 ratio of oxide activity coefficients in silicate melt (last term in Eq. 6) may be
 262 assumed independent of melt composition for low valence cations (e.g., Ni^{2+}
 263 and Co^{2+}) (O'Neill and Eggins, 2002; O'Neill and Berry, 2006), however,
 264 for high valence cations it may vary by a much higher degree. We thus in-
 265 troduced an empirical parameter to model the effect of silicate composition,
 266 particularly the degree of polymerization, which will be detailed in 3.3.2.

267 The activity coefficients in the metal are significantly influenced by the
 268 light elements dissolved in liquid iron, such as Si, O, S and C (Jana and
 269 Walker, 1997a,c; Tuff et al., 2011; Wood et al., 2014). To model the inter-
 270 actions in the metal and to correct the effects of the alloy composition on
 271 partitioning, we used the interaction parameter (ϵ) approach proposed by
 272 Ma (2001), to calculate the activity coefficients in the Fe-rich alloy. This has
 273 become standard practice in regard to metal-silicate partitioning (Wade and
 274 Wood, 2005; Corgne et al., 2009; Ricolleau et al., 2011; Siebert et al., 2013;
 275 Huang and Badro, 2018). Following this method, the activity coefficients of
 276 the solvent (Fe) and $N - 1$ solutes (i) for N components metallic solutions

277 can be expressed as

$$\begin{aligned}
\ln\gamma_{Fe} = & \sum_{i=1}^{N-1} \epsilon_i^i (x_i + \ln(1 - x_i)) \\
& - \sum_{j=1}^{N-2} \sum_{k=j+1}^{N-1} \epsilon_j^k x_j x_k \left(1 + \frac{\ln(1 - x_j)}{x_j} + \frac{\ln(1 - x_k)}{x_k} \right) \\
& + \sum_{i=1}^{N-1} \sum_{k=1(k \neq i)}^{N-1} \epsilon_i^k x_i x_k \left(1 + \frac{\ln(1 - x_k)}{x_k} - \frac{1}{1 - x_i} \right) \\
& + \frac{1}{2} \sum_{j=1}^{N-2} \sum_{k=j+1}^{N-1} \epsilon_j^k x_j^2 x_k^2 \left(\frac{1}{1 - x_j} + \frac{1}{1 - x_k} - 1 \right) \\
& - \sum_{i=1}^{N-1} \sum_{k=1(k \neq i)}^{N-1} \epsilon_i^k x_i^2 x_k^2 \left(\frac{1}{1 - x_i} + \frac{1}{1 - x_k} + \frac{x_i}{2(1 - x_i)^2} - 1 \right),
\end{aligned} \tag{7}$$

278 and

$$\begin{aligned}
\ln\gamma_i = & \ln\gamma_{Fe} + \ln\gamma_i^0 - \epsilon_i^i \ln(1 - x_i) \\
& - \sum_{j=1(j \neq i)}^{N-1} \epsilon_i^j x_j \left(1 + \frac{\ln(1 - x_j)}{x_j} - \frac{1}{1 - x_i} \right) \\
& + \sum_{j=1(j \neq i)}^{N-1} \epsilon_i^j x_j^2 x_i \left(\frac{1}{1 - x_i} + \frac{1}{1 - x_j} + \frac{x_i}{2(1 - x_i)^2} - 1 \right),
\end{aligned} \tag{8}$$

where γ_i^0 is the activity coefficient of solute i in liquid iron at infinite dilution, ϵ_i^j the interaction parameter of element j on element i and x_i the mole fraction of element i in the metal. Interactions between minor/trace metals (Mo and W) are not considered, since their influence on each other is supposed to be negligible due to the low abundances. We fit ϵ_i^j between light-element species (Si, O, C and S) and minor/trace metals, at the reference temperature 1873 K (T^0), together with γ_i^0 taken from Steelmaking Data Sourcebook (JSPSNCS, 1988). ϵ_i^j and γ_i^0 are then extrapolated to run temperatures according to

