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1 **A speciation model linking the fate of carbon and hydrogen during core –**
2 **magma ocean equilibration**

3

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5

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11

12

13 **Abstract.**

14 The core – mantle differentiation in the magma ocean constitutes a major planetary event that
15 involved two elements that are essential to life: carbon (C) and hydrogen (H). These two
16 elements are conventionally classified as volatiles (ie. atmophile), but they can also evolve into
17 being siderophile and lithophile at the extreme conditions found in planetary magma oceans.

18 We report here a model for H and C species dissolved in silicate melts in equilibrium with iron-
19 rich alloys under variable pressure, temperature and redox conditions. This speciation model is
20 able to reconcile and reproduce a large body of experimental data on metal-silicate partitioning
21 for H and C at carbon-saturation and in C-undersaturated systems. At low pressure, we conclude
22 that the prevailing species in a silicate magma ocean are CO₂, CO, H₂O, H₂, whereas CH₄
23 appears to dominate at high pressure. These speciation changes explain recent experimental
24 observations that (i) C evolves from being strongly siderophile at low pressure to moderately

25 siderophile at high pressure, and (ii) H is not siderophile at low pressure but becomes
26 increasingly so as pressure rises. Moreover, it shows that H becomes increasingly siderophile
27 as the total H content of the silicate melt and C-activity are lowered. Despite it offers a
28 promising reconciliation of a large set of experimental and molecular dynamics observations,
29 this model still suffers from large uncertainties when extrapolated to high pressure. In
30 particular, endmember and mixing properties in both the silicate melt and the molten metal
31 must be independently deciphered.

32 The enhanced CH₄ stability in the silicate melt at high pressure couples the fate of C and H in
33 deep magma oceans. In such cases, the solubility of C in the basal ocean depends on the H-
34 content and is higher than C-solubility at low pressure. This implies an increase in C activity as
35 the ascending convective cells of the magma ocean, which may cause C saturation as graphite
36 or diamond unless Fe-metal droplets, having a great C-solubility, are present in the shallow
37 magma ocean. Under certain conditions, enhanced siderophile behaviour for H can lead via a
38 runaway process to the desiccation of the magma ocean.

39

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41

42 **1. Introduction**

43 Terrestrial planets evolved through early magma ocean stages (Rubie et al. 2015). These magma
44 oceans were highly diverse on planetesimals, planetary embryos, and planets, implying
45 increasingly extreme temperature and pressure conditions (*eg.* Li et al., 2016; Siebert et al.,
46 2012). These molten stages are believed to provide an essential medium permitting planetary
47 differentiation into a core, mantle, early crust and early atmosphere. Magma ocean is a general
48 term embodying a silicate melt, with a varying fraction of silicate crystals, possibly coexisting

49 with molten metallic Fe-rich alloys, sulfide, carbide, graphite, diamond and a fluid phase. A
50 major part of our understanding of the magma ocean stages on Earth is deduced from the
51 interpretation of mantle depletion in variably siderophile elements through metal –silicate
52 equilibria (*e.g.* Wade and Wood, 2005; Siebert et al., 2012; Rubie et al., 2015; Badro et al.,
53 2015). The cause of mantle depletion of moderately siderophile elements with respect to
54 chondritic abundances is generally attributed to the sequestration of the depleted elements into
55 the core. Given the growing interest in the conditions defining habitable worlds, the distribution
56 of C and H, two life-essential elements, during the magma ocean stage has been thrust into the
57 scientific limelight (Okuchi, 1996; Hirschmann, 2012a; Sarafian et al., 2014; Li et al., 2016;
58 Clesi et al., 2018; Malavergne et al., 2019; Greenwood et al., 2018; Grewal et al., 2019; Fischer
59 et al., 2020; Li et al., 2020; Tagawa et al., 2021; Gaillard et al., 2021). At the pressure (P) –
60 temperature (T) – redox conditions (oxygen fugacity fO_2) of modern magmatic and volcanic
61 settings, C and H are considered as volatile elements or atmophile, ie. with a great affinity for
62 the vapor phase (Iacono-Marziano et al., 2012). However, during the magma ocean stages,
63 conditions were strongly reduced, and involved variable P-T conditions (1-60 GPa, 1500-
64 4000°C), implying that some supposedly volatile elements could become magmatophile or
65 siderophile and change the metal-silicate systematics (Ohtani et al., 2005; Hirschmann, 2012a;
66 Gaillard et al., 2021). Wood et al. (2013), in their review paper, used a combination of
67 thermodynamics, experimental data and isotopic constraints to predict a significant affinity of
68 C for the metallic phase (of about 1 wt%) during metal-silicate equilibria taking place during
69 the magma ocean stage. Okuchi (1996) reported experiments at high P and high-T (7 GPa,
70 1200-1500°C) revealing that H could be moderately siderophile. Capturing the behaviour of
71 these elements during core formation is therefore not only important for deciphering the origin
72 of a 5 to 10% density deficit in the Earth’s core, but also because it may be a major stage in the
73 construction of habitable worlds.

74 Recently, several research groups have produced experiments tackling the behaviour of C
75 during metal silicate equilibration (eg. Wetzel et al., 2013; Dasgupta et al., 2013; Kadik et al.,
76 2014; Stanley et al., 2014 ; Malavergne et al. 2019 ; Kuwahara et al. 2019; Fischer et al., 2020).
77 These studies have reported equilibrium partitioning of C between molten Fe-rich metal and
78 silicate melt at variable P, T, fO_2 and water (or H) contents. All these parameters affect the
79 partitioning of C between metal and silicate. Using empirical linear relationships between the
80 different variables (Eguchi and Dasgupta, 2018; Malavergne et al., 2019; Fisher et al., 2020),
81 the dependencies of C partitioning on fO_2 , T, P, water content and the amount of non-bridging
82 oxygen per tetrahedron (NBO/T) have been fitted (NBO/T is an empirical parameter long
83 known to control the solubility of carbon dioxide in molten silicates, eg. Iacono-Marziano et
84 al., 2012). Most of these experimental studies also involved H (ie. often reported as water) and
85 determined the H-content in the silicate melts, but so far, only three studies measured the
86 partitioning of H between metal and silicate melts (Okuchi, 1996; Clesi et al., 2018; Malavergne
87 et al., 2019) to 21 GPa, and recently, Tagawa et al (2021) indirectly estimated D^H at 30-60 GPa
88 3100-4600 K (using the phase proportions and the cell volume of FeH_x et ϵ - $FeOOH$ to get the
89 H content in metals). These studies reported significant effects of P, T and fO_2 on H metal-
90 silicate partitioning that are consistent with molecular dynamics calculations at extreme P and
91 T (Zhang and Yin, 2012; Li et al. 2020, Yuan and Steinle-Neumann, 2020). Finally, empirical
92 relationships have also been established to predict the molten metal – silicate liquid partitioning
93 of H (Clesi et al., 2018; Malavergne et al., 2019; Tagawa et al 2021).

94 All these linear empirical models are phenomenological laws that do not consider the C-O-H
95 chemical speciation in the silicate melts and their dependence on P, T and fO_2 , which control
96 H and C partition coefficients. These empirical approaches are interesting because they can
97 provide input for a timely discussion generalizing and interpolating the experimental data points
98 (eg. Fischer et al., 2020). However, equilibria related to the partition coefficient of an element

99 involving several species is, in principle, not constant and cannot be solved using a linear
100 relationship. In our case for example, partitioning of C involves at least three species in the
101 silicate melt: CO, CO₂, CH₄ (Armstrong et al., 2015), while the partitioning of H implies at least
102 OH, H₂O, H₂ and CH₄ as dissolved species in the silicate melts. Here, we establish a
103 thermochemical framework defining and linking the speciation of C and H in the silicate melt
104 at the extreme conditions of the magma ocean. Even if this formalism is simple, it allows us to
105 calculate with a unique formalism, the partitioning of both C and H between molten metal and
106 silicate liquid, including C-undersaturated cases. This formalism shows that the current dataset,
107 produced in various laboratories and covering a vast P-T-fO₂-volatile activity conditions, is
108 consistent. However, high pressure solubility C-O-H data in metals and silicate melts, as well
109 as some key thermodynamic parameters (such as compressibility) are missing rendering the
110 extrapolation of this model to pressure greater than 30 GPa more challenging and uncertain.
111 This approach paves the way for a broadened model to cover larger chemical systems (eg. to
112 include other volatile elements such as O, S, and N and a vapour phase).

113

114 **2. The database**

115 Table 1 summarizes the 161 experiments used for the present thermochemical modelling. These
116 experimental studies were conducted in the pressure range 1-21 GPa, in the temperature interval
117 1350 -2327 °C and with a fO₂ varying from -5.3 to +1.8 relative to the Iron-Wüstite (IW) redox
118 buffer. The entire database (but Clesi et al, 2018) gives the C and H content of silicate melts at
119 C-saturation. We have selected the experimental studies in which both H and C contents in the
120 silicate melt were determined, thus the recent high-P work by Fischer et al. (2020), Fichtner et
121 al. (2021) and Tagawa et al (2021) could not be used here (see the 2-next paragraphs). Clesi et
122 al. (2018) did not measure the C-content in the silicate melts but C-contents in silicate melts at
123 C-saturation under the P-T-fO₂-fH₂O conditions of their experiments is mostly provided by

124 other studies. The range of H-content in silicate melts (Table 1), converted into H₂O, is 0.009
125 (Armstrong et al. 2015) to 5 wt% (Kadik et al. 2014), which covers the expected conditions for
126 any magma ocean. All experiments are C-saturated and provide the C-content of metals, but
127 only two papers provide H concentrations in metals (20 experiments from Malavergne et al.,
128 2019 and Clesi et al, 2018). Some experiments were excluded because the metal compositions
129 were too rich in S (cut >1%) or Ni (cut at >10%), but this concerns only a four experiments in
130 Li et al. (2015).