$$\ln\gamma_i^0(T) = \frac{T^0}{T} \ln\gamma_i^0(T^0), \tag{9}$$

$$\epsilon_i^j(T) = \frac{T^0}{T} \epsilon_i^j(T^0). \tag{10}$$

279 *3.3. Partitioning of Mo and W*

280 In order to parameterize the effects of thermodynamic parameters on
 281 the partitioning of Mo and W during core formation, and to obtain better
 282 statistics for the parameterization, we compiled partitioning data from the
 283 literature on Mo (Hillgren et al., 1996; Jana and Walker, 1997a,b; Righter
 284 et al., 2010; Siebert et al., 2011; Tuff et al., 2011; Wade et al., 2012; Wood
 285 et al., 2014; Jennings et al., 2021) and W (Hillgren et al., 1996; Jana and
 286 Walker, 1997a,b; Righter and Shearer, 2003; Cottrell et al., 2009; Righter
 287 et al., 2010; Tuff et al., 2011; Siebert et al., 2011, 2012; Wade et al., 2012;
 288 Wood et al., 2014; Jennings et al., 2021). These data are plotted in Figs. 2-3,
 289 together with our data. It is notable that there is a lack of partitioning data
 290 for both Mo and W when pressure exceeds 25 GPa. By means of multivariate
 291 least-squares linear regression, the calculated nominal equilibrium constant
 292 ($\log K = \log K_D + \log \frac{\gamma_M}{\gamma_{Fe}^{n/2}}$, reported in Tables S3-S4) using the interaction
 293 parameter approach were fitted to the thermodynamic model described by

$$\log K = a + \frac{b}{T} + c \frac{P}{T} + d \cdot (nbo/t - 2.7), \quad (11)$$

294 where a is the entropy ($\Delta S^0/2.303R$), b the enthalpy ($-\Delta H^0/2.303R$), and
 295 c the volume ($-\Delta V^0/2.303R$) change of reaction 3 (superscript 0 denotes
 296 the standard state and R is the ideal gas constant). As discussed earlier,
 297 to account for the compositional effect of silicate melt (i.e., activity ratio,
 298 last term in Eq. 6) on partitioning of highly charged Mo (4+) and W (6+),
 299 we introduced an empirical parameter nbo/t (Mysen, 1983), the molar ra-
 300 tio of non-bridging oxygens (nbo) per tetrahedrally coordinated cations (t),
 301 which was corrected to a pyrolitic composition whose nbo/t equals 2.7. A
 302 stepwise regression was performed according to the following steps. Firstly,
 303 all coefficients, namely a , b , c , d , and interaction parameters (ϵ_i^j) between
 304 light elements (Si, O, C, and S) and the elements of interest (Mo and W),
 305 were fitted to the simultaneous equations (Eqs. 6-11) (step 1). After the
 306 statistically insignificant interaction parameters (see details in Section 3.3.3)
 307 were set to 0, the remaining coefficients were fitted again (step 2). The re-
 308 sulting interaction parameters from step 2 were then fixed (i.e., the ϵ_i^j values
 309 listed in Table 2), and a , b , c , and d were regressed a third time (step 3).
 310 The fitting results obtained in step 3 are consistent with the simultaneous
 311 fit of all the coefficients in step 1, whereas the uncertainties from the final
 312 regression are more relevant statistically. The parameterizations using Eq.

313 11 will enable us to evaluate individual effects of pressure, temperature and
 314 silicate composition on the partitioning of Mo and W, as follows.

Table 2: Thermodynamic parameters of the metal-silicate partitioning of Mo and W.

Element (i)	a	b (K)	c (K/GPa)	d	ϵ_i^O	ϵ_i^{Si}	ϵ_i^C	ϵ_i^S	ϵ_i^t	$\ln\gamma_i^0$	N	R ²
Mo	4.1(6)	-5563(1139)	-215(21)	-0.60(7)	-17(9)	29(1)	-8(1)	0	3.955	0	138	0.6
W	1.8(3)	-6942(596)	-84(11)	-0.69(4)	-15(6)	0	-9(1)	8(2)	0	0	259	0.6
O						-7	-20	-17.1	-1			
Si							3.6	9	12.4			
C								4.9	12.8			
S									-5.7			

Notes: Parameters of Eq. 11 for Mo and W partitioning: a , b and c represent the entropy, enthalpy and volume change of the reaction, and d the effect of silicate melt. Values in parenthesis are standard errors (1σ) obtained from the least-squares regressions. ϵ_i^j is the interaction parameter of element j on element i and γ_i^0 the activity coefficient of solute i at infinite dilution in liquid iron; interaction parameters are calculated from this study, except for those between light species (Si, O, C and S) which are from JSPSNCS (1988) (see Part II: Tables 2.1 and 2.3 therein). Self-interaction parameters ϵ_i^i and γ_i^0 are also taken from JSPSNCS (1988) (see Part II: Tables 1 and 2.1 therein). Interaction parameters and activity coefficients are reported at 1873 K (see details in section 3.2). N is the number of data used in each regression, and R² the coefficient of determination of the fitted model.

315 3.3.1. Pressure and temperature effect

316 Of the data compiled for Mo and W, most were obtained at experimental
 317 pressures well below 25 GPa (Fig. 2, blue dots). Our twelve experiments
 318 performed at higher pressures thus probe the partitioning behavior at the
 319 conditions of deep core formation. Under these extreme environments, we
 320 find that Mo and W more strongly partition into metallic liquid with increas-
 321 ing temperature (higher log K), while less so with pressure (lower log K), as
 322 can be found in Fig. 2.

323 The negative pressure effect ($c = -84 \pm 11$ K/GPa, Table 2) on W parti-
 324 tioning is indistinguishable from previous multi-anvil results by Siebert et al.
 325 (2011) ($c = -55 \pm 35$ K/GPa) and Wade et al. (2012) ($c = -77$ K/GPa), though
 326 to a more evident extent; the similar but more profound pressure effect on
 327 Mo partitioning ($c = -215 \pm 21$ K/GPa) is consistent with Wade et al. (2012)
 328 ($c = -167$ K/GPa). Recently, Jennings et al. (2021) found negligible and
 329 weak pressure terms on W and Mo, respectively. The reason is that their
 330 expressions may lose accuracy at higher pressures due to the limited pressure
 331 range, as provided in their own note of caution.

332 Similarly, for both Mo and W, temperature increases the affinity of these
 333 elements for the metallic phase ($b < 0$ K). The influence of temperature on
 334 partitioning was debated for both Mo (Siebert et al., 2011; Wade et al., 2012)
 335 and W (Cottrell et al., 2009; Wade et al., 2012). The increasing siderophily
 336 of W with temperature is well defined here, given the wide temperature
 337 range (from 1773 to 4700 K) covered by combining present and previous
 338 data: temperature dependence for Mo and W can be clearly seen if one