131

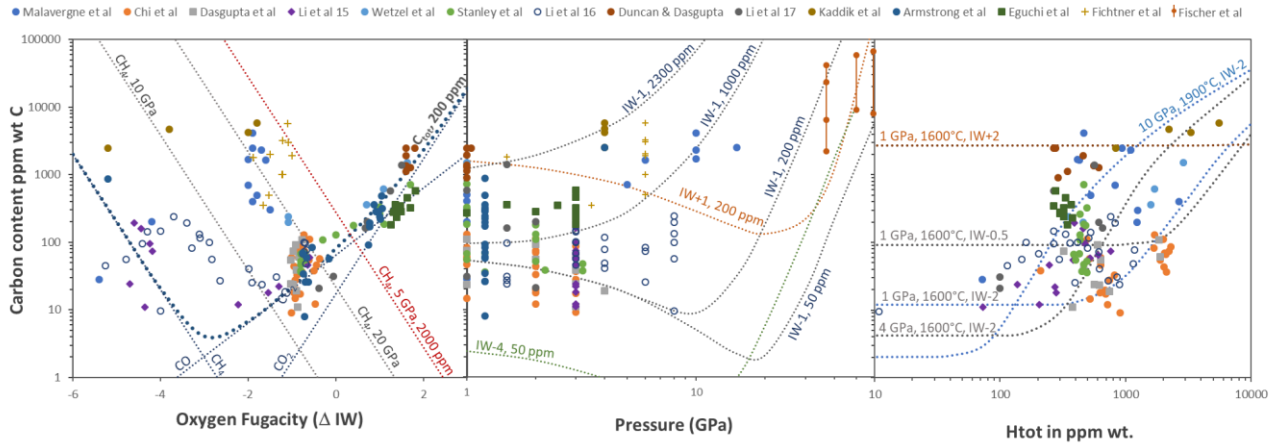
132 *Table 1. Summary of the experimental studies considered. All experiments are C-saturated.*

Authors	P range (GPa)	T (°C)	range	fO ₂ range	SILICATE MELT		METAL	
					C ppm	H ppm	C wt%	H ppm
Malavergne et al. 2019	1-15	1400-2300		-5.4 : -1.6	28-4100	277-1243	3.4-7	13-236
Clesi et al. 2018	5-21	1747-2427		-3.8 : -0.7	nd	402-1234	4.2-7.5	59-254
Eguchi & Dasgupta 2017	1-3	1425-1550		0.3 : 1.3	171 - 579	267-378	N.A.	N.A.
Li et al. 2017	1-2	1400-1550		-0.4 : 1.5	21 - 1388	100-656	N.A.	N.A.
Duncan et al., 2017	1	1600		1.6 : 1.8	900-2455	291-556	N.A.	N.A.
Li et al., 2016	1.5-8	1600-2200		-5.3 : -0.7	10-241	11-1172	3.03-5.7	N.A.
Stanley et al., 2014	1-3	1340-1617		-0.8 : 1.7	36-716	384-489	N.A.	N.A.
Wetzel et al., 2013	0.85 – 1	1500-1530		-1.1 : 1.6	199-1503	345-1698	7.6-8.3	N.A.
Armstrong et al., 2015*	1.2	1400		-1 : 1.5	8 - 864	10-1188*	6.2-7.7	N.A.
Li et al., 2015	3	1600		-4.7: -0.6	11 - 192	73 - 760	3.4-5.9	N.A.
Chi et al., 2014	1-3	1500-1800		-1 : -0.4	9-129	210-2284	4.9-7.2	N.A.
Dasgupta et al., 2013	1-4	1600-2000		-1 : -0.8	11-93	321-1890	4.8-8.5	N.A.
Kadik et al. 2014	4	1550		-1.8: -3.4	4200-5800	2200-5500	N.A.	N.A.

134 * Only water (OH bonds), measured by FTIR, are given in this paper.

135 Figure 1 reports the C-content in silicate melts at C-saturation vs. fO₂, P and total H contents in
 136 the melts. For the experiments at fO₂<IW, these silicate melts are saturated in metal Fe
 137 containing 5-7 wt% C. Considering these metal-saturated experiments, we distinguished two
 138 groups of datapoints: a group with ca. <200 ppm C (low pressure, 1-5 GPa and low H content)
 139 and another one with C-content > 200 ppm (high pressure and/or high H-content). Such a large
 140 range of C contents dissolved in silicate melts at graphite-saturation (8-5800 ppm, Table 1,

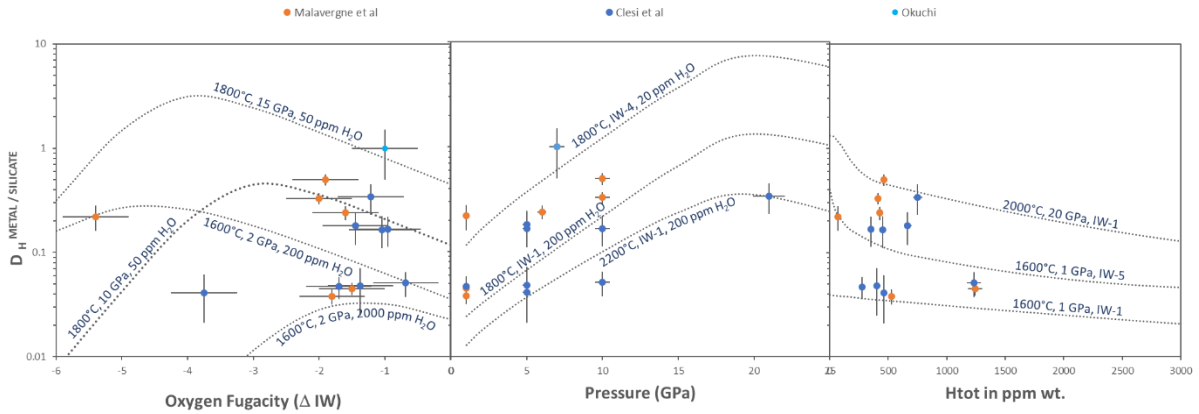
141 Figure 1) may then reflect a range of C-speciation (CO_2 , CO and CH_4 , eg. Armstrong et al.,
142 2015). But this large range has also cast doubt on the validity of some data. Recently, Fichtner
143 et al (2021) argued that most of the data in table 1 and figure 1 are flawed due to a poor
144 attainment of equilibrium. The point raised is that adding C as carbonate in the silicate starting
145 material is a necessity to enhance equilibration rates since graphite-melt reactions are otherwise
146 too sluggish. The datapoints of Fichtner et al. (2021) are indeed higher than most of the database
147 (Figure 1a,1b) leading to the suspicion of unequilibrated C-contents in the silicate melts of most
148 experimental data of table 1. In details, however, Fitchner et al. (2021) data indicates a range
149 of C-content that is comparable to the studies of Malavergne et al. (2019) and Kadik et al.
150 (2014) (see next paragraph). These three studies reported experiments that lasted ca. 10 minutes
151 to 1 hour, whereas most other experiments of table 1, which are suspected of problem of
152 equilibration, lasted a couple of hours: equilibration issues seem unlikely. It is also hardly
153 conceivable that the C content of the glass would be far below equilibrium (and very low, eg
154 $\ll 200$ ppm C), whereas the metal blobs spread in these glasses do show a high range of C-
155 content (5-7 wt% C) that are consistent with C-saturation: if isolated metal blobs are C-
156 saturated, the surrounding glass, connecting graphite to metal blobs, must also be equilibrated.
157 Here, we consider that deviation of equilibration is a possibility for some data, but the
158 generalisation of such a deviation is not justified by the existing experimental constraints taken
159 as a whole: the range of C-content in figure 1 must reflect speciation effects.



160

161 *Figure 1: C content at C-saturation versus f_{O_2} , P and H -content in the silicate melts. The*
 162 *database of Table 1 is shown here. The lines show calculations using the C-O-H speciation*
 163 *model for a range of P - T - H - f_{O_2} conditions that are representative of the conditions covered by*
 164 *the database. The data of Fichtner et al (2021) and Fischer et al (2020) are also shown though*
 165 *they have not been used to calibrate the speciation model. The data of Fichtner et al (2021) and*
 166 *Fischer et al (2020) can respectively be explained using the speciation model with ca. 1000-*
 167 *2000 ppm and ca. 50-200 ppm H_2O respectively.*

168 As noticed before, the datapoints of Kadik et al. (2014) and some of Malavergne et al (2019)
 169 display both high C and high H contents (dissolved in the melt). This may reflect a higher
 170 proportion of CH_4 . Regretfully, this assessment cannot be verified with the data of Fichtner et
 171 al (2021) since the H content of their samples is unknown. Fichtner et al. (2021) stated that their
 172 samples must be < 5000 ppm H_2O , which remains elevated, and they reported RAMAN spectra
 173 indicating dissolved CH_4 . Elevated C content reported in Fichtner et al (2021) may then also
 174 reflect a significant amount of CH_4 in the glass. Another study, Fischer et al (2020), also
 175 reported high amounts of dissolved C, whereas the H contents of the glass are unknown. These
 176 data were collected at very high P and T (Figure 1b). Noteworthy, the RAMAN spectra of these
 177 samples revealed that CH_4 is the dominant dissolved form of C.



178

179 *Figure 2: H metal-silicate partitioning versus f_{O_2} , P and H -content in the silicate melts. We*
 180 *show here the data of Clesi et al (2018), Malavergne et al (2019) and Okuchi (1996). The lines*
 181 *show calculations using the C-O-H speciation model for a range of P-T-H- f_{O_2} conditions that*
 182 *are representative of the conditions covered by the database. The high-pressure ($P > 30$ GPa)*
 183 *MD data of Li et al (2020) and that experimental data of Tagawa et al (2021) are not shown*
 184 *for sake of simplicity and because these were not used to calibrate our model.*

185 The 15 experimental H-partitioning data are shown in figure 2. Clesi et al (2018) and
 186 Malavergne et al (2019) have reported metal-silicate partitioning data at C-saturation in the
 187 pressure range 1-21 GPa, whereas Okuchi (1996) reported C-free data at 7 GPa. We can
 188 distinguish C-saturated data being in the range $D_H \sim 0.03-0.6$, whereas C-free data are in the
 189 range $D_H \sim 1$ or slightly higher. Using molecular dynamics calculations, Li et al (2020)
 190 corroborated that H is siderophile in C-free conditions (ie. $D_H > 1$) and they showed that D_H
 191 increases with increasing P (to 20-135 GPa). The recent study of Tagawa et al (2021) also
 192 confirms this result, though, we recall that the H-content in their Fe-alloys was indirectly
 193 estimated. This positive P dependence has also been reported in C-saturated conditions (Clesi
 194 et al., 2018; Malavergne et al., 2019) in the range 1-21 GPa (Figure 2).

195 To conclude on this brief review of available data on C and H metal-silicate partitioning, we
 196 see that the partitioning systematics of both elements are linked: C partitioning (or C-content at

197 C-saturation) depends on H-contents, and H-partitioning is different in C-free and C-saturated
 198 conditions. In both cases, a significant effect of P has been noticed, rendering H more
 199 siderophile and C less siderophile. Below we present a simple thermodynamic framework that
 200 relates C and H speciation in silicate melts to changes in metal-silicate partition coefficients in
 201 P-T-fO₂-fH₂O parameter space.

202

203 3. Data Reduction

204 Each of the treated equilibria follows a law of mass action involving the constant of the reaction
 205 (K), in which the P and T dependences of the reaction's Gibbs free energy (ΔG_r) are
 206 approximated by the relationship:

$$207 \log K = -\frac{\Delta G_r}{RT} = \frac{A}{T} + B + C \times \frac{P}{T} \quad (1)$$

208 A, B and C are respectively related to the changes in enthalpy, entropy and volume associated
 209 with the reaction. Accordingly, in C-saturated charges, the C-content in metal (C^{METAL}) is
 210 defined as follows:

$$211 C^{\text{GRAPHITE}} = C^{\text{METAL}} \quad \text{with} \quad \log K_2 = \log C^{\text{METAL}} + \log \gamma_C^{\text{METAL}} + \frac{A_2}{T} + B_2 + C_2 \times \frac{P}{T} \quad (2)$$

212 Here, γ_C^{METAL} stands for the activity coefficient of C in the Fe-metal (see supplementary
 213 section). At this stage, we consider γ_C^{METAL} to be P independent.

214 In the silicate melts of the C-O-H system, the total C-content is considered as being the sum of
 215 three species: CO₂, CO, and CH₄. Expressed in mass fraction, this yields:

$$216 C^{\text{tot}} = \frac{CO_2}{44} \times 12 + \frac{CO}{28} \times 12 + \frac{CH_4}{16} \times 12 \quad (3)$$

217 The total H content in the silicate melts is considered as being the sum of three species: H₂O,
 218 H₂, CH₄. Expressed as a mass fraction, this yields:

$$219 \quad H^{tot} = \frac{H_2O}{18} \times 2 + \frac{H_2}{2} \times 2 + \frac{CH_4}{16} \times 4 \quad (4)$$

220 In most of the experimental conditions (Table 1), all H₂O is dissolved in the silicate melt, mostly
 221 as OH (Newcombe et al., 2017), but we computed these OH as H₂O equivalent (eg. Iacono-
 222 Marziano et al., 2012). This C-O-H speciation appears to be consistent with current state-of-
 223 the-art surveys (eg. Kadik et al., 2014; Armstrong et al., 2015, Malavergne et al., 2019; Dalou
 224 et al., 2019; Fischer et al. 2020). However, we admit that, in view of the limited number of
 225 studies on HP-HT speciation of C-O-H species in silicate melts, additional species may need to
 226 be considered in future models (eg. FeCO, CH_x or CO_x species; see Wetzel et al., 2013 ; Ardia
 227 et al., 2014 ; Kadik et al., 2014; Dalou et al., 2019; Solomatova et al., 2019).

228 The solubility of CO₂, CO and CH₄ are defined at C-saturation as:



232 We considered CO₂ as an anionic species in the silicate (CO₃)²⁻, implying that its solubility
 233 depends on oxygen O²⁻ activities in the melt in addition to fO₂. Iacono-Marziano et al. (2012)
 234 did use the NBO/T parameter as a proxy of O²⁻ activity to model carbonate solubility in mafic
 235 melts. This approach has also been considered in recent models on the C content at graphite
 236 saturation (Li et al. 2017). Accordingly, equilibria (5) and (6) are respectively modelled as:

$$237 \quad \log K_5 = \log CO_2 + \frac{A_5}{T} + B_5 + C_5 \times \frac{P}{T} - \log fO_2 + D_5 \times \frac{nbo}{t} \quad (8)$$

$$238 \quad \log K_6 = \log CO + \frac{A_6}{T} + B_6 + C_6 \times \frac{P}{T} - 0.5 \times \log fO_2 \quad (9)$$

239 Equilibria (7) is described as follows:

$$240 \quad \log K_7 = \log CH_4 + \frac{A_7}{T} + B_7 + C_7 \times \frac{P}{T} + \log fO_2 + 2 \times \log H_2O \quad (10)$$

241 In equations (8-10), CO₂, CO, CH₄ and H₂O refer to the activity of these species in the silicate
242 melt. The activity of CO and CH₄ is equal to their mole fraction in the melt (assumed given the
243 low concentrations and the absence of proof of more complicated behaviour). The activity of
244 CO₂ depends on NBO, and that of H₂O in silicate melts has long been known to be proportional
245 to the square of the H₂O concentration (Newcombe et al., 2017 and references therein).
246 Accordingly, in all equilibria involving H₂O, its activity was computed as the square of the H₂O
247 melt content.

248 The total C content in silicate melts at C-saturation has been parameterized by merging eq. (3)
249 and eqs. (8-9-10). Since the activity of C, a_C , is 1, $\log a_C$ is null and is therefore absent in
250 equations (8) to (10), but C undersaturation in the metallic phase can be considered by adding
251 the term $-\log a_C$ to equations (8-10).

252 The H content in silicate melts is computed by merging eq. (4), eq. (7) and the following
253 equilibria:



255 The equilibrium constant for eq. (11) is written as:

$$256 \quad \log K_{11} = \log H_2O - \log H_2 + \frac{A_{11}}{T} + B_{11} + C_{11} \times \frac{P}{T} - 0.5 \times \log fO_2 \quad (12)$$

257 H₂ refers here to the mole fraction of H₂ dissolved in the silicate melt (Hirschmann, 2012b).

258 The partitioning of H between silicate melt and metal has been calculated as:



260 $\log K_{13} = 4 \times \log H + \log CO - \log CH_4 + \frac{A_{13}}{T} + B_{13} + C_{13} \times \frac{P}{T} - 0.5 \times \log fO_2$ (14)

261 Considering other stoichiometry (see Clesi et al., 2018) such as:



263 these are all equivalent, since all the species involved are linked by equilibria (5-6-7-11) and
 264 by the mass balance constraints (eqs. 3-4). This means that the partition coefficient of H can be
 265 computed as:

266 $D_H^{metal/silicate} = \frac{H^{metal}}{H^{silicate}} = \frac{H^{metal}}{\frac{CH_4^{silicate}}{16} \times 4 + \frac{H_2^{silicate}}{2} \times 2 + \frac{H_2O^{silicate}}{18} \times 2}$ (16)

267 All thermodynamic constants involved in equations (8-10 and 14) are simultaneously adjusted
 268 in order to reproduce the P-T-fO₂-H₂O dependences of the C-content in the silicate melt at C-
 269 saturation and the metal silicate partitioning of H. In practice, we minimized the following sum:

270 $S_{optimal} = f(H^{SILICATE}) + f(C^{SILICATE}) + f(H^{METAL}) + f(D_H^{METAL})$

271 with $f(H^{SILICATE}) = \frac{|H_{measured}^{tot} - H_{calculated}^{tot}|}{\partial_{H^{tot}}}$, $f(C^{SILICATE}) = \frac{|C_{measured}^{tot} - C_{calculated}^{tot}|}{\partial_{C^{tot}}}$,

272 $f(H^{METAL}) = \frac{|H_{measured}^{METAL} - H_{calculated}^{METAL}|}{\partial_{H^{METAL}}}$ and $f(D_H^{METAL}) = \frac{|D_{H_{measured}}^{METAL} - D_{H_{calculated}}^{METAL}|}{\partial_{D_H^{METAL}}}$

273 δ refers to the analytical error on the measured values as reported in the original study (we
 274 considered 2σ). This specific effort was justified by the fact that reported errors greatly vary
 275 from a study to another and from a sample to another.

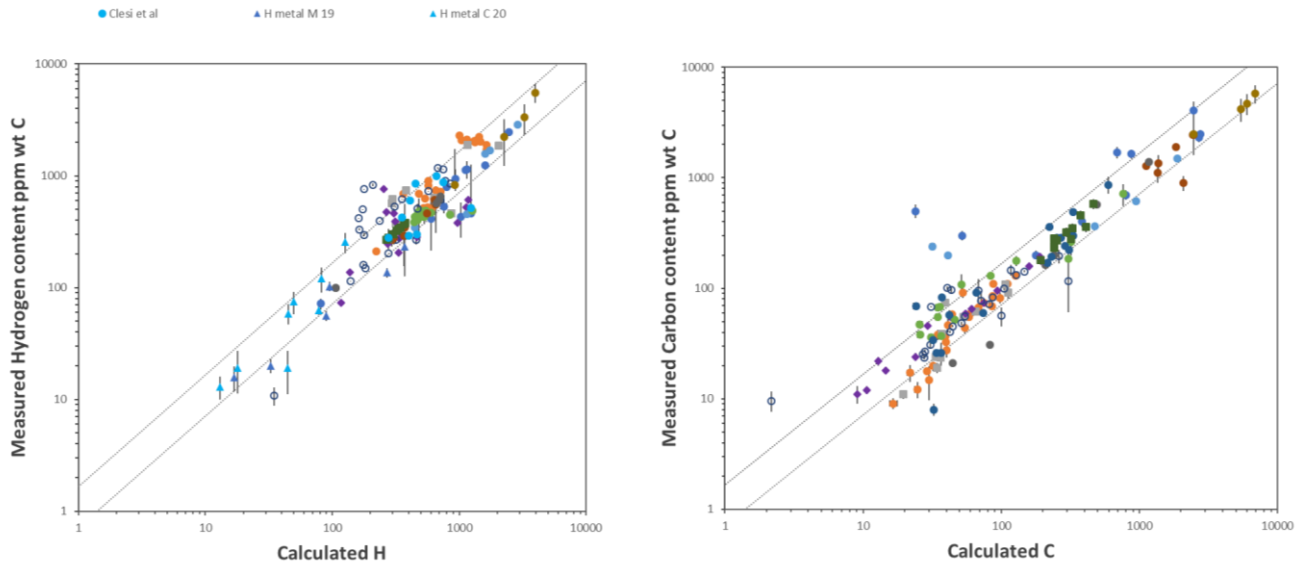
276

277 **4. Predicting partitioning data in the parameter space**

278 4.1. Accuracy

279 In a simultaneous fitting process, all thermodynamic constants A_i , B_i , C_i appearing in equations
280 (2, 8, 9, 10, 12, 14) have been parameterized in order to reproduce the P-T-fO₂ dependences of
281 the C and H contents in a silicate melt and metals at C-saturation. The list of parameters is given
282 in supplementary table S1. The results of the fit are given in figure 3 in terms of H and C-
283 contents in a silicate melt at C-saturation. Recalculated data for H- and C-contents at C-
284 saturation deviate on average by less than 33 % from the experimentally determined values (see
285 Fig. 3; see also figure S1). Outlier datapoints concern a few experiments that conflict with the
286 rest of the database, whereas P-T-H-fO₂-conditions are otherwise similar.

287 Uncertainties assessment on the A_i , B_i , C_i parameters adjusted using such non-linear multi-
288 parameter fitting has no unique solution. We performed sensitivity tests on each adjusted
289 parameter. This consists in varying each fitted parameter in order to probe its effect on the
290 function *Soptim* (eq. 17, see figure S2). The upper and lower bounds for the A_i , B_i , C_i parameters
291 were computed to match an increase of the *Soptim* function by 30% maximum (ie. an increase
292 of the misfit by 30%, see figures S2). This 30% value corresponds to the mean accuracy of our
293 model (see Fig. S1, where $1\sigma=15\%$). Quoted uncertainties are reported in table S1. Given the
294 reported experimental uncertainties (in P, T, fO₂, H and C-contents) and the possible issue of
295 calibration between different studies, we consider that the speciation model described here can
296 reproduce the observed saturation and partitioning data reasonably well. The C and H contents
297 and their uncertainties (a comprehensive error propagation formalism has been made available)
298 can be calculated using our model in an online application [http://calcul-isto.cnrs-](http://calcul-isto.cnrs-orleans.fr/apps/silicate_melt/)
299 [orleans.fr/apps/silicate_melt/](http://calcul-isto.cnrs-orleans.fr/apps/silicate_melt/)). Uncertainties in calculated C and H contents in silicate melts
300 range from ca. 10% at pressure of 1 GPa-1600°C, 15-25 % at 10 GPa-1800°C, 20-50% at 30-
301 2000°C GPa and 90-110% at 50 GPa, 3000°C. Uncertainties in calculated C and H contents in
302 metal and D_C and D_H are propagated on the web-application through the various equations listed
303 on section 3.