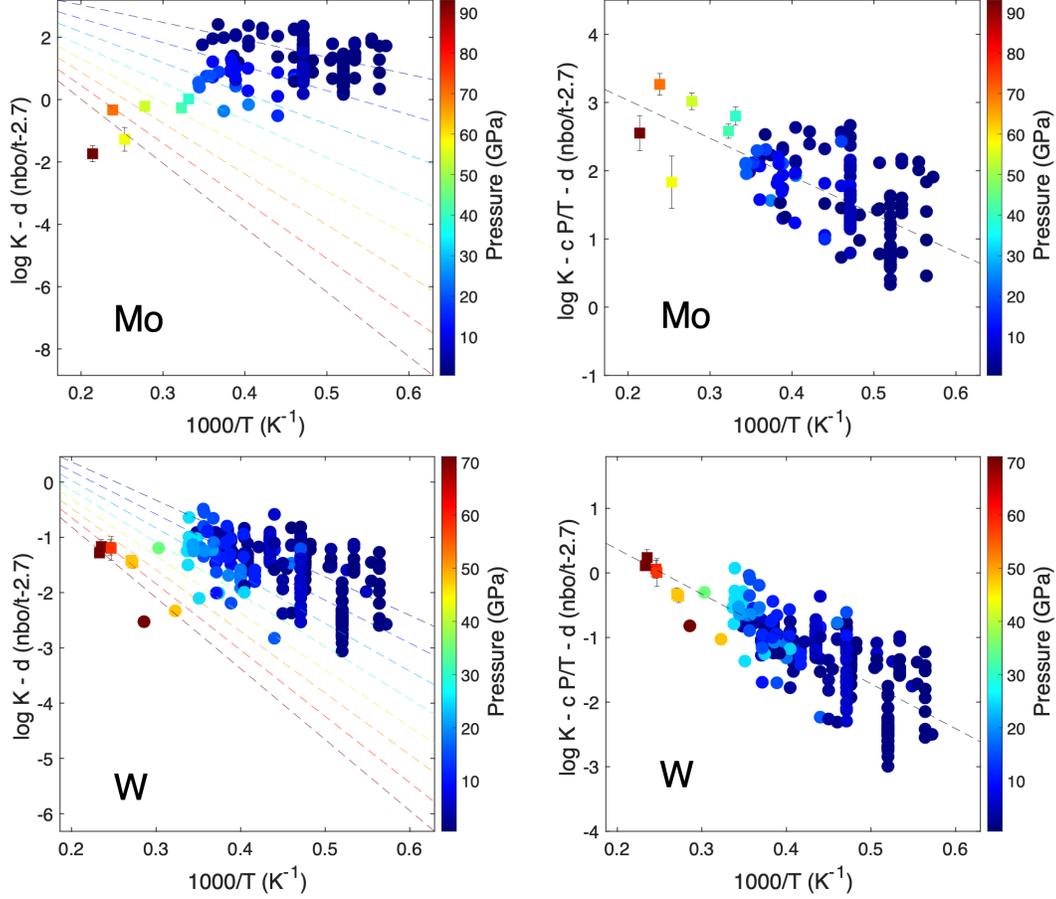


Figure 2: Pressure and temperature effect on the partitioning of Mo and W. Equilibrium constants ($\log K$) for Mo and W are plotted as a function of reciprocal temperature ($1000/T$). Pressure is reported in symbol color. Experimental data for Mo are taken from Hillgren et al. (1996); Jana and Walker (1997a,b); Righter et al. (2010); Siebert et al. (2011); Tuff et al. (2011); Wade et al. (2012); Wood et al. (2014); Jennings et al. (2021) and this study (squares). W data are taken from Hillgren et al. (1996); Jana and Walker (1997a,b); Righter and Shearer (2003); Cottrell et al. (2009); Righter et al. (2010); Tuff et al. (2011); Siebert et al. (2011, 2012); Wade et al. (2012); Wood et al. (2014); Jennings et al. (2021) and this study (squares). Error bars (shown where larger than symbols, for this study) were propagated from the analytical uncertainties in Table 2. In the left panels, equilibrium constants are corrected for silicate melt compositions ($\log K - d$ (nbo/t - 2.7), in order to show the P-T dependence; the dashed lines are isobars (color-coded as well) obtained from least-squares linear regressions (Eq. 11) to the data, showing temperature dependence at a given pressure, or pressure dependence at a fixed temperature. In the right panels, equilibrium constants are corrected for both pressure and silicate melt compositions ($\log K - c P/T - d$ (nbo/t - 2.7), the black dashed lines), to solely illustrate partitioning as a function of reciprocal temperature.

339 eliminates the effects of pressure and silicate composition by correcting for
340 the pressure and compositional (c and d) terms from the same dataset, as
341 shown in Fig. 2 (right panels).

342 Since pressure and temperature are correlated parameters in the regres-
343 sion, it would be useful to compare their effects together. Table S6 lists the
344 fitted parameters for b and c terms from present and previous studies. For
345 Mo, the combined P-T effects (c and b terms, Table S6) generally agree with
346 the recent work by Jennings et al. (2021), while differing from the extents to
347 which P and T affect the partitioning. The P-T effects on W partitioning,
348 on the other hand, are consistent with most previous results as regards the
349 signs (Siebert et al., 2011; Shofner et al., 2014), and within uncertainties are
350 identical to the results found in Wade et al. (2012) (Table S6).

351 3.3.2. Dependence on silicate melt composition

352 It has been shown that silicate melt composition, particularly the de-
353 gree of polymerization which is conveniently parameterized as a function of
354 nbo/t , can significantly affect the partitioning behavior between metal and
355 silicate (Walter and Thibault, 1995; Jana and Walker, 1997b; O’Neill and Eg-
356 gins, 2002; Chabot and Agee, 2003), especially for high valence state cations
357 like Mo and W. Since the coordination environment in silicate changes from
358 tetrahedra to octahedra at upper mantle conditions (10 to 20 GPa), the
359 nbo/t calculation is no longer applicable to our higher P data (> 40 GPa).
360 We therefore only calculated and fitted the nbo/t values for previous data
361 less than 25 GPa, and kept our nbo/t constant at the pyrolitic value of 2.7 in
362 all the regressions. The corrected (for pressure and temperature) equilibrium
363 constant K (< 25 GPa) in log units is plotted as a function of nbo/t in Figure
364 3.

365 In agreement with previous observations (Walter and Thibault, 1995;
366 Jana and Walker, 1997b; Cottrell et al., 2009; Siebert et al., 2011), Mo and
367 W become more lithophile in less polymerized melt (higher nbo/t). The rea-
368 son, since they are not considered tetrahedral cations, may be that highly
369 charged Mo and W cations require more non-bridging oxygen atoms in order
370 to be stably incorporated in the silicate network.

371 3.3.3. Influence of light elements in liquid metal

372 The effect of light species on the partitioning behavior of Mo and/or W
373 has been extensively characterized, to name only a few recent examples, for
374 carbon (Cottrell et al., 2009; Siebert et al., 2011; Jennings et al., 2021), sulfur