305

306 *Figure 3: Observed vs predicted Carbon Content at C-saturation (CCCS) and H content in*
 307 *silicate melts and metals. The legend is similar to that used in figure 1 and the additional data*
 308 *are specified just above the left figure; these include the H-data of Clesi et al (2018) and*
 309 *Malavergne et al (2019). The 33% misfit lines are reported here. Outlier datapoints concern a*
 310 *few experiments that conflict with the rest of the database (P-T-H-fO₂-conditions being*
 311 *otherwise similar).*

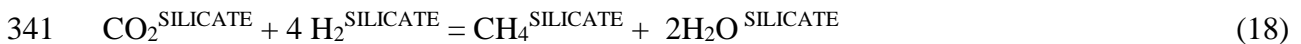
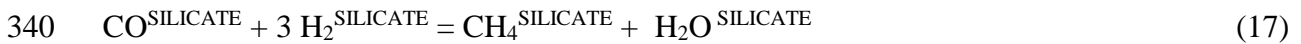
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313 4.2. C-speciation in P-T-fO₂ parameter space.

314 Figure 1 illustrates the speciation methodology used to capture the C-content in silicate melt at
 315 C-saturation in metal. It shows the silicate melt C-contents at C-saturation vs. fO₂, vs. P and vs.
 316 total H content in the silicate melts taken from the entire experimental database; it also
 317 superimposes the calculated C-speciation at various fO₂-P-T-H₂O conditions. In figure 1a, the
 318 thick dotted blue line shows the C_{tot} (the sum of C as CO₂+CO+CH₄) at 2 GPa, 1500°C and for
 319 a H₂O content in the melt of 200 ppm. The fO₂ dependences of the fraction of C as CO₂, CO
 320 and CH₄ are shown with the thin dotted blue straight lines. We clearly see CO₂ being the

321 dominant form of C at high fO_2 , CO at intermediate fO_2 and CH_4 at the lowest fO_2 . The
 322 crossover CO_2 -CO occurs at an fO_2 of about $IW+1$, as observed in specific experimental
 323 surveys (eg. Armstrong et al., 2015). The crossover CO- CH_4 occurs at ca. $IW-3$, but changing
 324 P or the H_2O content strongly modify this fO_2 values. For example, increasing P significantly
 325 increases the threshold fO_2 , which becomes ca. $IW-0.5$ at 20 GPa. This P effect explains some
 326 of the Malavergne et al (2019) data. Increasing H_2O content also greatly increases the amount
 327 of CH_4 , which can become the dominant form of dissolved C at 5 GPa- IW . This explains well
 328 the data of Kadik et al. (2014) that has so far been ignored in existing modelling (ie. Li et al.,
 329 2017; Eguchi et al., 2018; Fischer et al., 2020).

330 Figure 1b shows the P effect on C content at C-saturation. Calculated values bracket well the
 331 experimental data when considering a representative range of P-T- fO_2 conditions. These
 332 calculations also reveal two opposite trends. Moderately hydrated melts (≤ 200 ppm H_2O) show
 333 C-solubility that decreases with increasing P (to ca. 10-20 GPa), whereas hydrated melts show
 334 the opposite behaviour. C-decreasing with P is due to the fact that both CO and CO_2 have
 335 solubility at C-saturation that decrease with increasing P (Stanley et al., 2014; Li et al., 2017;
 336 Eguchi et al., 2018). For strongly hydrated samples, the C-solubility increases with P because
 337 our modelling implies that CH_4 is increasingly stabilized. This effect is data-driven since it
 338 results from the fitted values as described in section 3, but it must also reflect the volume change
 339 of the homogeneous reaction:



342 The volumes of the H_2O and CO_2 components and their P-T dependences are well-known and
 343 range, from 1 to 10 GPa, from 30 to 10 cc/mol and 34 to 22 cc/mol, respectively (ie. Gaillard
 344 et al., 2019). The volume of CH_4 and CO are, however, unknown. The solubility (ie. fluid-melt

345 equilibria) work of Ardia et al. (2014) and Armstrong et al. (2015) provides clues in the P range
346 1-5 GPa, that allowed us to estimate $V_{\text{CH}_4} \sim 27$ cc/mol and $V_{\text{CO}} \sim 22$ cc/mol. The molar volume
347 of H_2 is given in Hirschmann et al. (2012), $V_{\text{H}_2} = 11$ cc/mol. The volume changes of eq. (17) is
348 ca. 2cc at ca. 1 GPa and may strongly evolve negative with increasing P, given the high
349 compressibility of dissolved H_2O . We recall that the compressibility of CH_4 is unknown. We
350 expect similar P-evolution for eq. (18) given the poor compressibility of CO_2 vs H_2O . We admit
351 that independent and robust rationalization of the fact that CH_4 must dominate H-bearing
352 systems at HP is needed. At this stage, our model, that is data driven, cannot accurately account
353 for volume changes with P. Our sensitivity analyses make this clear (supplementary section).
354 The relatively simple formalism we adopted is justified by its capacity to capture the C-
355 solubility in the experimentally calibrated P-T-f O_2 -f H_2O parameter space.

356 A noteworthy feature is visible in figure 1b with the P extrapolation of our model: C-content in
357 H-poor silicate melts at C-saturation must first decrease with increasing P in the range 1-20
358 GPa (the domain where CO and CO_2 dominate) and then increase at higher P because of CH_4
359 formation. Note that the inflexion P depends on the H_2O content (ie. 20 GPa for 50 ppm H_2O ,
360 10 GPa for 200 ppm H_2O and 5 GPa for 500 ppm H_2O , the latter is not shown in fig. 1b). We
361 predict that above 35 GPa (though we calculate large uncertainties at such high P), C-content
362 should be in the range 100-60,000 ppm, depending on the H_2O content of the silicate melts. In
363 spite of the large uncertainties, this extrapolation is consistent with the data of Fischer et al.
364 (2020). Fischer et al (2020) data cannot be used in our calibration database because the H-
365 content in their silicate melts is unknown but they nevertheless reported RAMAN spectra
366 showing that CH_4 is the only C-species detected in their sample. This give credence to our
367 speciation model, but independent partial volume data and/or C-solubility experiments at high
368 P are needed.

369

370 4.3.H-speciation and partitioning in P-T-fO₂ space

371 The H metal-silicate partition coefficient is also implicitly controlled by the C-O-H speciation
372 and its P-T-fO₂ dependence. Figure 2 shows both experimental data and a range of calculation
373 covering the relevant P-T-fO₂-fH₂O conditions. Figure 2a illustrates the fO₂ effect on H
374 partitioning. This figure reveals two regimes:

- 375 - at oxidizing conditions, $D_H^{\text{METAL/SILICATE}}$ increases as fO₂ decreases, which reflects the
376 following reaction $\text{H}_2\text{O}^{\text{SILICATE}} = 2 \text{H}^{\text{METAL}} + \frac{1}{2} \text{O}_2$
377 - at reducing conditions, $D_H^{\text{METAL/SILICATE}}$ increases as fO₂ decreases, which reflects the
378 following reaction: $\text{CH}_4^{\text{SILICATE}} + \text{O}_2 = 4 \text{H}^{\text{METAL}} + \text{CO}_2^{\text{SILICATE}}$

379 The reaction $\text{H}_2^{\text{SILICATE}} = 2 \text{H}^{\text{METAL}}$ is necessarily operating but its effect (that should yield no
380 fO₂ dependence) is weak in figure 2a.

381 The P effects are highlighted in figure 2b. Increasing P makes H more siderophile (as observed
382 by Clesi et al, 2018 and Malavergne et al 2019), but this is strongly dependant on the fO₂, T
383 and the total H-content (see also Fig.2c). These effects are consistent with the recent HP-HT
384 experimental study of Tagawa et al (2021) and the molecular dynamics studies of Li et al.
385 (2020) and Yuan and Steinle-Neumann (2020) conducted on C-free systems that reported
386 increasing P makes H sensibly more siderophile. At ca. 20 GPa, however, the calculated D_H
387 values reach a sort of plateau or an inflexion point, indicating the domain where CH₄ dominates
388 in the silicate melt (see also fig. 1b for corresponding inflexion in the C-solubility vs P plot).
389 Such an inflexion is obviously not described in the recent works cited above on C-free systems.

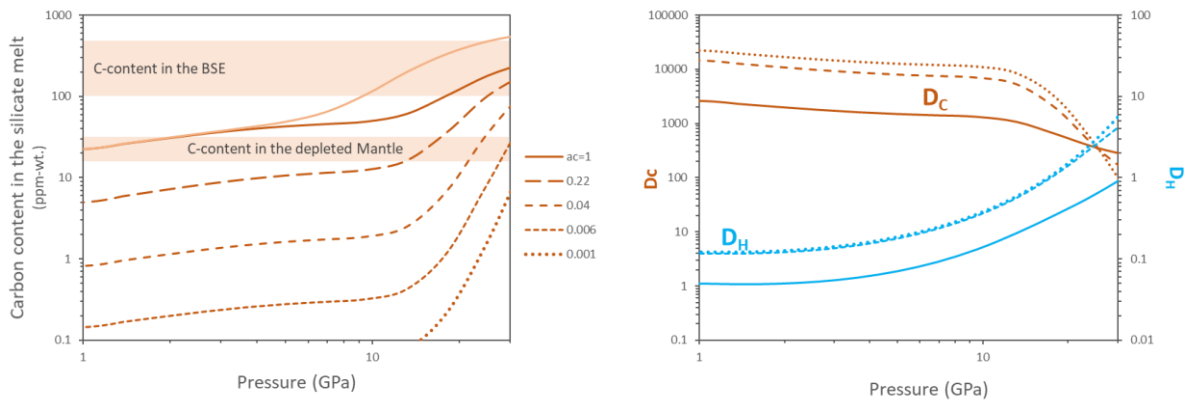
390 Figure 2c shows that lowering H-content in the silicate melt makes H more siderophile. This
391 dependence of H-partitioning on H-content is also described in Li et al (2020) for a C-free
392 system but not in other studies (Okuchi, 1998; Clesi et al., 2018; Malavergne et al., 2019). The
393 effect of the H content is twofold: first, in reactions (13) and (15), ruling H-partitioning, 1 mole

394 of H-bearing species in the silicate melt reacts into 2 or 4 moles of H in the metal, a
395 stoichiometry implying that the partitioning changes with H-content; second, the relationship
396 between H₂O mole fraction in the silicate and activity of H₂O is a square function, which cancels
397 the stoichiometric effect for reaction 15 at low P (ie. when all H is H₂O). Figure 2c shows that
398 the effect of H-content is critical at high P and low fO₂ conditions, where CH₄ dominates. At
399 low P, where H₂O dominates the H-speciation, the effect of H-content is insignificant. All this
400 implies that the experiments must be collected in the expected range of H-content of the magma
401 ocean in order to be directly applicable. The range of H₂O content of the bulk silicate Earth
402 given in Marty (2012) (1000-3000 ppm H₂O, ca. 100-300 ppm H) and in Hirschmann (2018)
403 (620-800 ppm H₂O, ca. 60-80 ppm H) is the domain where small changes in the H-content of
404 the silicate melt is predicted to have an important effect on H metal-silicate partitioning. Most
405 current experimental data have been conducted above this range of H-content (Fig. 2c).