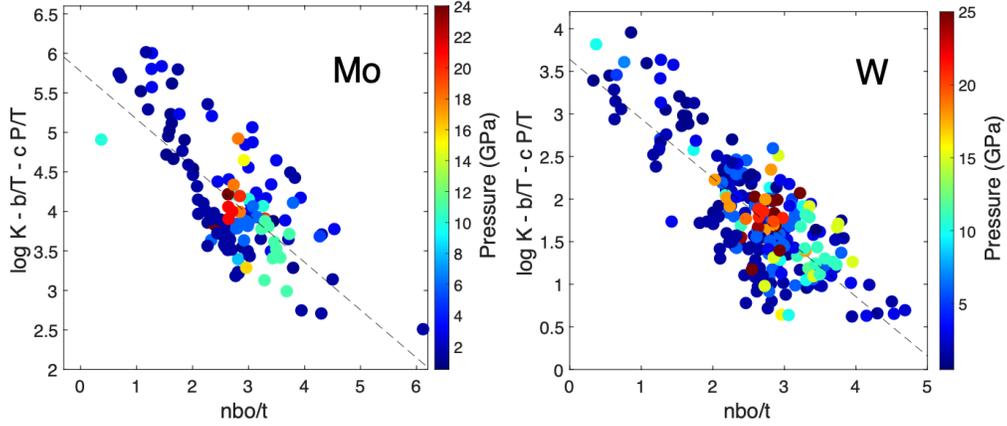


Figure 3: Equilibrium constants ($\log K$) for experiments conducted under 25 GPa as a function of nbo/t for Mo and W. Following the same rationale as in Fig. 2, P and T effect (c and b terms in Eq. 11) are removed, i.e., $\log K - b/T - c P/T$ (solid dots), to reveal the effect of nbo/t . The partitioning of Mo and W is both strongly influenced by the degree of polymerization of silicate melt: both elements become more siderophile with decreasing nbo/t , consistent with previous results from Walter and Thibault (1995); Jana and Walker (1997b); Cottrell et al. (2009); Siebert et al. (2011).

375 (Wade et al., 2012) and silicon (Tuff et al., 2011). Recently, it becomes possible to
 376 quantify that of oxygen, when partitioning experiments under much higher P-T conditions are available in LHDACs: because such conditions
 377 greatly promote the partitioning of FeO into liquid metal. This can be seen by the fact that, while the starting metal contained neither oxygen nor any
 378 lithophile elements (see Table S1), oxygen, magnesium and aluminum were observed along with siderophile elements in recovered metal (Table S2).
 379

382 The minor amounts of oxygen in our metals, between 3 to 8 wt%, allow for characterization of its interactions with Mo and W. Using the activity
 383 model described above and combining Eqs. 6-11, we have modeled the effect of oxygen, along with Si, C and S, by fitting the interaction parameter ϵ . The
 384 fitting results are listed in Table 2. We find the absolute values of ϵ_{Mo}^O ($=-17$) and ϵ_W^O ($=-15$) to be significantly larger than those tabulated in JSPSNCS
 385 (1988), where $\epsilon_{Mo}^O=1.3$ and $\epsilon_W^O=4.1$. This means that oxygen dissolved in liquid iron has more pronounced influence on the partitioning of Mo and W
 386 than previously thought. Meanwhile, the negative signs of ϵ_i^O indicate that oxygen increases the siderophily of both elements.
 387
 388
 389
 390
 391

392 Si is another important light element in Earth's core, and is known to

393 interact strongly with Mo, as the value of 933 for ϵ_{Mo}^{Si} listed in JSPSNCS
 394 (1988) indicates. Our experiments show a wide range of Si contents in the
 395 metal, 1.5-12.8 wt%; when augmented by all available data (Table S3), we
 396 find ϵ_{Mo}^{Si} of 29(1), a value much lower than 933 but close to the recent value
 397 of 22(5) found by Tuff et al. (2011). In contrast to Tuff et al. (2011) who
 398 reported ϵ_W^{Si} of 18.3, we find it statistically insignificant ($\epsilon_W^{Si}=0$). This is
 399 because the strong correlation between ϵ_W^{Si} and ϵ_W^O (Pearson correlation coef-
 400 ficient $r=0.84$), revealed by our higher pressure results, determines that only
 401 ϵ_W^O remains significant in the linear regression. Although carbon concentra-
 402 tion is assumed negligible in our metal (see Methods), we have fit ϵ_i^C based
 403 on a large C-containing dataset with up to 38 mol% C in the metal, which
 404 yields $\epsilon_{Mo}^C=-8(1)$, $\epsilon_W^C=-9(1)$, consistent with the values of -6 and -3 for Mo
 405 and W by JSPSNCS (1988), and identical to -7.0(3) and -7.4(6) for Mo and
 406 W by Jennings et al. (2021) within uncertainties.

407 S was intentionally added to nearly half of our experiments (Table 1),
 408 which ended up with 3-8 wt% in the metals. Combining with 57 and 55 S-
 409 containing data for Mo and W respectively from the literature (Table S3-S4),
 410 we find ϵ_{Mo}^S insignificant in the thermodynamic regression, slightly differing
 411 from the value of 2.27 Wood et al. (2014), but in line with $\epsilon_{Mo}^S(=0.3)$ close
 412 to zero in JSPSNCS (1988). Unlike Mo, the S-W interaction is much more
 413 remarkable, and our value of 8(2) for ϵ_W^S is in good agreement with 5.94 and
 414 6.47 found in JSPSNCS (1988) and Wood et al. (2014).