406 4.4.C-undersaturation at variable pressures

407 Calculations in fig 1-3 are conducted for C activity of unity (i.e., graphite/diamond-bearing
408 systems), however, in the absence of graphite/diamond, the activity of C is < 1 in metal, and
409 hence activity-composition models are required to quantify C partitioning between metal and
410 silicate. Such models must be confronted to experimental data at pressure. The experimental
411 work of Kuwahara et al. (2019) provided C-partitioning data at C-undersaturation.
412 Unfortunately, these experiments contain as much N as C, implying that the metal is a ternary
413 Fe-C-N with complex activity-composition relationships. Furthermore, these experiments are
414 massively contaminated with B (several wt % from the experimental assemblage). This makes
415 it difficult to use the Kuwahara et al. (2019) data as absolute C-partitioning data. Nevertheless,
416 this experimental work indicates that C tends to become less siderophile as the activity of C in
417 the metal is reduced. Note that the existing low P activity-composition relationships for C in
418 Fe-C (see supplementary section) implies that C should become more siderophile as C-activity

419 decreases (the activity coefficient of C in Fe-metal increases as C-activity increases). This effect
 420 is actually visible in figure 4b, where $D_C^{\text{metal-silicate}}$ is higher for C-undersaturated cases at $P < 10$
 421 GPa. At higher P , when CH_4 dominates, we notice an inversion of the effect of C-activity on
 422 $D_C^{\text{metal-silicate}}$. Here (Fig. 4b), the calculation is done for a fixed H_{tot} content (80 ppm H that is the
 423 Bulk Silicate Earth H-content after Hirschmann, 2018), and this H is essentially balanced
 424 between H_2O and CH_4 . When CH_4 is involved, the total C-content does not only depend on a_C
 425 and $f\text{O}_2$, but it also depends on the fraction of H_2O (eq. 7). For a system containing more H_{tot} ,
 426 the crossover, described in fig. 4b at 10 GPa, must occur at lower P . This simple analysis reveals
 427 that the effect of C-undersaturation on $D_C^{\text{metal-silicate}}$ is complex since it depends on P and H -
 428 contents in the silicate melt.



429
 430 *Figure 4: The effect of P and C-activity on the C-solubility in silicate melt and on the metal-*
 431 *silicate partitioning for C and H. As P increases from 1 to 30 GPa, T increases from 1600 to*
 432 *2800°C. The H content is fixed to 80 ppm H (H-mantle after Hirschmann, 2018) in all curves*
 433 *but the pink one on the top of the left panel, which shows C-solubility for a silicate melt*
 434 *containing 160 ppm H.*

435 The effect of C-activity on $D_H^{\text{metal-silicate}}$ is also addressed in Figure 4b, showing that H becomes
 436 increasingly siderophile as the metal C-activity is reduced. This is consistent with the results
 437 from the four available experimental studies (Okuchi, 1998; Clesi et al., 2018; Malavergne et
 438 al., 2019; Tagawa et al, 2021), indicating that H is more siderophile in C-free ($D_H > 1$) than in

439 C-saturated systems ($D_H < 1$). This is also consistent with the molecular dynamics data of Li et
440 al. (2020) which demonstrate that partitioning of H between molten metal and silicate melt
441 exceeds 10 at extreme P-T conditions (up to > 100 GPa and $> 3000^\circ\text{C}$) in C-free systems. The
442 driving force that makes H increasingly siderophile with C-undersaturation is captured by the
443 following equilibrium, which dominates the metal-silicate partitioning of H at high P:



445 As the activity of C in metal is reduced, the above equilibrium is shifted to the right-hand side,
446 making H more siderophile.

447 The behaviour of C-O-H species during metal – silicate equilibria under C-undersaturated
448 conditions is currently under-constrained by experimental surveys. Whereas we are confident
449 of the effect of C-undersaturation on D_H described here, its effect on D_C appears to be multiple
450 and more difficult to capture. Experiments with C under-saturation conditions are essential to
451 test the validity of the important conclusions reached at this stage.

452

453 **5. Geochemical Implications for mantle - core differentiation on Earth**

454 A series of calculations investigate the fate of H and C in the P-T-X parameter space permitted
455 by our model. We limit our calculations to 30 GPa. Outside of this P-range, excessively large
456 uncertainties prevent any sound discussion. These calculations nevertheless allow us to discuss
457 the effect of variable values of C-activities and the effect of P. We consider two endmember
458 cases:

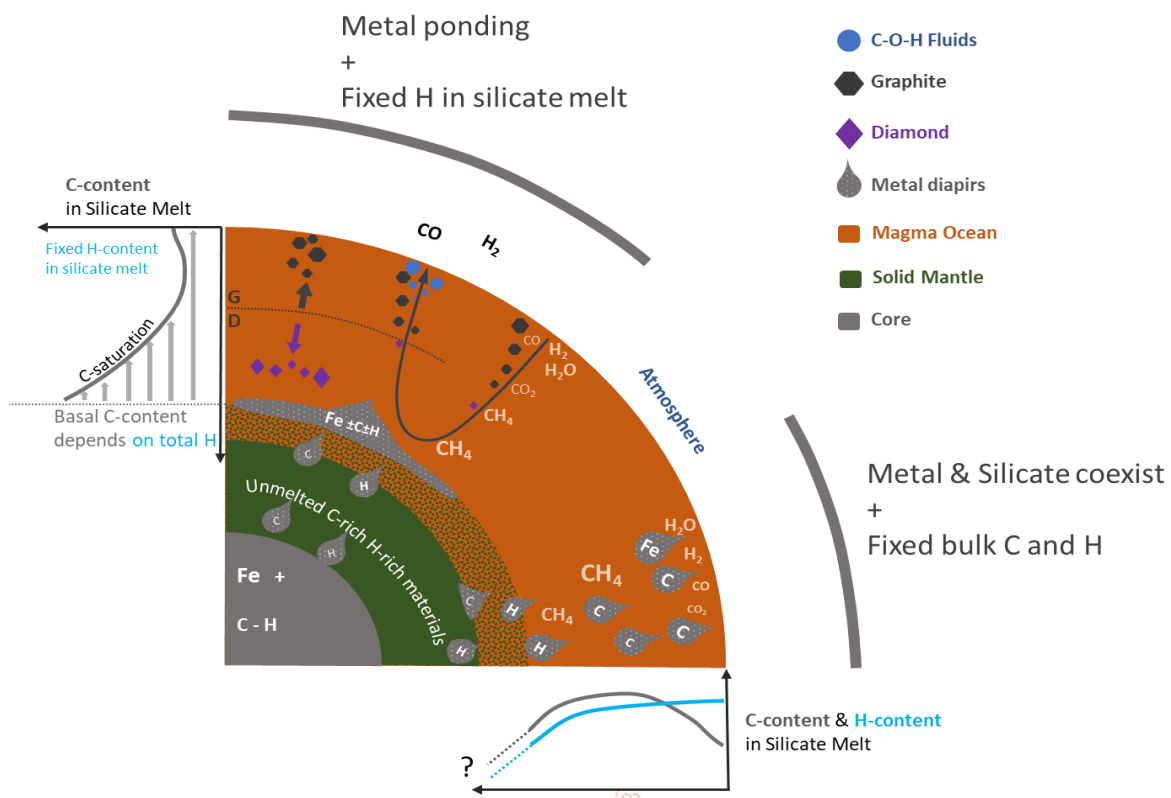
459 (i) metal efficiently sinks and ponds at the base of the magma ocean (fig. 5, top-left side).

460 The C and H partitioning at high-P high-T will control the activity of C and H in the entire
461 magma ocean.

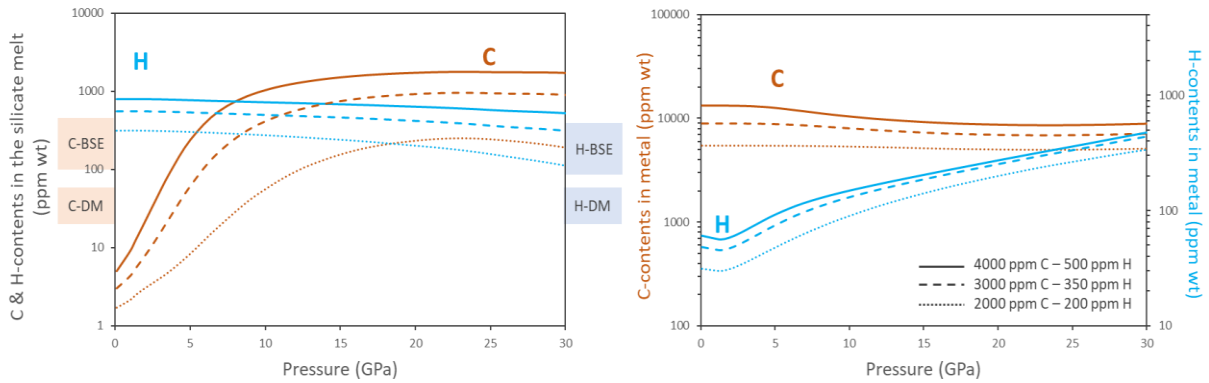
462 (ii) metal and silicate coexist all along the magma ocean vertical section (fig. 5, bottom-
463 right side); in that case, C and H partition between metal and silicate at all depths.

464 Figure 4a shows the C-solubility in silicate melt vs. P (or depth) in a magma ocean. Variable
465 values of C-activity are computed, whereas the H-content in the magma is fixed to 80 ppm H
466 (Bulk Silicate Earth after Hirschmann, 2018; in addition, a sensitivity test shows the effect of
467 doubling this amount of H). This means that we neglect H degassing as suggested by previous
468 studies (Sossi et al., 2020; Gaillard et al., 2021). The C solubility increases with increasing P
469 from ca. 20 ± 5 ppm at 1 GPa to a maximum value of ca. 293 ± 95 ppm at 30 GPa-2800°C. In the
470 latter case, C is mostly as CH₄. Accordingly, most H (ie. 70 ppm H) is in the CH₄ form. The C
471 content in the basal magma ocean is therefore controlled by the H availability. At low P, in
472 contrast, most H occurs as H₂O (75 ppm H), most C occurs as dissolved CO (max. 13 ppm) and
473 the remaining C occurs as CO₂ (4 ppm). A first conclusion must be highlighted here, the depth
474 of the magma ocean controls its C content, implying that shallow magma oceans must have low
475 C-contents (~ca. tens of ppm), whereas deep magma oceans enable high C-content (ca. >100
476 ppm C). At such high-P, the affinity of C for the metal is not as strong as at low P (Fig. 4b)
477 implying that C assimilation by the core in large planet must weaken, whereas the core of small
478 planets must massively take C. This point is consistent with the experimental model of Fischer
479 et al (2020). The second conclusion is that convection-driven upward transfer of such C-rich
480 basal magma ocean regions implies decompression-induced speciation changes, with C & H,
481 shifting from CH₄-dominant to CO-H₂O dominant during ascent. Such a speciation change is
482 not redox neutral and must consume oxygen (lowering the fO_2). In addition, as indicated in
483 figure 4a, the solubility of C must decrease, implying that C saturation may be reached as the
484 melt moves toward the surface of the magma ocean. This scenario is illustrated on the left part
485 of figure 5, where a vertical gradient in C-solubility causes C-saturation in upwelling regions
486 of the magma ocean, while downwelling regions must dissolve graphite or diamond. The C-

487 content in the basal silicate melt, where deep metal-silicate equilibration takes place, is
 488 controlled by the availability of H to form CH₄. In the case of figure 4, we recall that the H
 489 content in the silicate melt is constant (80 ppm), and it corresponds to the H-content in the bulk
 490 silicate Earth. If this H content is doubled, it greatly impacts the C-solubility in the P domain
 491 where CH₄ dominates (fig. 4a). Marty (2012) reported much greater values (up to 290 ppm)
 492 than Hirschmann (2018) for the H-contents in the BSE. We therefore conclude that a large range
 493 of C-solubility in the basal magma ocean is possible (from ca. 200 to 1000 ppm) reflecting the
 494 uncertainties in H-content in the BSE (fig. 4a). In any case, we see that the calculated range of
 495 C-contents is comparable to the C-content of the depleted mantle in the P-range < 10 GPa and
 496 with C-content of the BSE (ie. Hirschmann, 2018; Marty, 2012) at P> 10 GPa.



497
 498 *Figure 5: Diagram illustrating the two simulated magma ocean configurations, involving a*
 499 *basal layer of metal (top-left) and metal droplets being spread in the magma ocean (bottom-*
 500 *right). The top-left case is simulated in fig. 4, whereas the bottom-right one is shown in fig.6.*



501

502 *Figure 6: The fate of C & H in a magma ocean that contains Fe-metal at all depth. Here, we*
 503 *fixed the bulk C and H contents (in metal + silicate) as indicated in the legend. C solubility in*
 504 *the magma ocean increases with increasing P until a critical depth, where H becomes*
 505 *siderophile. Beyond this threshold P, we propose that the magma may get increasingly*
 506 *desiccated. P-T evolution similar to figure 4.*

507 As illustrated in the right side of figure 5, if one considers that metal and silicate coexist all
 508 along the magma ocean vertical section, C-saturation is, in contrast, unlikely since the metal
 509 takes most C. We simulated in figure 6 such a case with fixed bulk C and H contents along the
 510 magma ocean profile (several runs were done with 4000-3000-2000 ppm C and 500-350-200
 511 ppm H). Here, we focus on a somewhat simple, but increasingly popular model of accretion for
 512 planet Earth made up mainly of enstatite chondrites (eg. Javoy et al., 2010; Piani et al., 2020).
 513 Enstatite chondrites contain 4000 ppm C and 490 ppm H (Piani et al., 2020). We conducted
 514 calculations at a fixed fO_2 of IW-2 (no significant difference with simulations done at IW-4)
 515 for a set of P-T conditions similar to figure 4. At low pressure (ie. less than 5GPa), one sees
 516 that most C is sequestered in the molten metal phase, leaving only a few tens of ppm C in the
 517 silicate melt. In contrast, H is mainly partitioned in the silicate melt. As P increases, C becomes
 518 less siderophile, reaching contents of ca. 200-1000 ppm-wt. in the silicate magma ocean,
 519 depending on the H content, at 20 GPa. This is because CH_4 becomes increasingly stable. In
 520 the meantime, H becomes increasingly siderophile. As P increases further, this can lead to the

521 dehydrogenation of the silicate melt, which may evolve dry at $P > 30$ GPa, but our model does
522 not allow calculations to be conducted at such pressure due to too large uncertainties. Whereas
523 we are confident in the enhanced stability of CH_4 at high P , and the geochemical consequences
524 we briefly expose here, reducing the uncertainties of predicted values is a necessity in order to
525 quantitatively link chondritic C-H abundances and the distribution of these elements during
526 the magma ocean stages. In order to do so, we need independent constraints on C-O-H species
527 compressibility and $a\text{-X}$ relationships in a metal that become multicomponent and increasingly
528 O-rich as pressure increase (eg. Tagawa et al., 2021)

529

530 **6. Conclusions and perspectives**

531 A growing body of experimental and molecular dynamics data have recently been produced in
532 the literature on the partitioning of C and H during metal – silicate equilibria. Whereas these
533 data originated from a number of laboratories, used different methods and produced different
534 results, the modelling carried out here shows that all the data can be reconciled within the
535 framework of a melt speciation model, involving the C-H-species H_2O , H_2 , CO_2 , CO , and CH_4
536 dissolved in a silicate melt. The dependence of the stability of these species on P , T and $f\text{O}_2$ can
537 be related to previously determined values of H and C metal – silicate partition coefficients.

538 The use of this model allows us to distinguish two types of magma ocean: shallow and deep
539 ones. In shallow magma oceans, C is strongly siderophile, while H is not siderophile. In deep
540 magma oceans, C evolves to become less siderophile, while H becomes increasingly
541 siderophile. The partitioning of H into metal depends on both P and C activity. In a C-poor,
542 deep magma ocean, H incorporation into the core could lead to desiccation of the magma ocean.

543 Experimental and MD tests of this model are, however, needed since there are not enough
544 constraints at this stage in certain regions of the parameter space (eg. low C-activity, high P)

545 /low H content). Investigation of both C and H during partitioning are required since these are
546 coupled through speciation relationships. This model is ultimately expected to evolve towards
547 a multicomponent mixture taking into account all possible stoichiometric interactions between
548 species in the C-H-O-N-S system (eg. Tsuno et al., 2018).

549

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669

670 **8. Acknowledgment**

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673 by M Hirschmann and Paolo Sossi.

674

675 **9. Supplementary information**

676

677 **H & C activity coefficient in metal**

678 The behaviour of H in metals is not thought to be ideal but its activity coefficient follows the
679 empirical relationships given in Lob et al (2011):

680 $\log \gamma_H = 0.169 \times C^{METAL} - 0.2516$ (17)

681 Where C^{metal} stands for the mass fraction of C in metal. Activity-composition relationships for
682 C in metals have been defined in the metallurgy literature (eg. Wang et al. 1991). These are
683 used with the calculations for C-undersaturated systems below (see section 4.4). The presence
684 of <20% Ni is not considered to affect the activity of H as shown by previous thermodynamic
685 analyses of the 1-atm database (Jiang et al., 2011). We must specify at this stage that the non-
686 ideality laws for H and C in the metal as suggested from 1-atm studies have not yet been verified
687 by HP data. We suggest that specific HP experimental studies be devoted to this purpose (eg.
688 Li et al., 2016 for C-S interactions in metals).

689

690 **Regressed parameters**

691 Regressed parameters and their uncertainties are shown in table S1. These constants can be used
692 to compute the log K of each reactions as follows:

693 $\log K = -\frac{\Delta G_r}{RT} = \frac{A}{T} + B + C \times \frac{P}{T} + D \times NBO$

694 In table S1, the A terms must be multiplied by 1000. Note that the C terms is in some cases
695 modified as $C^{mod} = C + C' \times P/T$ in order to allow the volume change of the reaction to change

696 with P and T. In most of these cases, the uncertainties are very large underlining the need of
 697 getting robust compressibility data for C-O-H species in silicate melts.

698 Our procedure for getting uncertainties imply that these are not symmetrical so we give in table
 699 S1 the lower and upper bound values for each fitted value.

700

701

702 Table S1: Regressed parameters and their upper and lower bounds. Units allow the log K of
 703 each reaction to be calculated in molar ratios.

Reaction	Constant	Best fit	Bounds
C metal	A2	-0.487	-0.52 / -0.41
	B2	1.022	1.11 / 0.85
	C2	-0.006	-0.007 / -0.005
CO2	A5	-8.794	-9.3 / -8.5
	B5	-0.054	-0.35 / 0.1
	C5	-0.201	-0.6 / 0.05
	C5'	9.512	2 / 21
CO	D5	0.784	0.57 / 0.9
	A6	-1.658	-1.83 / -1.53
	B6	-2.220	-2.31 / -2.15
CH4	C6	-0.287	-0.38 / -0.2
	A7	-9.760	-9.96 / -9.62
	B7	0.019	-0.07 / 0.081
	C7	0.441	0.406 / 0.465
	C7'	-6.382	-16.8 / 0.9

H2	A11	-6.867	-20 / -6
	B11	-0.165	-4 / 0.25
	C11	-0.638	-4 / -0.3
	A13	15.470	12.8 / 16.6
	B13	0.612	-0.7 / 1.2
	C13	0.012	-0.35 / 0.15
H metal	C13'	7.085	-2 / 15

704

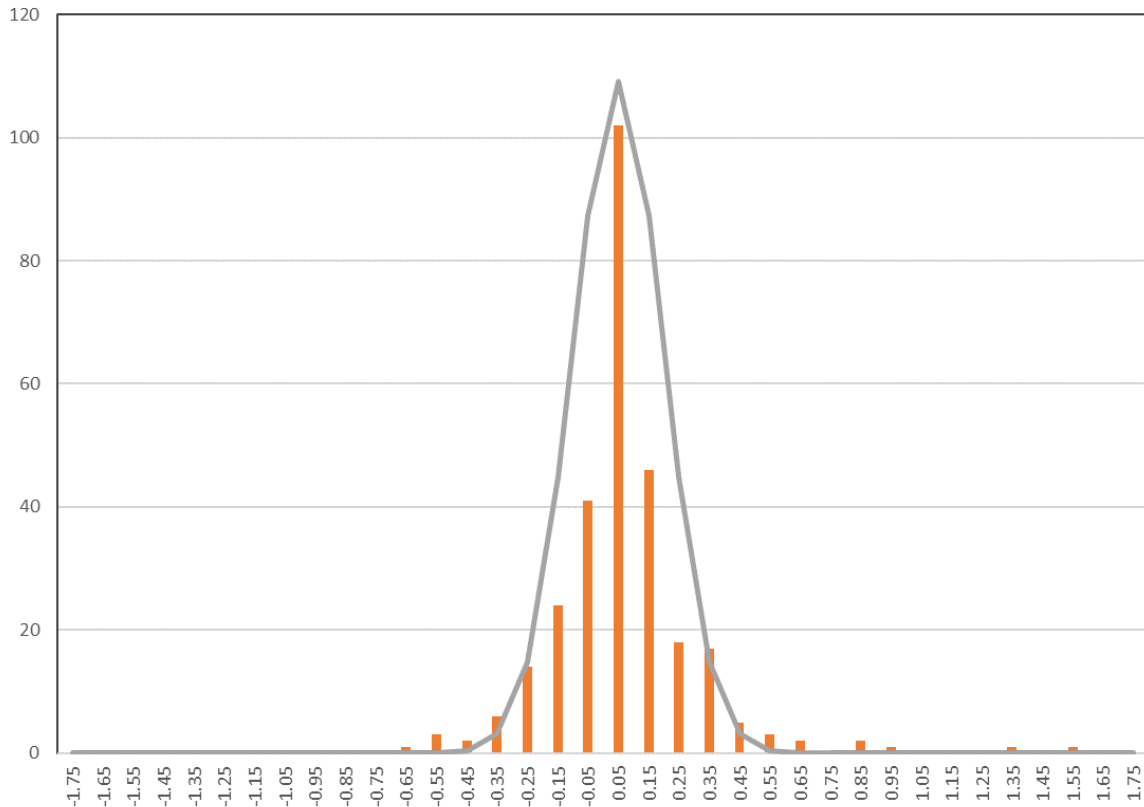
705 The online calculation tools use the numbers provided in table S1 to calculate the various
706 equilibria. The uncertainty propagations use an average error (lower bound – upper bound
707 divided by 2).

708 The ability of our model to reproduce the experimental observations has been quantified in
709 figure S1, which shown the distribution of residues expressed as deviation per data, in fraction,
710 expressed as follows:

$$711 \text{ Deviation} = (\text{observation} - \text{computed}) / \text{observation}$$

712 A value of 1 means that the misfit is 100 %. The distribution of residues (fig. S1) indicates a
713 one sigma value of 0.15 (15 %), which explains the 30 % uncertainties (2 sigma) announced in
714 section 4.1.

715

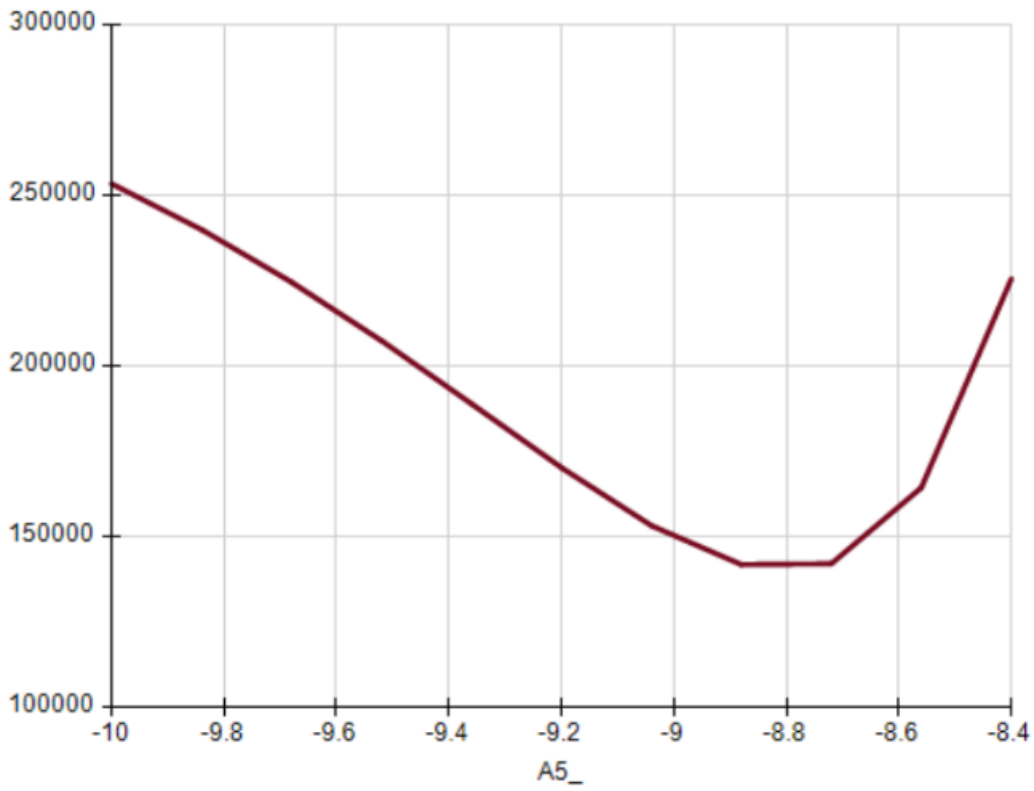


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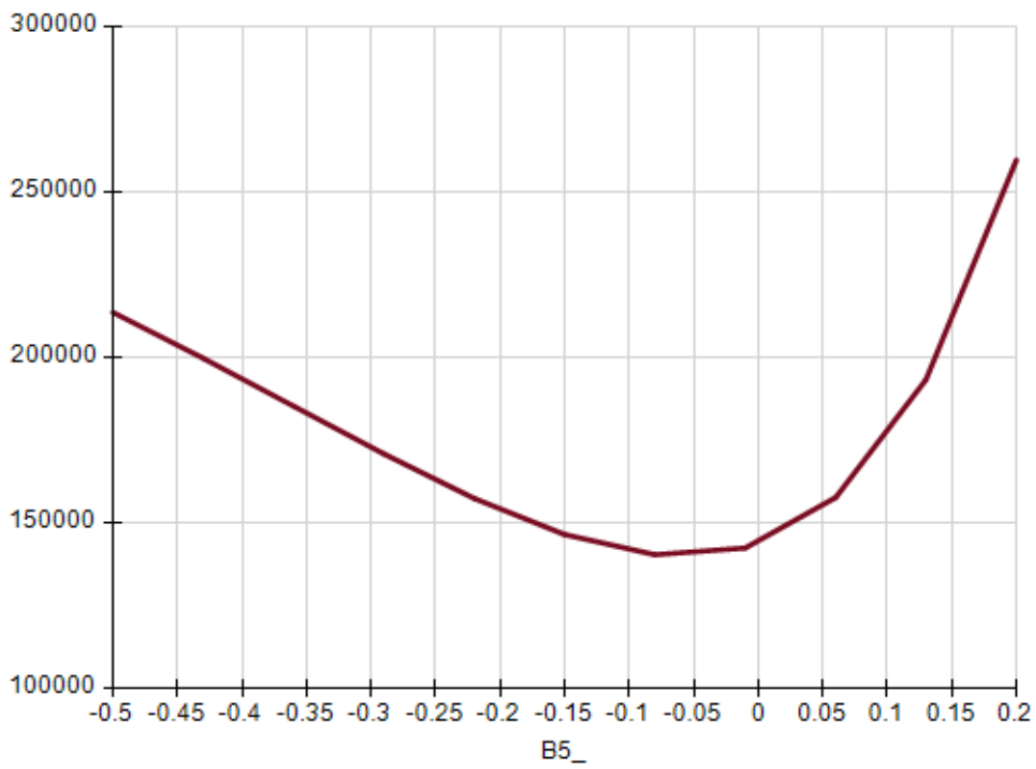
717 *Figure S1: Frequency diagram showing the distribution of misfit per data. The horizontal scale*
 718 *is expressed as fraction of the value to fit. In practice, this must be read as more than 100*
 719 *experimental observations are reproduced to within 5%. In grey is shown a log-normal curve*
 720 *calculated for a 1-sigma of 0.15.*

721 Figure S2 illustrates the sensitivity tests for some of the regressed parameters. The values of
 722 the Soptim function (residues normalized to experimental uncertainties) vary as the regressed
 723 parameters are changed, with a minimum centred on the regressed values. In most cases, the
 724 error a non-symmetrical. We considered that values of the Soptim function below 180,000 (30%
 725 variation relative to the minimum) correspond to the acceptable range for the regressed
 726 parameters.

727



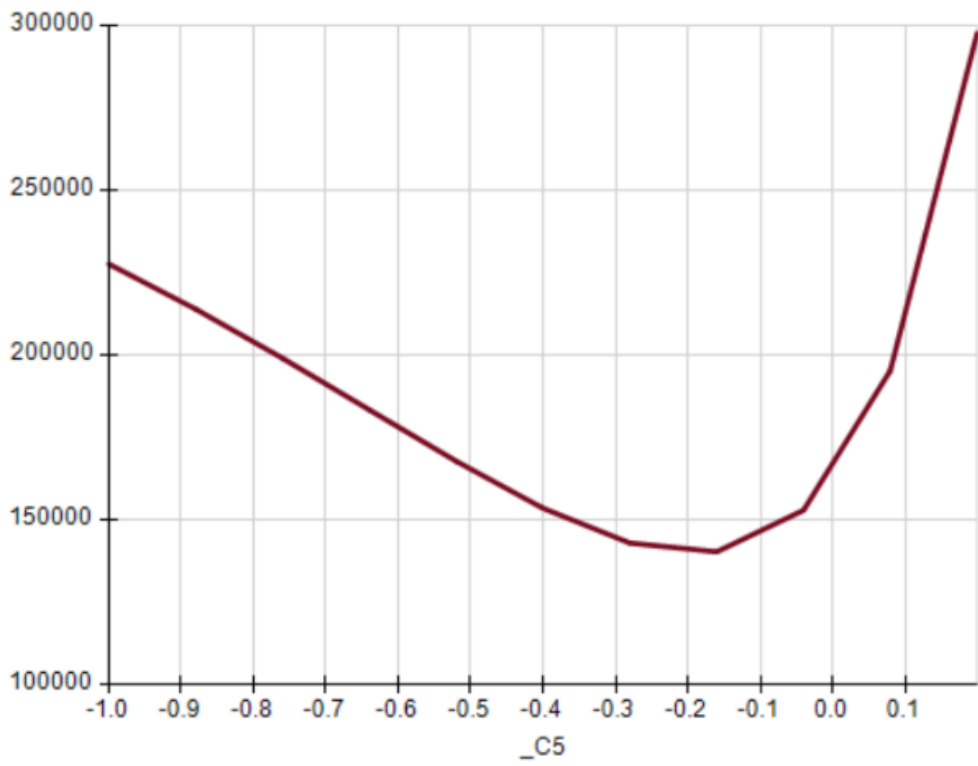
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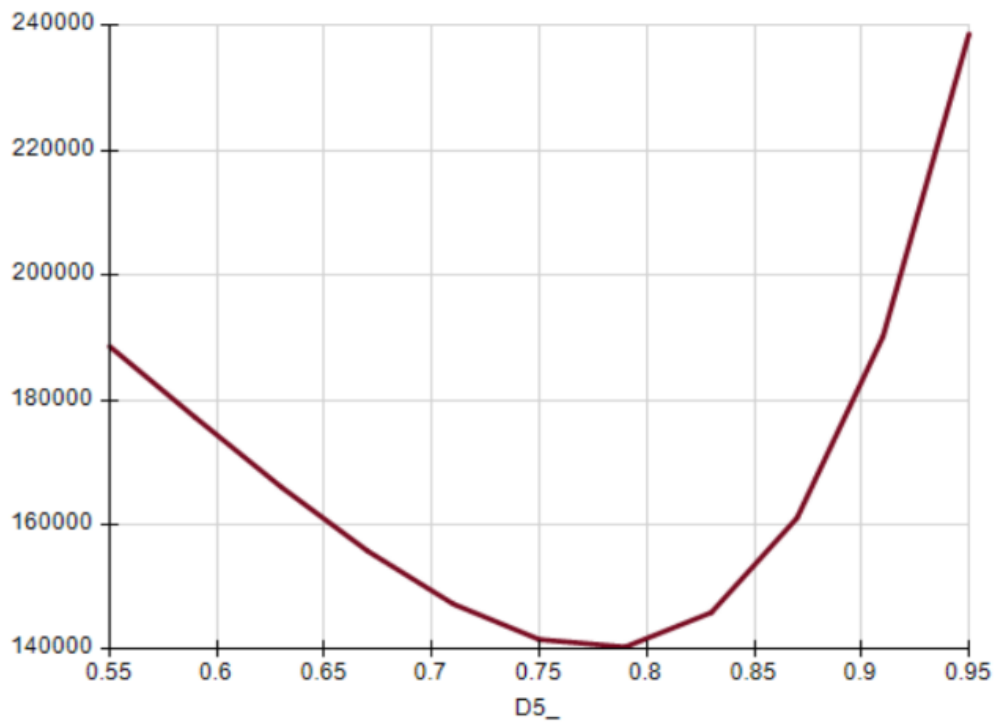
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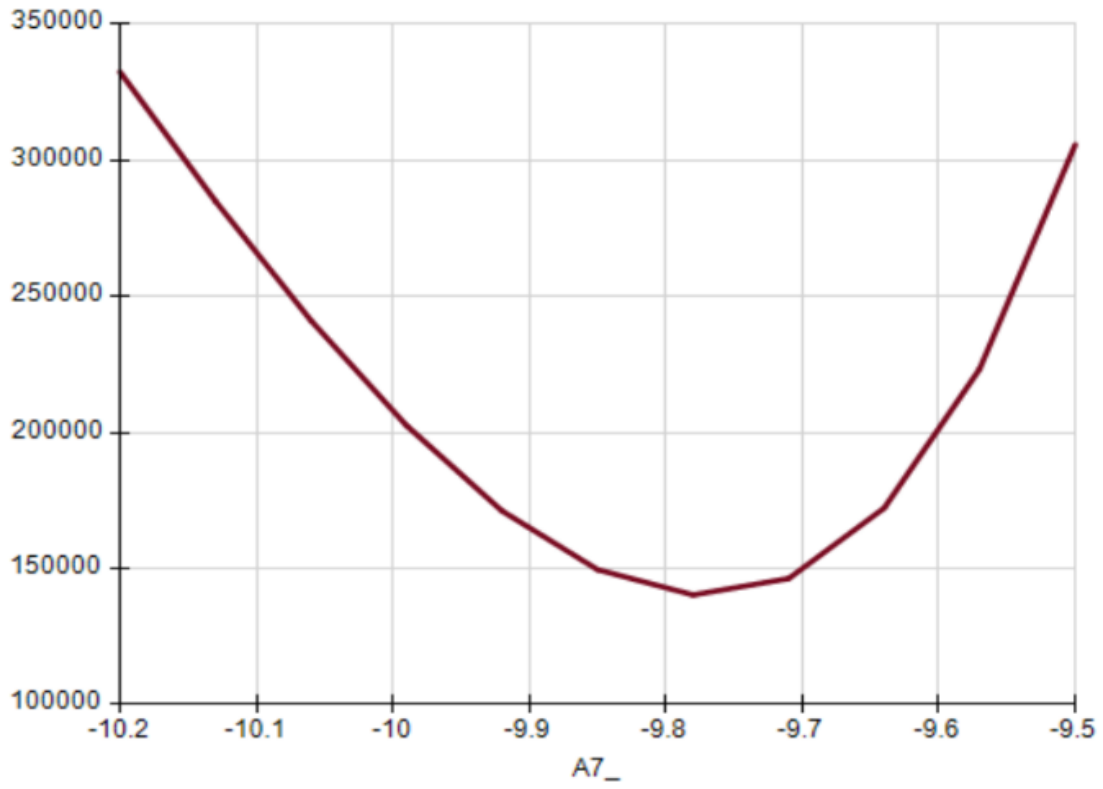
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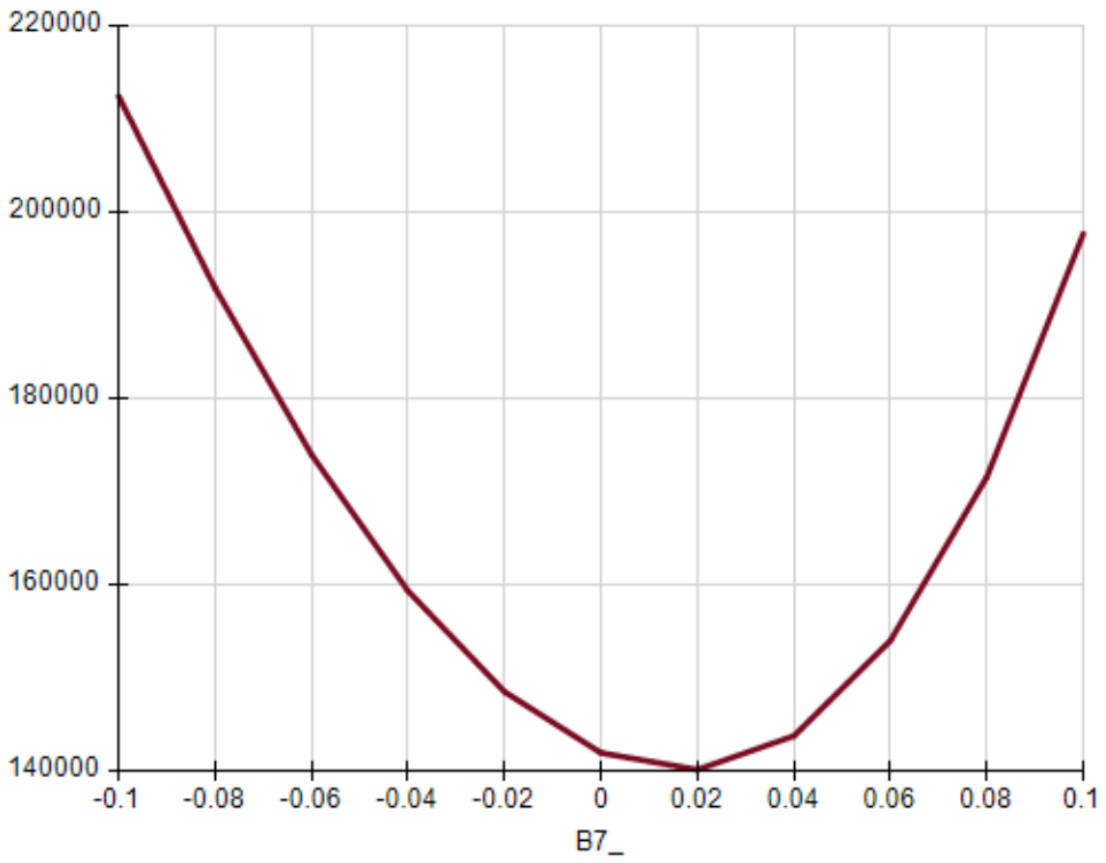
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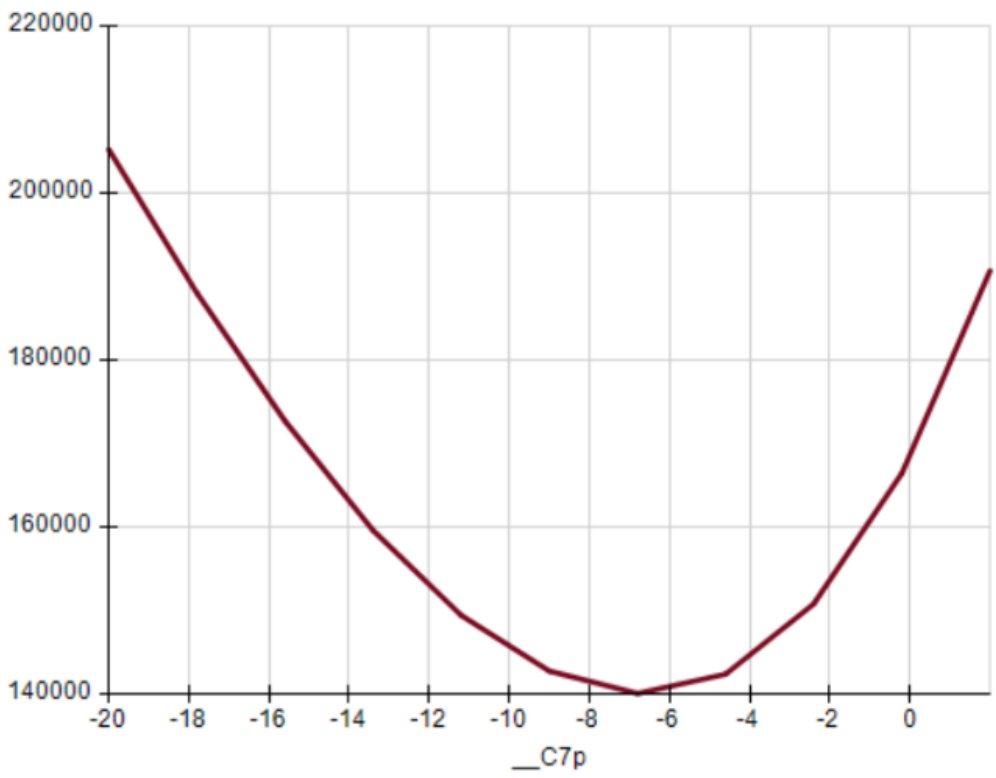
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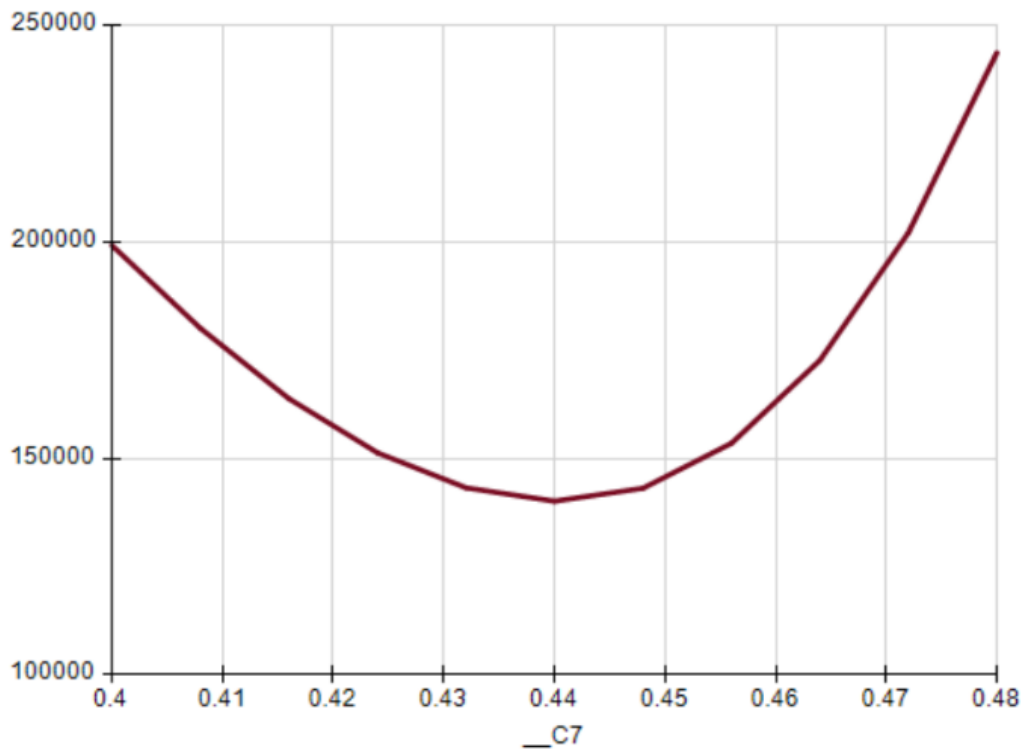
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771 Figure S2: Example of sensitivity tests on some regressed parameters. The vertical axis is the
772 Soptim value. Soptim values < 180,000 define the acceptable range of regressed parameters.

773

774

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