415 4. Discussion: applications to core formation

416 Equations 6 and 11 can be combined and rearranged as follows:

$$\log D_M = a + \frac{b}{T} + c \frac{P}{T} - \frac{n}{2} \log \frac{x_{FeO}}{x_{Fe}} - \log \frac{\gamma_M}{\gamma_{Fe}^{n/2}}, \quad (12)$$

417 where the ratio of activity coefficients in silicate melt in Eq. 6 has been
 418 approximated by fitting the nbo/t in Eq. 11, which is canceled by assuming
 419 a pyrolitic silicate melt ($nbo/t = 2.7$) in the magma ocean. Using Eq. 12,
 420 in principle, the elemental distribution between metal and silicate can be
 421 predicted at a given P, T, fO_2 and metal composition.

422 Since the Earth's core formation is thought to take place in a continuous
 423 fashion during its accretion, we model a multistage core formation process
 424 where the Earth is accreted in 100 steps (Fig. 4). At each step, the metal

425 from the accreted material fully equilibrates with the entire magma ocean
 426 at its base, whose pressure and temperature are calculated as a function
 427 of total accreted mass and magma ocean depth and by using the mantle
 428 liquidus in Andraut et al. (2011). In order to reach the observed Ni and Co
 429 abundances in the mantle, the final equilibrium pressure and temperature at
 430 the end of Earth’s accretion is determined to be 50 GPa and 3280 K (Fig.
 431 4a), consistent with recent estimates from single-stage (Siebert et al., 2012;
 432 Fischer et al., 2015) and multi-stage core formation models (Badro et al.,
 433 2015; Huang et al., 2020), as well as N-body accretion simulations (Rubie
 434 et al., 2015). The FeO content of the magma ocean (mantle) is imposed to
 435 follow a given redox path. The ratio of activity coefficients in the metallic
 436 phase is calculated self-consistently by predicting the amount of Si and O
 437 dissolved in liquid Fe following the Si-O model in (Siebert et al., 2013).
 438 Recent N-body simulations (Jennings et al., 2021) took account of i) partial
 439 equilibrium between the impacting cores and Earth’s mantle, and ii) a range
 440 of composition as regards redox state in accreting bodies, such that it may
 441 explain their overabundant W in the mantle. However, our accretion model
 442 does not include these two aspects, because we consider that i) the nature
 443 of impacting bodies might not be well constrained, and ii) full equilibration
 444 hypothesis works well here and hence does not require partial equilibrium,
 445 which would add more free parameters than already desired in this study.

446 Based on the results of our regression (Table 2) for Mo and W, their
 447 elemental distribution between metal and silicate is calculated at each accre-
 448 tion step and integrated until the core is fully formed. We firstly find that a
 449 growing Earth, taking only Si and O as major light components in its core
 450 (dashed lines in Fig. 4b), would be too much enriched in Mo relative to W
 451 in its mantle (low D_{Mo} and high D_W). This would result in a retreat to
 452 the old dilemma where W is found too siderophile compared to Mo by the
 453 end of accretion (Wade et al., 2012; Wood et al., 2014), which leads to an
 454 overestimated Mo/W ratio in Earth’s mantle (dashed lines in Fig. 4, lower
 455 panels). Although, in contrary to the above-mentioned studies, Mo remains
 456 more siderophile than W during most of the accretion (during which Mo/W
 457 ratio is faithfully reproduced too, Fig. 4f); it only becomes less so (mainly
 458 affected by pressure, whose effect is now better constrained) by the end of
 459 core formation where pressures are higher.

460 Fig. 4 shows results of core formation at constant fO_2 with FeO con-
 461 tent in the mantle equal to that of present-day Earth (Fig. 4c). Keeping a
 462 constant fO_2 is a simple but effective way to examine the effects of other

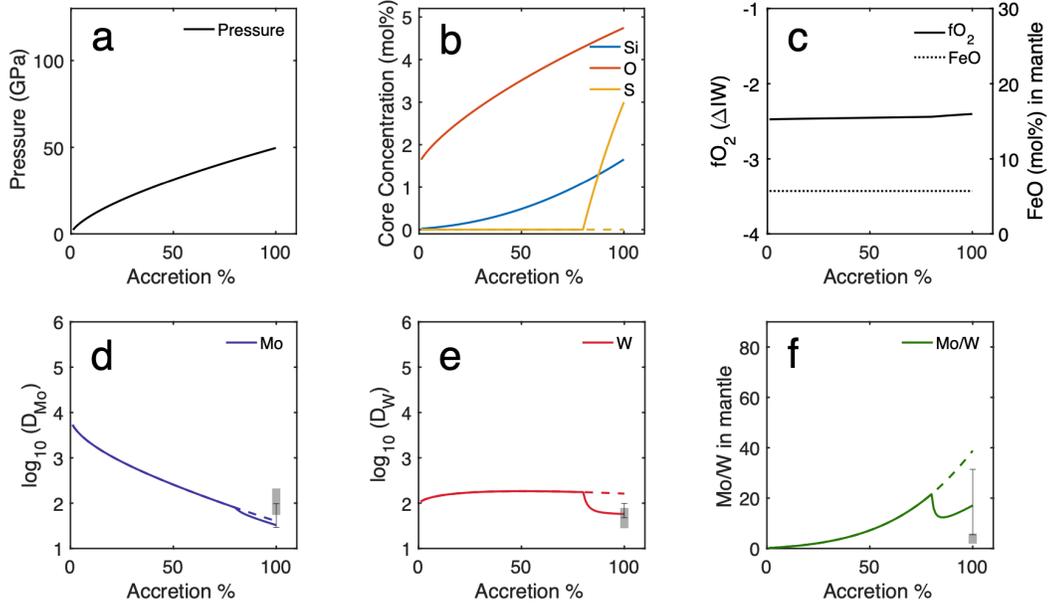


Figure 4: Results of Earth's core formation modeling as a function of accreted Earth's mass (%) with (solid lines) and without (dashed lines) S addition during the last 20% accretion. Upper panel (from left to right): the evolution of (a) pressure for metal-silicate equilibration, (b) concentrations of light elements (Si, O and S) in the core (mol%), and (c) bulk fO_2 (relative to IW buffer, solid line) between Earth's core and mantle as well as FeO content in the mantle (dotted line). Lower panel (from left to right): Core-mantle partition coefficients (in log unit) of (d) Mo (blue) and (e) W (red), and (f) Mo/W ratio (green) in the mantle. Dashed lines: S-free throughout the accretion. Solid lines: S is added only during the last 20% of the accretion. Grey shaded rectangles represent Earth targets to match from McDonough and Sun (1995) and Palme and O'Neill (2014). Error bars are propagated from the uncertainties on the thermodynamic parameters in Table 2 using Monte-Carlo simulation. The observables, D_{Mo} , D_W and Mo/W ratio in the mantle, are simultaneously matched only when S is accreted during late accretion.

463 variables (P, T and composition); alternatively, evolving the Earth under re-
464 ducing or oxidizing conditions may offer a solution. However, after extensive
465 experimenting, we find that modifications to the redox path, by building the
466 Earth from either oxidized or reduced materials, do not alleviate the Mo/W
467 ratio problem. Although a previous study found the same (Wade et al., 2012),
468 it seems counter-intuitive given the valence difference between W (6+) and
469 Mo (4+). The reason may be that the partitioning between core and mantle
470 is not entirely controlled by fO_2 , but determined by the interplay of P, T,
471 fO_2 , and composition. Since pressure and temperature conditions of Earth's
472 core formation are predetermined by Ni and Co partitioning (Li and Agee,
473 1996; Siebert et al., 2012; Fischer et al., 2015; Huang and Badro, 2018) and
474 mantle liquidus, we are inevitably led to look into the effect of light species
475 in the core.

476 The partitioning of Si and O is calculated using the Si-O solution model
477 as in Siebert et al. (2013) (Fig. 4b), and their influence on the behavior of
478 Mo and W has been incorporated in our model through the calculations of
479 activities γ_{Mo} and γ_W . On the other hand, interaction parameters in Table
480 2 indicate a strong negative interaction between S and W, $\epsilon_W^S=8$, in stark
481 contrast to Mo, which should be little affected by S content in the metal
482 ($\epsilon_{Mo}^S=0$). The solution seems to reside in S.

483 Based on cosmo/geochemical observations, S content of Earth's core is
484 estimated ~ 2 wt% (McDonough, 2003). We thus devised a model where the
485 delivery of 2% S begins at different stages of the accretion. As can be seen in
486 Fig. 5, if S is accreted throughout the process ($x=0$, i.e., homogeneous accre-
487 tion), the effect of S would be minimal and W would be overly siderophile.
488 However, when S is to be enriched in the metal towards the end, particularly
489 after 80% of the accretion, we find that D_W drops significantly, while D_{Mo}
490 remains almost unaltered, such that all three observables being reproduced.
491 One of our best fits where 2 wt% (3 mol%) S is added during the last 20%
492 accretion is shown in Fig. 4 in solid lines. Interestingly, despite the up-
493 dated effects of pressure, temperature and metal composition resolved from
494 our high pressure data combined with all available literature data, we coin-
495 cide in the late addition of S with previous work at lower pressures (Wade
496 et al., 2012; Wood et al., 2014). Apart from this consistency from lower to
497 higher pressures for Mo and W partitioning, the late addition of sulfur finds
498 supports in their mantle abundances estimated from the partitioning of S
499 (Suer et al., 2017), Zn (Mahan et al., 2018), and moderately volatile and
500 siderophile elements (Kubik et al., 2021), as well as dynamical simulations

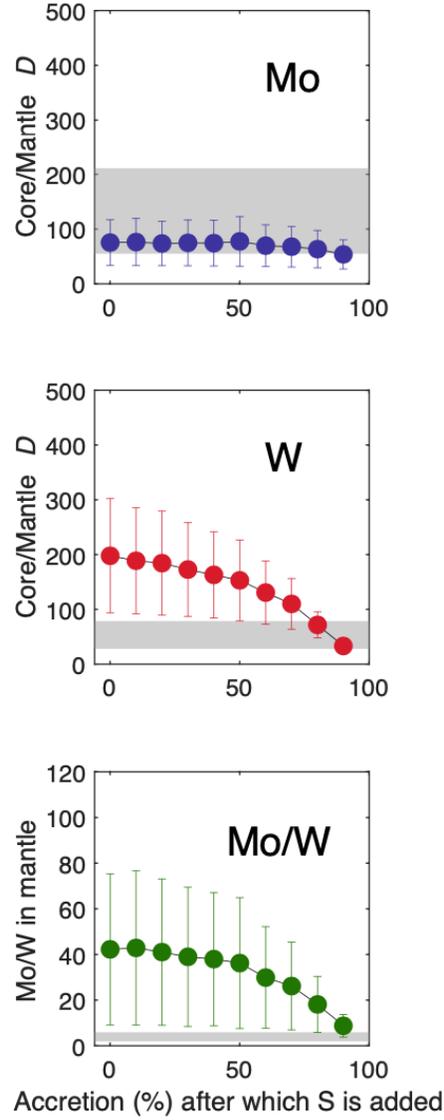


Figure 5: Bulk partition coefficients for Mo and W between Earth’s core and mantle, and Mo/W ratio in the mantle, versus timing of S addition to the core. Each point corresponds to an endpoint of the same multistage core formation model as in Fig. 4. The uncertainties are the intervals of partition coefficient calculated by Monte-Carlo simulation. Horizontal grey patches represent Earth targets from McDonough and Sun (1995) and Palme and O’Neill (2014). The addition of 2 wt% S towards the end of accretion greatly decreases D_W , resulting in the correct reproduction of the observed Mo/W ratio.

501 (Raymond et al., 2009) and recent volatile data for chondrites (Braukmüller
502 et al., 2019) that favor a late delivery of volatile-rich materials to the Earth.
503 Moreover, our findings are compatible with heterogeneous accretion models
504 that could explain various isotopic signatures of the Earth and other bodies
505 alike (Albarède, 2009; Schönbächler et al., 2010).

506 The influence of C on Mo and W partitioning is also tested. However, due
507 to the nearly equivalent interactions between C-W and C-Mo (ϵ_i^C in Table
508 2), the sequestration of small amount of C, ~ 1 wt% in the core (Wood et al.,
509 2013), equally adjusts D_W and D_{Mo} . Carbon therefore does not offer an
510 effective solution. As regards the light-element candidates in the core, to
511 this study it would seem likely a mixture of Si, O, S and probably C (which
512 we are unable to discriminate).

513 5. Conclusions

514 Superliquidus metal-silicate partitioning experiments have been performed
515 on Mo and W in twelve diamond anvil cells under high P-T conditions up
516 to 93 GPa and 4700 K. When combined with available literature data, both
517 Mo and W are found to be less siderophile with increasing pressure, with
518 Mo being more significantly influenced. In contrast, temperature similarly
519 promotes the partitioning of Mo and W into the metal. At pressures lower
520 than 25 GPa, the non-bridging oxygen/tetrahedral cation (*nbo/t*) adequately
521 models the effect of silicate melt composition on highly charged Mo and W
522 cations. Oxygen dissolved in liquid metal interacts more strongly with Mo
523 and W than previously considered. W partitioning is notably more sensitive
524 to S content of the metallic liquid than Mo.

525 The application of our results to a multi-stage core formation model shows
526 that homogeneous accretion of the Earth produces the observed Mo concen-
527 tration in its mantle, but underestimates W abundance and thus ends up
528 with an overestimation of the Mo/W ratio. The late addition of 2 wt% S to
529 the core after 80 % of Earth's accretion reconciles the 3-observable problem
530 by making W less siderophile. Parameterizations for Mo, and especially W,
531 can be used in the future to model physical conditions as well as timing of
532 core formation.

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Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: