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1 **Redox Controls during Magma Ocean Degassing**

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10 **Nitrogen, carbon, hydrogen and sulfur are essential elements for life and comprise about 1 %**
11 **of terrestrial planet masses. These elements dominate planetary surfaces due to their volatile**
12 **nature, but the Earth's interior also constitutes a major C-H-N-S reservoir. Resolving the**
13 **origin of the surficial versus deep volatile reservoirs requires the past 4.5 Giga-years of mantle**
14 **outgassing and ingassing processes to be reconstructed, involving many unknowns. As an**
15 **alternative, we propose to define the primordial distribution of volatiles resulting from**
16 **degassing of the Earth's magma ocean (MO). The equilibrium partitioning of C-H-O-N-S**
17 **elements between the MO and its atmosphere is calculated by means of solubility laws,**
18 **extrapolated to high temperatures and over a large range of redox conditions. Depending on**
19 **the redox conditions, the amount of volatiles, and the size of the MO considered, we show that**
20 **the last MO episode may have degassed 40-220 bar atmospheres, whereas hundreds to**
21 **thousands of ppm of C-H-O-N-S can be retained in the magma. Two contrasting scenarios**
22 **are investigated: reduced vs. oxidized MO. For reduced cases (<IW-2), an H-C±N-rich**
23 **atmosphere can be formed, whereas the atmosphere under oxidizing conditions (>IW+2)**
24 **would be dry and C-N-S-rich. An intermediate redox state produces a C-N atmosphere. In**
25 **many cases, the present-day surficial abundances (atmosphere+ocean+crust) of C and N, the**
26 **most volatile elements, are very close to the calculated primordial MO - atmosphere**
27 **distribution. This probably means that lithospheric recycling and post-magma ocean**
28 **degassing only moderately alter the surficial abundances of these elements. Sulfur, in**
29 **contrast, must have been mostly outgassed by post-MO events. Changes in redox conditions**
30 **during magma ocean degassing played a first order role in the composition of the primordial**
31 **atmosphere of planets. We suggest that the more oxidized conditions on Venus due to H-loss**
32 **may have played a role in the growth of a dry MO atmosphere on this planet compared to an**
33 **H-bearing one on Earth. To verify these first order assertions, constraints on volatile**
34 **behaviour under extreme magma ocean conditions and upon magma ocean solidification are**
35 **urgently needed.**

36 1. Introduction

37 The life-forming elements (carbon, hydrogen, oxygen, nitrogen and sulfur; hereafter CHONS)
38 are abundant on the Earth's surface and dominate most surficial biogeochemical cycles.
39 However, it is known that the planetary interior represents at least an equivalent CHONS
40 reservoir (Marty et al., 2020; Hirschmann, 2018; Gaillard et al., 2021). Two CHONS mantle
41 reservoirs have been identified: (i) depleted mantle (DM), corresponding to the source of mid-
42 ocean ridge magmatism (Hirschmann and Dasgupta, 2009; Saal et al., 2002; LeVoyer et al.,
43 2017), and (ii) deep enriched mantle (EM) reservoirs, fueling most hotspots (Hofmann, 2003;
44 Hirschmann and Dasgupta, 2009; Marty et al, 2020; Miller et al., 2019). Historically, these
45 reservoirs have not been defined in terms of volatile CHONS components, but on various trace
46 element and isotope ratios that are linked to the formation of the crust (Hofmann, 2003). Their
47 definition in terms of volatile reservoirs is therefore a work in progress. Difficulties arise partly
48 from the fact that these two reservoirs are not homogeneous, making their definition and their
49 CHONS contents highly debated. Their respective volumes are also poorly known. The volume
50 of the depleted mantle (DM) is at least equivalent to that of the upper mantle and may extend
51 down to a region just above the core – mantle boundary (Hoffman, 2003; Miller et al., 2019),
52 where puzzling geophysical discontinuities possibly delineate deep geochemical reservoirs.
53 The deep EM contains primordial material with unusual Sun-like He, Ne and N isotopic
54 compositions that are significantly distinct from those of the DM (Marty et al., 2016, 2020;
55 Tucker and Mukopadhyay, 2014). The EM is enriched with respect to the DM in both carbon
56 and hydrogen but the magnitude of this enrichment remains unclear (e.g. Miller et al., 2019 vs.
57 Hirschmann 2018 for C, and Marty et al., 2020 vs. Hirschmann, 2018 for H).

58 The origin and evolution of the distribution of the CHONS elements between the depleted and
59 enriched mantles and how they connect to CHONS abundances at the Earth' surface is also a
60 matter of lively debate. The deep enriched mantle may have been isolated for a long time from
61 the mantle convection sourcing mid-ocean-ridge magma (linked to plate tectonics, e.g. Ballmer
62 et al., 2017; Tucker and Mukhopdhyay 2014). However, mantle plumes, mantle degassing and
63 lithospheric recycling (i.e. ingassing) have been operating for a long time and potentially caused
64 extensive redistribution of CHONS between mantle and surface reservoirs (Hirschmann and
65 Dasgupta, 2009; Sleep, 2011; Hirschmann, 2018). There is, however, no consensus on the
66 CHONS reservoirs and fluxes associated with subduction processes and mantle outgassing. For
67 example, published estimations of the present-day amount of subducted carbon range from 0 to
68 52 Mt C / years (Kelemen and Manning, 2016). All these uncertainties mean that the estimation

69 of the primordial distribution of volatile elements, as well as their evolution within the different
70 reservoirs, remains highly hypothetical (Hirschmann, 2018).

71 As an alternative approach to this question, we propose to reconstruct the primordial volatile
72 distributions inherited from planetary accretion and early differentiation stages making up the
73 Hadean. Although no rock specimens have survived from the Hadean eon, some zircon crystals
74 indicate that an early atmosphere, crust, oceans, and possibly life, were most likely established
75 within the first 100 million years of the Earth's history (Catling and Zahnle, 2020). Consistent
76 with such an early evolution, geochemical surveys indicate that most of the CHONS elements
77 were delivered during accretion (Marty et al., 2016; Sarafian et al., 2014; Greenwood et al.,
78 2018; Piani et al., 2020) and were thus processed by the various differentiation events, in
79 particular the magma ocean stages (Pahlevan et al., 2019; Grewal et al., 2020; Sossi et al., 2020)
80 (see Fig. 1). In this context, even if a significant late veneer has contributed to refining the final
81 volatile reservoirs of the Earth, its contribution would not be greater than 10% (Marty et al.,
82 2013), which would not alter the conclusion that volatiles were efficiently processed during the
83 early magma ocean stages. Here, we present a model that predicts CHONS partitioning between
84 magma and gas in the context of magma ocean – atmosphere interaction. We show that oxygen
85 fugacity is the key parameter ruling such partitioning. We found that for N and C, i.e. the most
86 volatile elements, the magma ocean outgassed a mass similar to the present-day surficial
87 reservoirs. Hydrogen can only be degassed under reduced conditions, whereas sulfur is only
88 volatile in conditions as oxidized as the present-day mantle. This pushes back the prerequisite
89 conditions for life to the early stages of planetary systems.

90 **2. Conditions of MO degassing.**

91 2.1. General framework and assumptions

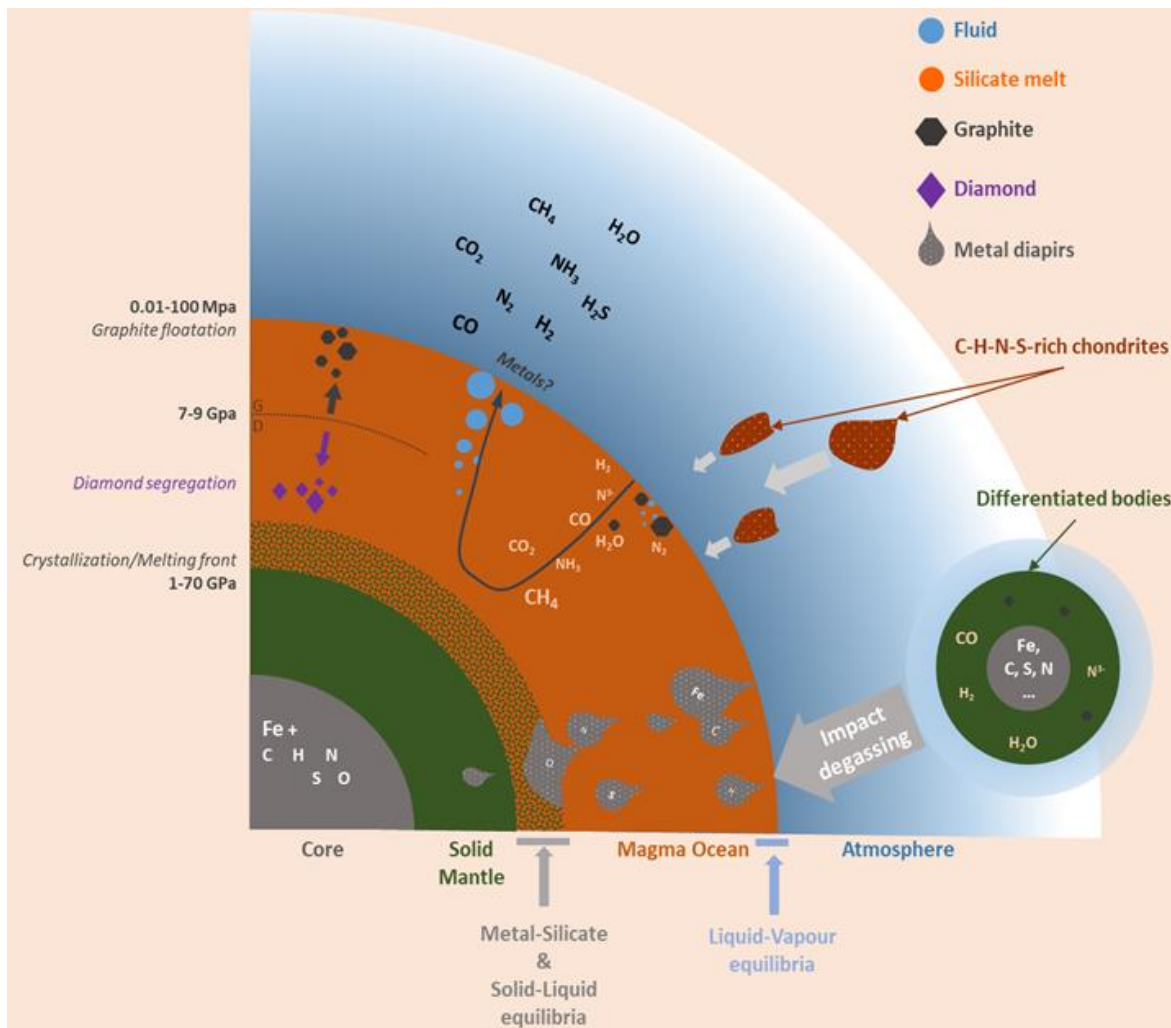
92 Magma oceans (MO) experienced extreme thermodynamic conditions: high temperature, low
93 viscosity, and vigorous convection enabled efficient mass transfer and large-scale chemical
94 equilibration during planetary differentiation (Fig. 1) (eg. Elkins-Tanton, 2012; Rubie et al.,
95 2015). Gas-melt equilibration certainly occurred at the MO – atmosphere interface (Lebrun et
96 al., 2013; Hamano et al., 2013; Sossi et al., 2020; Katyal et al., 2020). The equilibrium CHONS
97 partitioning was thus governed by speciation in both the melt and gas, which was in turn
98 controlled by the pressure (P), temperature (T) and oxygen fugacity (f_{O_2}) conditions prevailing
99 at this interface. This simplification holds as long as convection in both the MO and its
100 overlying atmosphere is fast enough. However, fast convection also implies rapid cooling,

101 which would have caused rapid crystallization of the MO (ie. Elkins-Tanton, 2012 ; Lebrun et
102 al., 2013 ; Hamano et al., 2013 ; Rubie et al., 2015 ; Hier-Majumder and Hirschmann, 2017).
103 In this respect, most simulations suggest that the cooling and solidification of the Earth's last
104 MO occurred rapidly, within less than ca. 4-5 millions of years (Myrs) (Hamano et al., 2013).
105 Alternatively, degassing and greenhouse effects may extend the lifetime of a MO to several
106 tens of millions of years, but in any case, crystallization must have been relatively fast. Two
107 end-member cases can be identified: (a) crystallization is so rapid that the molten MO –
108 atmosphere partitioning is preserved, and (b) CHONS volatiles can be segregated during
109 crystallization of the MO (eg. Hier-Majumder and Hirschmann, 2017) producing deep volatile
110 reservoirs. The possibility of deep segregation of volatiles is not explored in this study. We will
111 mainly discuss situation (a), where gas – melt equilibria are controlled by the prevailing P-T-
112 fO_2 at the MO – atmosphere interface.

113 The temperature is set at $T=1500^{\circ}C$, which is low when considering MO conditions (Sossi et
114 al., 2020). Such a temperature avoids an unreasonable extrapolation of COHNS solubility laws
115 that have been defined at $<1300^{\circ}C$ (see Supplementary methods, Iacono-Marziano et al., 2012;
116 Bernadou et al., 2021). For the sake of completeness, tests up to $T=1920^{\circ}C$ (fig. S1) were
117 carried out. It shows a weak model sensitivity at this temperature. It would be good to carry out
118 accurate calibrations of speciation and solubility laws during melt - gas equilibria at $\sim 2000^{\circ}C$
119 in the future.

120 Pressure is defined by the weight of the atmosphere applied at the surface of the MO as
121 explained below. Finally, oxygen fugacity is treated as a variable input parameter.

122



123

124 *Figure 1. The early fate of C-H-O-N-S elements in a MO. Life-essential elements are processed*
 125 *through a three-body problem involving the core, the silicate MO and the atmosphere. The*
 126 *delivery of C-H-O-N-S elements is carried out via accretion of both chondritic material and*
 127 *differentiated small bodies. The incorporated C-H-O-N-S elements partition between the*
 128 *convective silicate MO, the sinking metal diapirs, and the rising fluids (bubbles). A variety of*
 129 *species can dissolve in the MO and the atmosphere. In addition, under the typically reducing*
 130 *conditions of the MO, graphite (G) and/or diamond (D) saturation in the MO can store a*
 131 *significant part of the carbon that is present in the system. These carbon phases respectively*
 132 *float to the surface and sink to a depth in the MO, thus indirectly impacting the MO outgassing*
 133 *dynamics. This study uses gas – silicate melt equilibria to predict the MO–atmosphere*
 134 *exchanges. The pressure at the MO – atmosphere interface is controlled by the weight of the*
 135 *atmosphere, which is determined by the mass of the MO atmosphere.*

136

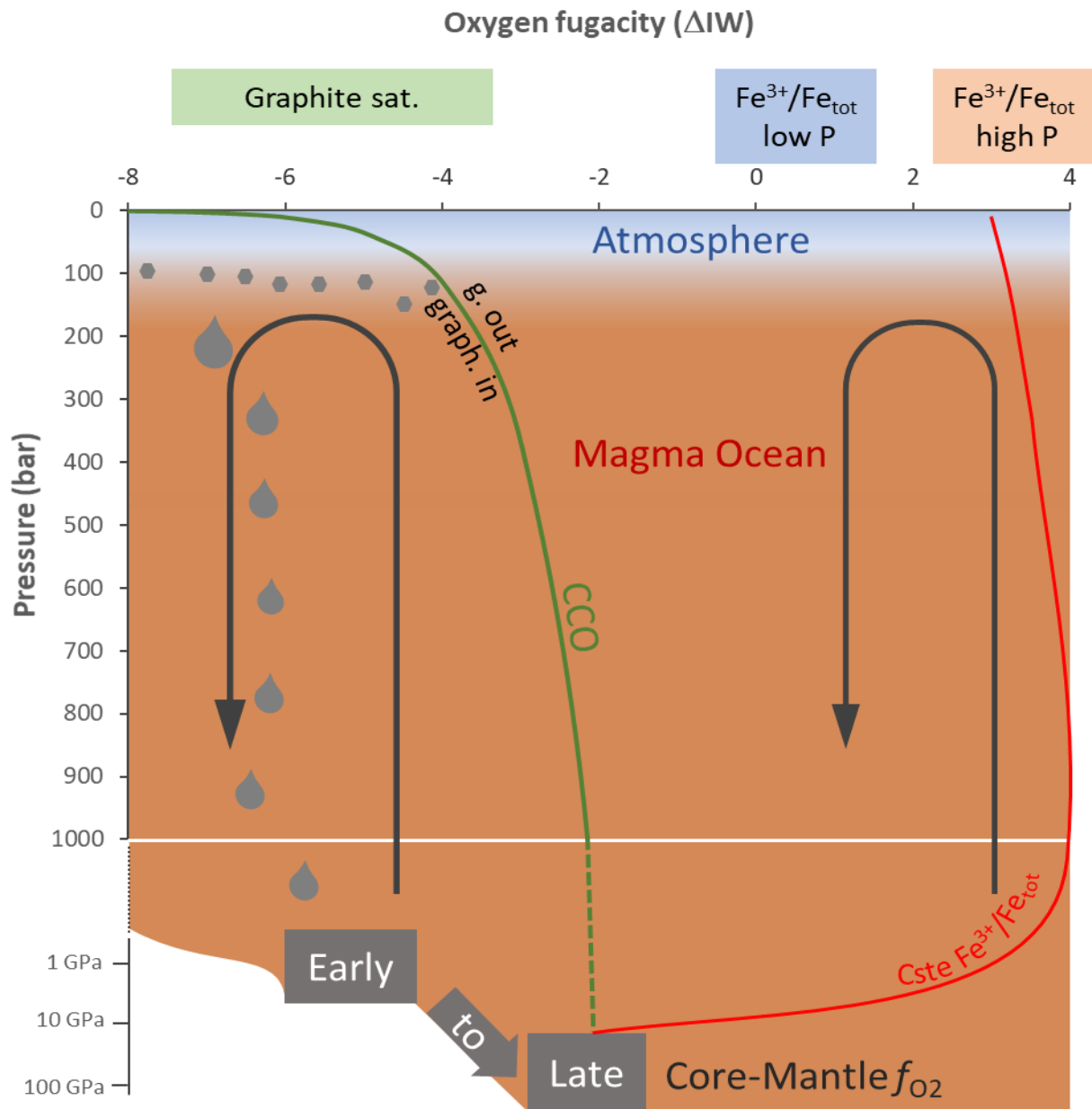
137 Mantle depletion in different siderophile elements suggests that strongly reducing conditions
 138 prevailed during the early differentiation of the Earth, i.e. IW-5, before they turned more
 139 oxidizing during the final stages of core formation, i.e. IW-2 (Wade and Wood, 2005; Rubie et
 140 al., 2015). This is deduced from metal-silicate equilibria taking place at the base of the MO
 141 (Fig.1). However, the actual redox state that prevailed at the MO surface, where degassing took

142 place (Fig. 1), is still under debate (eg. Pahlevan et al., 2019; Armstrong et al., 2019; Keppler
143 and Gobalek, 2019; Sossi et al., 2020):

144 (i) On the one hand, Armstrong et al. (2019) reports the enhanced stability of ferric iron
145 in silicate melts at elevated pressure (ie. >10 GPa). This implies that if metal –
146 silicate equilibrium buffers the f_{O_2} at great depth in the MO (>500 km), a surficial
147 MO with f_{O_2} conditions similar to that of the present-day mantle (i.e. close to the
148 FMQ buffer) must have prevailed. This suggests that the MO ferric iron content was
149 in the range 3-10% relative iron ($Fe^{3+}/Fe_{tot}=0.03-0.1$). Such an oxidized MO would
150 be broadly consistent with conditions required to prevent hydrogen escape
151 (Pahlevan et al., 2019).

152 (ii) On the other hand, Keppler and Gobalek (2019) suggest that graphite flotation may
153 have prevailed during most of the MO stage. If true, the f_{O_2} conditions prevailing
154 in the shallow mantle were not necessarily buffered by ferric-ferrous equilibria. The
155 combination of graphite buoyancy and the particular f_{O_2} -depth relationships of the
156 C-CO equilibria, may have imposed f_{O_2} conditions in the shallow MO as low as IW-
157 5 (Fig. 2., Shirayev and Gaillard, 2014). In fact, the prevailing f_{O_2} would be
158 inversely proportional to the pressure at the MO – atmosphere interface (Shirayev
159 and Gaillard, 2014). Whether such low f_{O_2} would cause massive H_2 escape remains
160 uncertain since the predicted timescales of both H-escape and cooling of a MO in
161 putative H_2 -rich atmosphere are of similar orders (ie. Katyal et al., 2020). These
162 rates should, in addition, be controlled by the ratio of H dissolved in the MO vs. H
163 outgassed into the atmosphere, which is not considered in models of atmospheric
164 escape.

165 (iii) In between, Sossi et al. (2020) use the present-day mantle ferric-ferrous iron fraction
166 in the solid upper mantle ($Fe^{3+}/Fe_{tot} \sim 0.04$) to propose an MO at an f_{O_2} of ca.
167 IW+0.5±0.7. This MO model does not assume any particular prevailing redox
168 mechanism, but takes the present-day mantle oxidation state as being representative
169 of the MO.



170

171 *Figure 2. The range of fO_2 conditions prevailing in the basal and surficial MO. The three top-*
 172 *boxes illustrate the three cases discussed in the text, from high to low fO_2 : Armstrong et al*
 173 *(2019) propose high fO_2 conditions in the surficial MO based on high pressure*
 174 *disproportionation reactions involving iron, Sossi et al (2020) propose a moderately reduced*
 175 *MO based on low pressure ferric-ferrous equilibria, and finally, assuming graphite floatation*
 176 *(Keppler and Gobalek, 2019), we consider the most reduced case when the CCO buffer prevails*
 177 *at low pressure. At low pressure, the CCO buffer can be as reduced as IW-5 (calculation done*
 178 *at 1750°C). One can nevertheless see that, at high pressure, the fO_2 of the CCO buffer can be*
 179 *reconciled with that of metal-silicate equilibration implying that graphite saturation imposes*
 180 *very low fO_2 at the surface of the MO, while the mantle body itself can remain more oxidized.*

181 These contrasting views require f_{O_2} to be considered as a variable in our model of MO
182 degassing. State of the art models for MOs simultaneously calculate crystallization and
183 degassing, but are limited to CO_2 - H_2O atmospheres (eg. Elkins-Tanton, 2012; Le Brun et al.,
184 2013; Hamano et al., 2013), implicitly restricting models to a 2-volatile component system and
185 assuming that the redox conditions in the surficial MO were similar to the present-day mantle.
186 Addressing the multi-component nature and the variation in oxidation state of species in the
187 CHONS system is an important step towards addressing the diversity of possible conditions
188 prevailing in early MOs. Here, we deploy a model where graphite and C-H-O-N-S species
189 dissolved in the MO depend on the partial pressure and mass of coexisting gas species,
190 including oxygen (O_2 , see section 3).

191

192 2.2. Volatile contents as a function of the MO size

193 The aim of this study is to quantify the volatile budgets formed during the last magma –
194 atmosphere equilibration stages. For this purpose, a summary of the mass and size of these
195 surficial and deep volatile reservoirs is available in Table 1, together with the four types of
196 simulated runs. An Earth-sized planet is considered, and results for variable MO masses (from
197 1/4 to the full bulk silicate Earth (BSE)) are shown. The surficial volatile inventory, (i.e.
198 atmosphere + ocean + crust, after Marty, 2012; Hirschmann, 2018) was systematically
199 considered in our calculations. We added to this surficial CHNS inventory the volatiles in
200 various mantle reservoirs: Case 1 - Only the volatiles of the depleted mantle (DM, supposedly
201 the most well-known) are considered; Case 2 - Volatiles of the bulk silicate mantle (BSM =
202 DM+EM) are considered, as used recently by Sossi et al., (2020). The integration of multiple
203 earlier MO stages, nebular capture processes, and impact degassing (Tucker and
204 Mukhopadhyay, 2014) are not addressed here.

205 Case 1 implicitly considers that the deep enriched mantle was never involved in the last MO
206 (Fig. 1). This assumption is consistent with the N, He and Ne isotopic signatures of plumes
207 compared to MOR basalts (Tucker and Mukhopadhyay, 2014; Labidi et al., 2020). The mass of
208 the DM is unspecified, but its CHNS concentrations as estimated in literature data (Table 1) are
209 used here. The mass of the MO is set to that of the depleted mantle and is assumed to vary from
210 10^{27} to $3 \cdot 10^{27}$ g (1/4 to 3/4 of the BSM) (Hofmann, 2003; Miller et al., 2019).

211 Case 2 relies on the fact that the bulk silicate Earth (BSE) was fully molten. The CHNS masses
212 of the surface + bulk silicate mantle (BSM) were thus processed through the MO and its

213 atmosphere. In this context, the MO has the size and mass of the BSE. Sossi et al (2020) recently
 214 simulated a similar case at $fO_2 \sim IW+0.5$. Because the amount of volatiles in the deep enriched
 215 mantle is much less well-known and debated, we considered both extreme options: a strongly
 216 (Marty, 2012) and a moderately enriched deep mantle (Hirschmann, 2018).

217

218 *Table 1: the distribution of CHNS volatiles in the different Earth reservoirs and a summary of*
 219 *the run conditions used in our simulations.*

Elements	Surficial reservoirs ¹ (g)	Bulk Silicate Mantle BSM ² (ppm)	Depleted Mantle DM ³ (ppm)
C after H 2018	1.06×10^{23}	110	37
after M 2020		211-646	
H after H 2018	1.7×10^{23}	33	15
after M 2012		100-300	
N	6.4×10^{21}	1.1	0.1-0.3
S	1.5×10^{22}	118-200	120-220

Runs with variable MO sizes

Cases	1. MO = DM + Surficial reservoirs ⁵			2. MO = BSE + Surf. Res. ⁴
MO size	¼ BSM	½ BSM	¾ BSM	BSM
C (ppm)	143	90	72	140-400
H (ppm)	191	102	73	79-333
N (ppm)	6.5	3.3	2.2	2.8
S (ppm)	126	123	120	119

220 Data after Hirschmann (2018) for the surficial reservoirs and the bulk silicate mantle (BSM). For C and H, the
 221 data of Marty al. (2020) have also been considered. Data after Marty et al. (2020) for N in the BSM and DM. The
 222 depleted mantle is after Saal et al. (2002) and Le Voyer et al (2017).

223 1: Mass of atmosphere + sediments + crust

224 2: Volatile contents in ppm-wt normalized to the bulk silicate Mantle (BSM = 4×10^{27} g)

225 3: Volatile contents in the depleted mantle

226 4: Here we considered that the entire CHNS content of Earth (surface + BSM) has been processed by an MO with
 227 the size of the bulk silicate Earth (BSM).

228 5: Here, we considered that the CHNS contents of the Earth's surface plus DM have been processed and the MO
 229 had the size of the DM.

230

231

232 **3.**

4. Mass balance and chemical equilibria calculations

The mass of the system (M^{tot}) is the sum of masses of both MO (M^{MO}) and its atmosphere (M^{MOATM}):

$$M^{tot} = M^{MO} + M^{MOATM} \quad (1)$$

The total mass fractions in C-H-N-S of the system were calculated as:

$$S_i^{tot} \times M^{tot} = S_i^M \times M^M + M_i^{ATM} = S_i^{MO} \times M^{MO} + S_i^{MOATM} \times M^{MOATM} \quad (2)$$

where i is the element, S_i^{tot} is the total mass fraction of the element i in the system, M^M represents the mass of the considered mantle (respectively BSM for case #2 and DM for case #1), S_i^M is the mass fraction of i in the considered mantle, and M_i^{ATM} the mass of element i in the present-day atmosphere+ocean+crust. S_i^{MO} and S_i^{MOATM} correspond to the mass fraction of the element i in the MO and its atmosphere, respectively.

In Case 1, we assumed $M^{MO} = M^{DM}$, implying that variable MO sizes change the total mass fractions of C-H-N-S of the system: the larger the DM (or MO) the larger the quantity of CHONS available to partition between the MO and its atmosphere (Table 1).

A gas-melt equilibrium is assumed to occur at the MO-atmosphere interface. This interface is characterized by a fixed temperature (1500°C, see figure S1 for a test on the effect of higher T), a varying oxygen fugacity (from IW-6 to IW+4) and a pressure (P^{MOATM}) given by:

$$P^{MOATM} = \frac{g \times m^{gas} \times M^{tot}}{4 \times \pi \times r^2} \quad (3)$$

Where g is the gravitational acceleration, 9.8 m.s^{-2} , m^{gas} is the mass fraction of gas in the system and r the radius of the planet. There is therefore no *a priori* assumption about the mass of the atmosphere formed, which is calculated from the abundances of volatile species in the system, the size of the planet and its MO, and g .

The relationship between the atmospheric pressure and the composition of the atmosphere is given as:

$$P^{atm} = \sum P_i = P_{CO_2} + P_{CO} + P_{CH_4} + P_{H_2O} + P_{H_2} + P_{N_2} + P_{H_2S} + P_{S_2} + P_{SO_2} \quad (4)$$

The relationship between gas partial pressure (P_i) and the content of dissolved species (S_i) in the melt is simplified to:

$$S_i = \sum a_i \times P_i^{b_i} \quad (5)$$

261 Where a and b are empirical constants specific to each species (see Supplementary methods).
262 These constants were taken from Iacono-Marziano et al., (2012a) for H₂O-CO₂, Gaillard et al.,
263 (2003) and Hirschmann et al., (2012) for H₂, Armstrong et al., (2015) for CO, Bernadou et al.,
264 (2021) for N₂, and primarily O'Neill and Mavrogenes (2002) for sulfur (see Supplementary
265 methods). Some approximation was necessary because none of these solubility laws were
266 calibrated for the composition and high-T of the MO (see Supplementary methods).

267 Finally, these solubility laws are coupled to a gas speciation model that has been presented in
268 previous work (see Iacono-Marziano et al., 2012b) and used to solve the equilibria involving
269 the O₂ component and the following redox couples C/CO, CO/CO₂, H₂/H₂O, H₂S/SO₂, CH₄/CO
270 (Holloway, 1987). The relationship between f_{O₂} and Fe³⁺/Fe²⁺ is taken from Kress and
271 Carmichael (1991) in order to mass balance O between gas and melt.

272 The MO degassing code is available at <http://calcul-isto.cnrs-orleans.fr/apps/planet/>.

273 **5. Results.**

274 5.1. The speciation – f_{O₂} relationships and its planetary significance

275 Here we provide a broad picture of the volatility and speciation of the C-O-H-N-S elements as
276 a function of oxygen fugacity. Our results provide the gas species' partial pressures in the
277 atmosphere (Fig. 3A), and the equilibrium speciation of the C-H-O-N-S dissolved in the MO
278 (Fig. 3B) at the MO-atmosphere interface. The CHNS abundances and the MO mass considered
279 correspond to case (1), MO= ½ BSM (Table 1). In the most reduced conditions, C (stable as
280 graphite), N and S are not volatile and remain in the MO, while H is efficiently degassed (as
281 H₂). In more detail, at f_{O₂} of about IW-6, the atmosphere is dominated by 40 bar H₂ with about
282 1 bar resulting from CH₄ outgassing (the CH₄ fraction should vary with C/H). In spite of the
283 high H volatility, 100-200 ppm H₂O remains dissolved in the MO together with ~30 ppm H₂.
284 This means that >50% of H remains dissolved in the MO even in the most reduced cases. As
285 f_{O₂} becomes oxidizing, i.e. >IW, N₂, CO₂, H₂O and SO₂ become increasingly dominant in the
286 system. In these conditions N₂ and CO₂ are highly volatile, while H₂O is still not due to its high
287 solubility in silicate melts. Sulfur only becomes volatile at the uppermost f_{O₂}, close to that of
288 the present-day mantle. Moreover, with increasing f_{O₂}, graphite and CH₄ are oxidized to CO,
289 resulting in an increase in atmospheric pressure until graphite is exhausted. A pressure of ~80-
290 90 bar is reached at f_{O₂} ~IW-3.5, when all graphite is oxidized (Fig.3). In a system containing
291 more C, this threshold f_{O₂} is raised, as discussed in section 4.2. Consequently, reduced bodies,
292 such as enstatite achondrite parent bodies or planet Mercury, must undergo surficial graphite

293 saturation as a rule. Given the low graphite density and the low C-solubility in silicate melts,
294 this would explain the graphite-rich rocks observed by the Messenger mission to Mercury's
295 surface (Charlier and Namur, 2019; Keppler and Gobalek, 2019). In contrast, under oxidizing
296 MO conditions, i.e. > IW-2, all H remains dissolved as H₂O, while C is significantly outgassed.
297 This has fundamental implications for the capacity of this MO to accrete under wet conditions:
298 reduced, enstatite-like MO had ca. 30-40% of accreted H as H₂ in the vapour state, implying a
299 greater exposure to H-loss to space (eg. Pahlevan et al., 2020; Katyal et al., 2020; H-escape or
300 atmospheric blow), while more oxidized MOs were able to prevent their hydrogen inventory
301 from escape, since >99% of their H was dissolved in the MO. In summary, a reduced MO can
302 largely retain N, C, and S, as these elements are not efficiently degassed at low oxygen fugacity.
303 An oxidized MO could evolve wet, while it must outgas most of its C and N. Sulfur outgassing
304 is not expected unless under oxidized f_{O2} conditions similar to the present-day mantle.

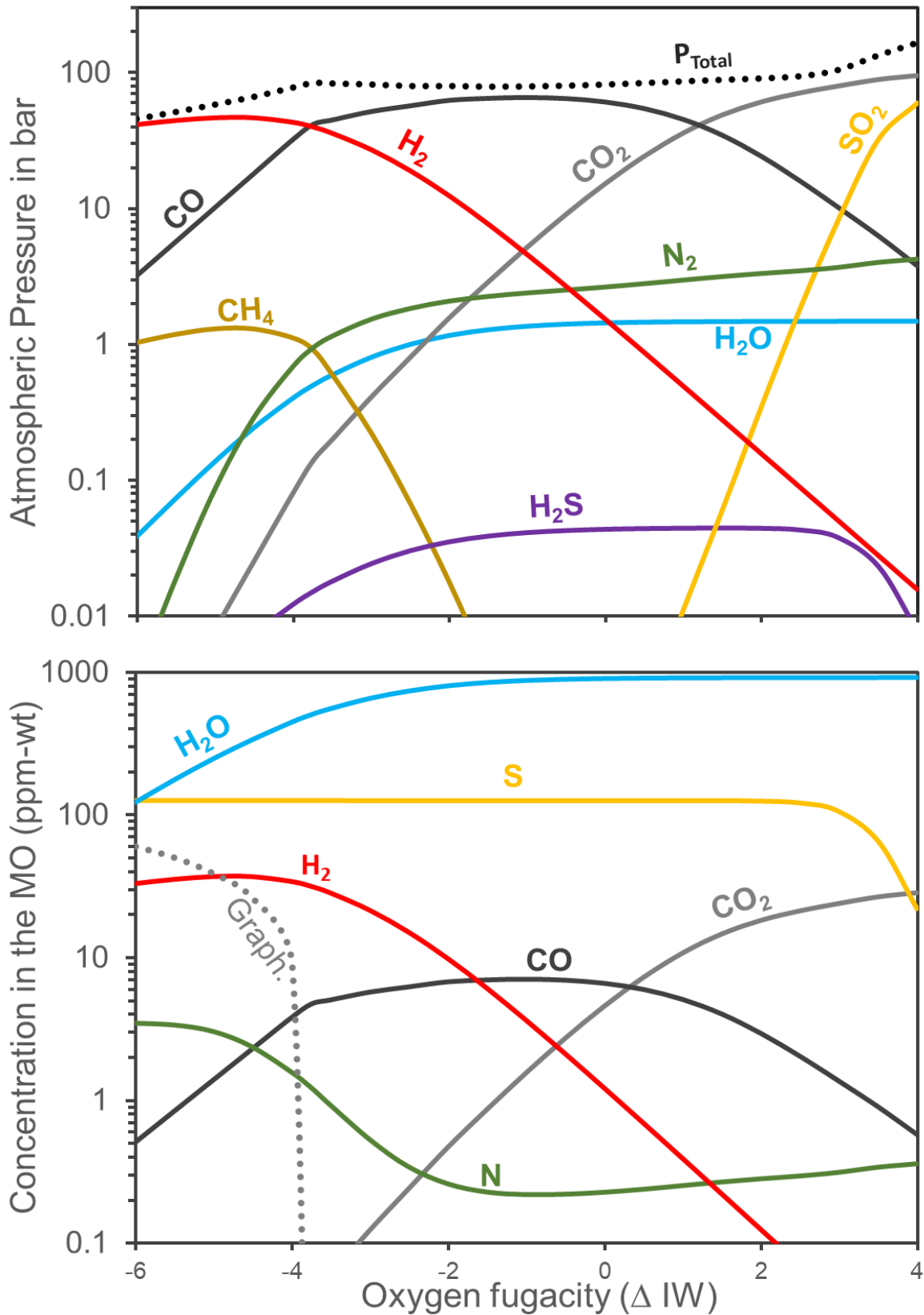
305 5.2. Mass balancing the MO – Atmosphere CHONS distribution

306 On an element-by-element basis, we quantitatively discuss the MO - atmosphere mass transfers
307 caused by the speciation relationships shown in figure 3. We first discuss Case 1 (MO = DM +
308 atmosphere), and then Case 2 (MO = BSE).

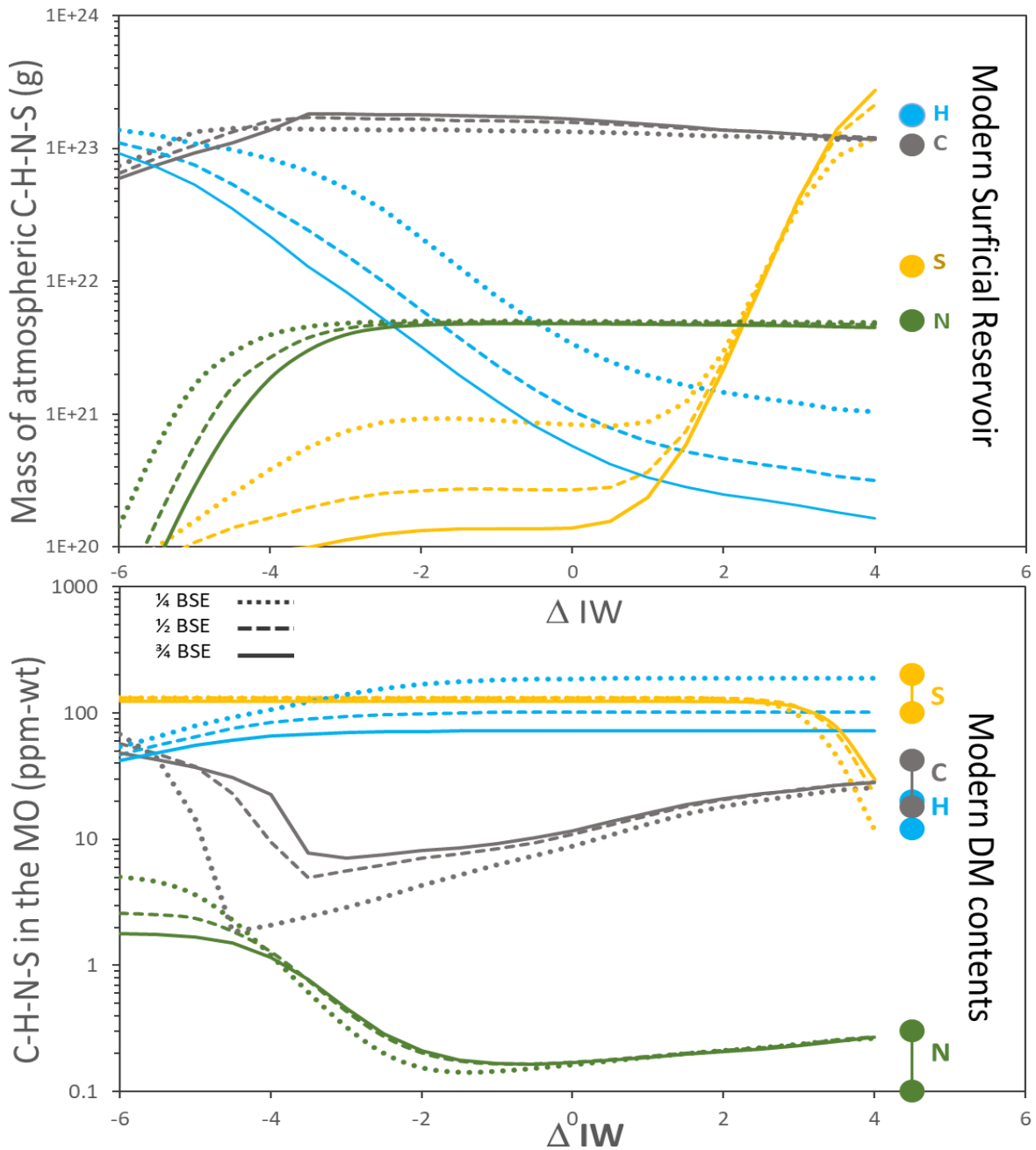
309 Case 1: Melting the Depleted Mantle (Table 1)

310 Figure 4 illustrates Case 1, where the MO is the same size as the depleted mantle. In this figure,
311 the masses of outgassed and preserved CHONS remaining dissolved in the MO are shown for
312 variable f_{O2} conditions and variable MO sizes.

313



314
 315 *Figure 3. C-H-O-N-S speciation in the gas and the melt as a function of fO_2 during the MO –*
 316 *atmosphere equilibration (Case 1, $\frac{1}{2}$ BSM in Table 1) at 1500°C. A: Partial atmospheric*
 317 *pressures and speciation of the C-H-O-N-S elements in the basal atmosphere. B: Concentration*
 318 *in ppm-wt of the C-H-O-N-S species dissolved in the shallow MO.*



319

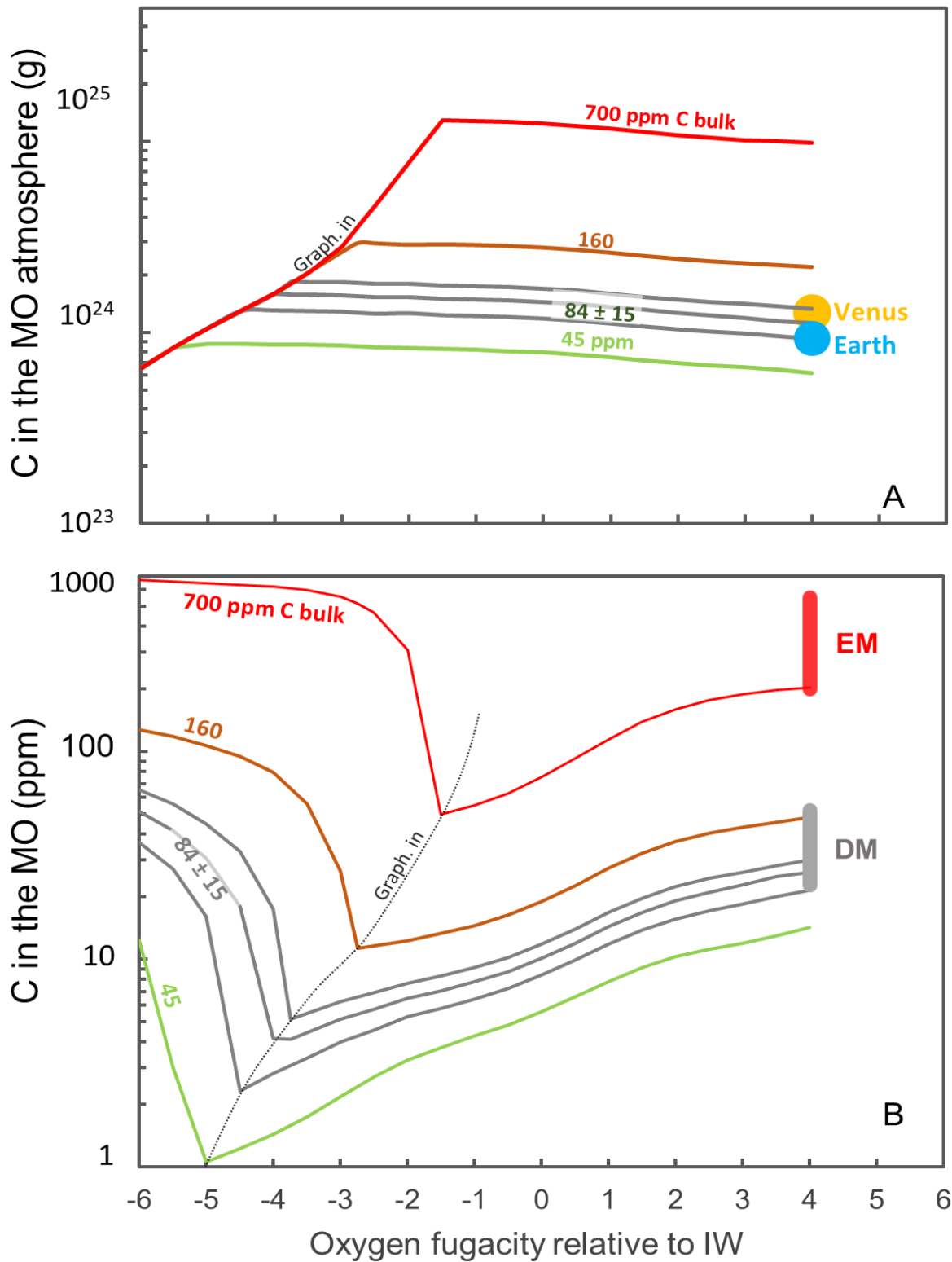
320 *Figure 4. Mass distribution of the C-H-O-N-S elements as a function of fO_2 during the MO –*
 321 *atmosphere equilibration cases 1, DM = MO. Top: Calculated masses of C-H-O-N-S outgassed*
 322 *in the MO atmosphere and comparison with the present-day surficial mass of C-H-N-S on*
 323 *Earth. Bottom: Calculated concentrations of C-H-N-S (ppm-wt) in the shallow MO and*
 324 *comparison with the present day CHNS content in the depleted mantle (DM).*

325 The present-day mass of carbon in the Earth's surficial reservoir is 1.06×10^{23} g (Hirschmann,
 326 2018). Figure 4 indicates that the calculated mass of C outgassed from the MO varies slightly
 327 with fO_2 but remains in the range $6.4 \times 10^{22} - 1.7 \times 10^{23}$ g. It should be noted that the outgassed
 328 mass of C is insensitive to the mass of the MO. This calculated degassed C mass brackets,
 329 within a 50% relative variation, the present-day mass of carbon in the Earth's surficial reservoir.

330 The carbon content in the depleted mantle is highly variable (19-1,200 ppm), but recent
331 estimates give an average value of $37 \pm 12(1\sigma)$ ppm-wt (Le Voyer et al., 2017; Hirschmann,
332 2018). The calculated C content in the equilibrium MO varies from 2 to 70 ppm-wt depending
333 on fO_2 and the size of the MO. At low fO_2 ($<IW-3$), graphite saturation implies that most C in
334 the MO is present as graphite. At higher fO_2 , C dissolves in the silicate melt as CO ($fO_2 < IW$)
335 and as CO_3^{2-} (at $fO_2 > IW+1$) (see also Fig.3). The C-content of the MO perfectly matches the C
336 content of the depleted mantle if degassing occurs at $fO_2 > IW$ or at $<IW-4$. If degassing of the
337 MO occurs at intermediate fO_2 ($IW-4 / IW$), the C-content of the MO is significantly lower (2-
338 15 ppm C) than the average C-content of the depleted mantle (37 ± 12 ppm C). When the large
339 uncertainty in carbon content of the depleted mantle is propagated through the calculation, a
340 moderate impact on the mass of outgassed C and on the C-content of the MO is observed (Fig.
341 5). Additional sensitivity tests are shown in Fig. 5A, using lower and higher bulk C contents
342 (45-700 ppm C in the bulk system). All calculations converge at low fO_2 , where graphite
343 saturation occurs but the domain of graphite saturation changes with the bulk C content (the
344 MO is systematically graphite-saturated in the C-rich case if $fO_2 < IW-1$). In this C-rich system,
345 the C-content of the MO can become as high as that of the enriched mantle (in both reduced
346 and oxidized cases). The mass of outgassed C in such a case would be around 10^{25} g, (i.e. 10
347 times greater than the present-day surficial mass of C).

348 The present-day mass of nitrogen in the Earth's exosphere is 5×10^{21} g. The calculated mass of
349 nitrogen outgassed by the MO is in the range of 6.3×10^{19} to 6.5×10^{21} g (for a total N mass of
350 7×10^{21} g for Case 1, ie. DM size= $\frac{1}{2}$ BSM, Table 1). The lowest value was calculated for the
351 lowermost fO_2 (Fig.4A). This indicates that MO outgassing at $fO_2 \geq IW-3$ would yield an
352 outgassed mass of N that matches the present-day Earth's surficial mass of N perfectly. The
353 calculated N-content dissolved in the MO (Fig. 4B) varies with fO_2 from values greater than 1
354 ppm at $<IW-4$, to within the range 0.2-0.3 ppm N at $fO_2 > IW-2$. The N content of the DM is
355 currently estimated to lie within the range 0.1-0.3 ppm (Marty, 2020), which is similar to our
356 prediction for the N-content in the MO at $>IW-2$. To summarise, we conclude that the present-
357 day distribution of carbon and nitrogen between the Earth's surface and depleted mantle could
358 have been attained by outgassing of the MO formed by the Moon-forming impact, if the fO_2 of
359 the MO-atmosphere interface was $\geq IW-3$. This could be coincidental, but the similarities are
360 striking.

361



362
 363 *Figure 5. Sensitivity tests on the effect of bulk C-content on the partitioning of carbon between*
 364 *the MO and its atmosphere. The C-content of the depleted (DM) and the enriched mantle (EM)*
 365 *is shown for comparison in the bottom diagram while the C-mass of the Earth's and Venus's*
 366 *atmosphere are shown in the top diagram. The domain of graphite saturation is marked by the*
 367 *dashed line.*

368 The present-day mass of hydrogen at the Earth's surface is 1.8×10^{23} g. At IW-6, the mass of
369 outgassed H is $1.1 \pm 0.2 \times 10^{23}$ g, which makes up 60% of the present-day surficial mass of H
370 (Fig. 4). Under such conditions, the H content of the MO is ca. 50 ppm (Fig. 3), which is
371 equivalent to ~ 400 ppm H_2O . Massive degassing of hydrogen therefore requires strongly
372 reducing conditions at the surface of the MO. In contrast, MO degassing at (even moderately)
373 oxidizing conditions prevents the outgassing of hydrogen. Notably, degassing at the $f\text{O}_2$ of the
374 present-day Earth's mantle would produce a dry atmosphere, containing 500 times less H than
375 today. Interestingly, contrary to C and N, the H balance of outgassing/ingassing is affected by
376 the size of the MO: smaller MOs tend to outgas more H (Fig. 4). This is because the atmospheric
377 pressure is lower for small MOs. To summarize, apart from in strongly reduced conditions,
378 hydrogen is hardly outgassed.

379 The present-day mass of sulfur at the Earth's surface is 1.2×10^{22} g (Canfield, 2004). The mass
380 of outgassed S from the MO is strongly $f\text{O}_2$ dependant and remains well below 10^{22} g for $f\text{O}_2$
381 $< \text{IW}+2$, whereas at $f\text{O}_2$ of ca. $\text{IW}+2.5$, the amount of S outgassed by the MO would perfectly
382 match the present-day surficial S budget (Fig.4). On the one hand, a negligible fraction of S is
383 degassed if $f\text{O}_2 < \text{IW}+2$. On the other hand, at a surficial MO $f\text{O}_2$ similar to that of the present-
384 day mantle (Armstrong et al., 2019), the outgassed mass of S would exceed the modern Earth's
385 surficial sulfur content by an order of magnitude, leaving behind a sulfur-poor mantle.

386 Thus it can be seen that strongly atmophile elements such as C and N are unaffected by the size
387 of the MO, whereas moderately atmophile elements, such as H and S, are more significantly
388 affected. However, the most important parameter controlling CHNS outgassing remains the
389 oxygen fugacity of the shallow magma ocean.

390

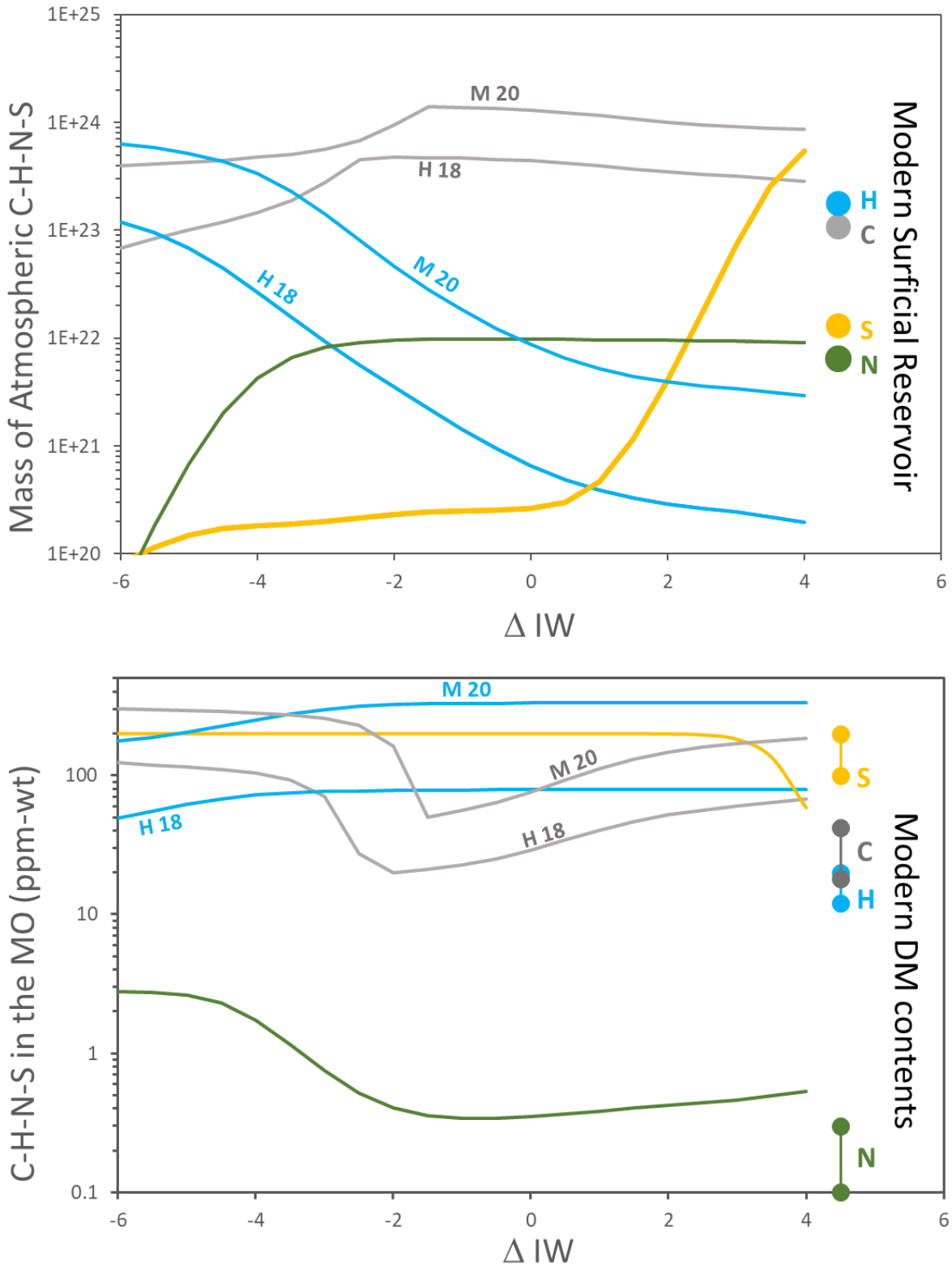
391 Case 2: Melting the Bulk Silicate Earth (Table 1)

392 Figure 6 illustrates calculated masses of outgassed CHONS for the case of a fully molten silicate
393 Earth, together with the CHNS content of the MO in equilibrium with this atmosphere. For
394 most $f\text{O}_2$ conditions, and for the two bulk C-contents considered (Hirschmann 2018 and Marty
395 et al., 2020, respectively), the outgassed masses of C significantly exceed present-day Earth's
396 surficial reservoir (by a factor of 5 to 10). The C-content in the MO lies within the range 20-
397 300 ppm C, depending on the $f\text{O}_2$ and the bulk C-content. Such a concentration range is
398 intermediate between the C-content of the depleted mantle and that of the deep enriched mantle.
399 We therefore conclude here that a MO of the size of the BSE would produce an atmosphere and

400 a MO significantly exceeding the present-day C reservoirs of the Earth's surface and the
401 depleted mantle.

402 The mass of outgassed hydrogen shows similar trends to Case 1, in that it decreases with
403 increasing fO_2 . Yet due to the much higher H content of the BSE compared to that of the DM
404 (Hirschmann 2018 vs. Saal et al., 2003), we predict a much greater mass of outgassed H and a
405 higher H content in the MO than for Case 1. The H content in the MO lies within the range of
406 50 to 330 ppm (ie. 450 – 3000 ppm H_2O), which largely exceeds the H content of the depleted
407 mantle. The mass of outgassed H ranges from 7×10^{23} to 2×10^{20} g, which implies that a mass
408 similar to the present-day Earth's surface (Mass H = 1.8×10^{23} g) may have been outgassed
409 during the MO stage of Case 2.

410 The results for S and N are marginally different from those discussed in Case 1. It is of particular
411 note, however, that the N contents in the MO always exceed the N content in the DM, whereas
412 the mass of outgassed N approaches the present-day N surficial mass, though the agreement is
413 not as striking as in Case 1.



414

415 *Figure 6. Mass distribution of the C-H-O-N-S elements as a function of fO_2 during the MO –*
 416 *atmosphere equilibration Case 2, BSE = MO. Top: Calculated masses of C-H-O-N-S outgassed*
 417 *into the MO atmosphere and comparison with the present-day surficial mass of C-H-N-S on*
 418 *Earth. Bottom: Calculated concentration in C-H-N-S (ppm-wt) in the shallow MO and*
 419 *comparison with the present day CHNS content in the depleted mantle (DM). H 18 refers to*
 420 *Hirschmann (2018) and M 20 refers to Marty et al (2020).*

421 6. Discussion.

422 6.1. Melting the BSE.

423 Case 2 involves the partitioning of COHNS elements between the MO and its atmosphere, and
424 assumes that the BSE was once fully molten. We found the abundance of all elements, in both
425 the atmosphere and MO, exceeded that of the present-day surficial and DM reservoirs. Though
426 this might be interpreted as a circular reasoning (because the way the BSE C-H-N-content has
427 been estimated implies the existence of deep reservoirs, see Hirschmann, 2018 and Marty et al.,
428 2020), this experimental scenario suggests that a hidden (deep) sink must have formed either
429 during the solidification of the MO or during the subsequent 4.5 Gyrs of mass transfer governed
430 by mantle geodynamics (eg. Ballmer et al., 2017). This deep reservoir is also required by
431 independent CHNS-noble gas isotopic constraints (eg. Tucker and Mukhopdhay, 2014; Labidi
432 et al., 2020). Given that our model does not address mass transfer processes conducive to deep
433 CHNS reservoirs, there is no purpose in looking at Case 2 in more detail. We simply state that
434 our calculations define the starting distribution of CHONS elements prior to MO solidification
435 (Fig.6). These starting conditions could then be used in geodynamical models addressing
436 volatile mass transfer during MO solidification and subsequent geodynamic processes.

437 Recently, Sossi et al. (2020) conducted similar calculations, and estimated the atmospheric
438 pressure resulting from vaporisation of the BSE volatiles at fO_2 close to IW. Case 2, using the
439 BSE values of Hirschmann (2018), at fO_2 of IW, is similar to the case studied by Sossi et al.
440 (2020). Accordingly, the estimations of atmospheric pressure only slightly differ between the
441 two studies ($P^{atm} = 220$ bar in the present study compared to 190 bar in Sossi et al., 2020). The
442 small difference might be related to the use of different solubility laws for N_2 and CO_2 and/or
443 that H_2 and CO solubility laws are neglected in Sossi et al. (2020).

444 6.2. Does the depleted mantle delineate the MO?

445 The atmosphere / MO distributions of carbon and nitrogen perfectly match the present-day
446 surficial / DM ones if $fO_2 > IW-2$. This may be purely coincidental, yet the fingerprint of the
447 MO outgassing stage for the most volatile elements is striking. If true, the C-N mantle and
448 surficial reservoirs created following MO degassing seem to have been only marginally affected
449 by 4.5 Gyrs of mantle geodynamics. The present-day outgassing rates for nitrogen are very low
450 and would require longer than the Earth's lifetime to build the surficial N reservoir
451 (Hirschmann, 2018). This corroborates our finding that the N surficial budget was set by the
452 primordial N outgassing. Present-day outgassing rates for carbon, on the other hand, are much

453 greater, enabling the surficial reservoir to be refilled within the time-scale of the Earth's lifetime
454 (Hirschmann, 2018). We propose that a steady state balance between ingassing and outgassing
455 may have operated over geological eons. The C content of the DM mantle would then be
456 directly inherited from the C content of the degassed MO as defined in Figure 4, which has
457 been (and continues to be) progressively enriched by subducted C-rich lithospheric slabs. The
458 C content of the DM must therefore have increased over time. In this context, MORB samples
459 these heterogeneities but remains broadly dominated by strongly C-depleted lithology (Le
460 Voyer et al., 2017).

461

462 6.3. Earth—Venus MO atmospheres

463 As also noted by Sossi et al. (2020), our results indicate that atmospheres calculated under
464 moderately reducing conditions (i.e. $IW-2 < fO_2 < IW+2$) broadly share many features with the
465 modern atmosphere of Venus (though the bulk volatile budget is based on the Earth's reservoir).
466 Calculated atmospheres are dry, with CO or CO₂ pressure of about 80-220 bar, N₂ pressure of
467 about 2-4 bar, and only small amounts of sulfur (Fig. 3). In particular, degassing of Earth's MO
468 in Case 1 (melting of the DM) produces an atmosphere that perfectly matches the Venusian one
469 (see Table 1 and Fig. 3), which differs from the conclusions of Sossi et al. (2020) in which
470 melting of the BSE is used. We recall here the striking Earth-Venus similarities in terms of
471 surficial reservoirs. The mass of carbon in Venus's atmosphere is 1.25×10^{23} g and the Earth's
472 surface contains 1.03×10^{23} g C. The mass of nitrogen in Venus's atmosphere is 4.8×10^{21} g and
473 Earth's surficial mass of nitrogen is estimated to be 5×10^{21} g. This corroborates the multiple
474 similarities already noted elsewhere (Kasting et al., 1988; Lecuyer et al., 2000; Wordsworth
475 2016; Gilman et al. 2020; Sossi et al., 2020) between planet Earth and Venus. It may also
476 indicate that, for both planets, the carbon and nitrogen surficial inventories were likely formed
477 during the MO stage. However, the present-day forms of surficial C and N differ on the two
478 planets. This is because a range of biotic and abiotic mechanisms have fixed C and N in the
479 Earth's soil, sediments and crust, but since these mechanisms did not operate on Venus
480 (Wordsworth, 2016) these elements remained in Venus's atmosphere. This is likely related to
481 the presence of liquid water on the Earth's surface and its absence on Venus.

482 The divergence in composition of the atmospheres of Venus and Earth has long been discussed
483 in terms of distance to the Sun, which has major effects on atmospheric temperatures and
484 hydrogen escape processes (Kasting, 1988; Hamano et al., 2013; Gillmann et al., 2020). Here,
485 our redox analysis shows that degassing under oxidized conditions (ie. $fO_2 > IW-2$) prevents H

486 emission into the atmosphere. The atmosphere is therefore dominated by C and N species with
487 total atmospheric pressures of ca. 80-200 bar (according to the MO sizes and the volatile
488 contents investigated in this study). This may define a Venusian scenario, in which the
489 atmosphere was dry from the beginning (ie. it contains ca. 1% H₂O, Figure 2, see also Sossi et
490 al., 2020). Conversely, degassing under reduced conditions produces an atmosphere that is
491 significantly enriched in hydrogen. Such reduced degassing conditions are possible if the
492 surface of the MO is graphite-saturated because of floatation processes (ie. Keppler and
493 Gobalek, 2019). However, this does not mean that the whole MO is subject to graphite-
494 saturation or the same degree of reducing conditions. For example, one may consider a MO that
495 is overall at IW (eg. Sossi et al., 2020) that is C-saturated at the surface because of graphite
496 floatation (Keppler and Gobalek, 2019). As pressure decreases, graphite-gas equilibria can
497 buffer fO₂ as low as IW-5 at P<10 bar, whereas the same system at P> 1000 bar would buffer
498 fO₂ ~ IW-2 (Fig. 2, see Iacono-Marziano et al., 2012). This graphite-saturated case may define
499 a terrestrial scenario, in which the atmosphere was H-rich from the beginning, ie. containing
500 half to 1/10th of the present-day amount of the Earth's surficial water (Fig. 4), which in turn
501 implies that a significant amount of H remains in the MO. The transition from a strongly
502 reducing to a moderately oxidizing situation may be viewed in the framework of hydrogen
503 escape processes (Kasting, 1988; Hamano et al., 2013; Gillmann et al., 2020). In this context,
504 a more efficient H-loss on Venus as compared to Earth must have caused a shift toward more
505 oxidizing conditions (ie. H₂-loss). Such loss must also consider that a large fraction of the H
506 remains dissolved in the MO, which is not taken into account in such models (eg. Katyal et al.,
507 2020). In a scenario where Earth and Venus have received similar quantities of CHONS during
508 accretion (eg. Gillman et al., 2020 and ref. therein), an atmospheric divergence during the MO
509 stage is possible. This would be due to enhanced H-loss on Venus, which increased fO₂ and H
510 solubility in the MO. In other words, both H-loss and H-incorporation in the MO may have
511 contributed to the drying of the Venusian atmosphere. It seems unlikely that post-MO-stage
512 degassing would alter this conclusion, as detailed in section 5.5.

513

514 6.4. Cooling, solidification and degassing of the MO

515 In the absence of experimental data, the effect of temperature remains difficult to define on the
516 solubility of volatiles at T>1300°C. In figure S1, we illustrate a moderate effect calculated over
517 the T range 1500-2000°C. Graphite saturation is, however, significantly enhanced as T

518 decreases. This implies high atmospheric pressures at high T, even for very low fO_2 conditions,
519 in contrast to the data shown in Figure 4. Maintaining high atmospheric pressure makes
520 hydrogen less volatile. However, we must keep in mind that there is no constraint on the effect
521 of T on H_2 and H_2O solubility in mafic compositions.

522 The question of the extent of CHONS outgassing or ingassing during solidification of the MO
523 is beyond the scope of this study. Nevertheless, some aspects must be discussed here because
524 the incompatible nature of hydrogen might have enhanced its degassing during MO
525 crystallization. Figure S2 shows the calculation of an upper bound assuming perfect crystal
526 settling and incompatible behaviour for C-H-N during the solidification of the MO. Following
527 90% crystallisation in an extreme configuration such as this, the H-content in the residual melt
528 can reach 0.5-0.7wt%, but H outgassing would remain moderate. Furthermore, Hier-Majumder
529 and Hirschmann (2017) calculated that the entrapment of water-rich interstitial melt at the MO
530 crystallization front could limit the extent of H-enrichment in the residual liquid of a solidifying
531 MO. It therefore appears that the process of MO solidification itself would not necessarily
532 enhance hydrogen outgassing. Significant hydrogen degassing at the MO stage seemingly
533 requires strongly reduced conditions and the entrapment of a major part of the primordial water
534 in the deep mantle is very likely. This implies that early hydrated komatiites (3.3 Ga, Sobolev
535 et al., 2019) may not require early subduction processes.

536

537 6.5. Post-MO outgassing

538 Once the MO solidified, mantle convection and associated volcanism may have contributed to
539 the degassing of the planetary interior. Gaillard and Scaillet (2014) have shown that the
540 degassing of magmatic water is limited by a dense atmosphere such as that formed by the MO.
541 If water remained trapped in the mantle after the magma ocean stage, the basalt produced by
542 melting of post-magma-ocean mantle containing 300-600 ppm (Table 1), could emit a gas phase
543 containing ca. 10% H_2O at ca. 100 bar. In contrast, in a 1-bar atmosphere, the gas phase would
544 be dominated by H_2O . Carbonate precipitation may reduce the amount of atmospheric CO_2 and
545 decrease the atmospheric pressure, but this would require the presence of oceans (Sleep, 2011)
546 and therefore the outgassing of H at an earlier stage. This should be addressed by specific
547 studies in the future, but it appears that if hydrogen was not degassed from the MO, the
548 atmosphere would have likely remained dry.

549 Finally, in most cases discussed here, sulfur is not degassed from the MO. Only an unexpectedly
550 highly oxidizing MO could significantly outgas sulfur. Here again, MO solidification would
551 not significantly increase the mass of degassed sulfur because sulfur is strongly compatible in
552 sulfides and the high density of molten sulfides would cause deep S sequestration. Sulfur
553 outgassing associated to post-MO volcanism (Gaillard et al., 2011) must thus be considered,
554 although a quantitative assessment of the amount of sulfur outgassed during the Archaean is
555 beyond the scope of this paper.

556 7. Conclusions

557 The influence of oxygen fugacity on the degassing of the MO is quantified in this study.
558 Varying the fO_2 , MO size and volatile content results in a great diversity of primary atmosphere
559 composition. Two end-member cases can be distinguished: oxidizing and reduced. In the
560 oxidizing case, C-N-S are outgassed from the MO, leaving an S-poor mantle, whereas H is not
561 volatile and is likely efficiently entrapped in the mantle during MO solidification. In the reduced
562 case, C-H±N are outgassed from the MO. We suggest that the deep enriched mantle (with
563 primordial He and Ne) was probably not involved in the last MO stage and represents a
564 fossilized pre-moon forming impact (Fig. 1). The last MO degassing most likely defined the C-
565 N distributions between the Earth's surface and the depleted mantle. Moderate post MO
566 recycling of surficial C via subduction of oceanic lithosphere may explain the heterogeneities
567 in C contents (and other trace and isotope elements) of the depleted mantle.

568 The surficial masses of C and N are identical on Venus and Earth and were most likely formed
569 during the MO degassing. The Earth-Venus divergence, with Venus's surface evolving to be
570 dry, may be linked to H-loss during the MO stage, which counterintuitively implies that the
571 interior of Venus could be wetter than its counterpart, the Earth. Finally, the geological
572 processes that are taken to define a habitable world must include the MO's central role in
573 generating the initial range of planetary environments.

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700

701 **Supplementary Methods.**

702 The relationship between gas partial pressure (P_i) and the content of the gas (S_i) in the melt is
703 simplified as:

$$704 \quad S_i = \sum a_i \times P_i^{b_i} \quad (6)$$

705 Where a and b are empirical constants specific to each species that the I component could form
706 in the silicate. H_2O solubility is independent of the melt composition, while CO_2 solubility
707 depends merely on the degree of polymerisation of the melt (Iacono-Marziano et al., 2012a).
708 Since no experimental data defines the CO_2 solubility in molten peridotite, we used the
709 estimation for komatiites of Iacono-Marziano et al. (2012a):

$$710 \quad S_{CO_2} = 1.1 \pm 0.15 \times P_{CO_2} \quad (7)$$

711 For H_2 solubility, we used a combination of low pressure (Gaillard et al., 2003) and high
712 pressure (Hirschmann et al., 2012) data. This yielded the following relationships with a 20%
713 accuracy on the calculated S_{H_2} :

$$714 \quad S_{H_2} = \exp\left(-\left(1.51 + P_{tot} \times \frac{9.43}{RT}\right)\right) \times P_{H_2} \quad (8)$$

715 The CO solubility law was taken from Armstrong et al. (2015) that we verified to be consistent
716 with recent data (Yoshioka et al. 2019). The solubility law of Bernadou et al. (2020) was used
717 for nitrogen.

$$718 \quad [S_N] = K_1 \times P_{N_2} + f_{O_2}^{-3/4} \times K_2 \times P_{N_2}^{1/2} \quad (9)$$

719 Where K_1 and K_2 are two thermodynamic constants fitted to account for the P and T
720 dependences of N solubility. These constants have long been established (Libourel et al., 2004)
721 at 1400°C, 1 bar in the C-O-N system, and Bernadou et al. have shown that eq. (8) remains
722 almost unchanged from 1 atm to 3000 bar in the C-H-O-N system.

723 For sulfur, we used the following relationship:

$$724 \quad \ln(S_S) = 13.8426 - \frac{26.476 \times 1000}{T_k} + 0.124 \times S_{FeO} + 0.5 \times \ln\left(\frac{f_{S_2}}{f_{O_2}}\right) \quad (10)$$

725 S_{FeO} stands for the concentration of iron (as FeO wt%) in the silicate melt. This equation is a
726 rearrangement of the model used in O'Neill and Mavrogenes (2002) that has been refitted for
727 the FeO content in the melt in wt% and the temperature in K. To calibrate equation (10), we
728 used 369 experimental data from 9 papers (Haughton et al., 1974; Buchanan and Nolan, 1979;

729 Danckwerth et al., 1979; Gaetani and Grove, 1997; O'Neill and Mavrogenes, 2002; Ripley et
730 al., 2002; Bockrath et al., 2004; Zajacz et al., 2013; Mungall and Brenan, 2014; Nash et al.,
731 2019), linking sulfur content in silicate melts equilibrated with gas at 1 atm having known
732 values of fO_2 and fS_2 , in the fO_2 range IW-1 to FMQ+0.1.

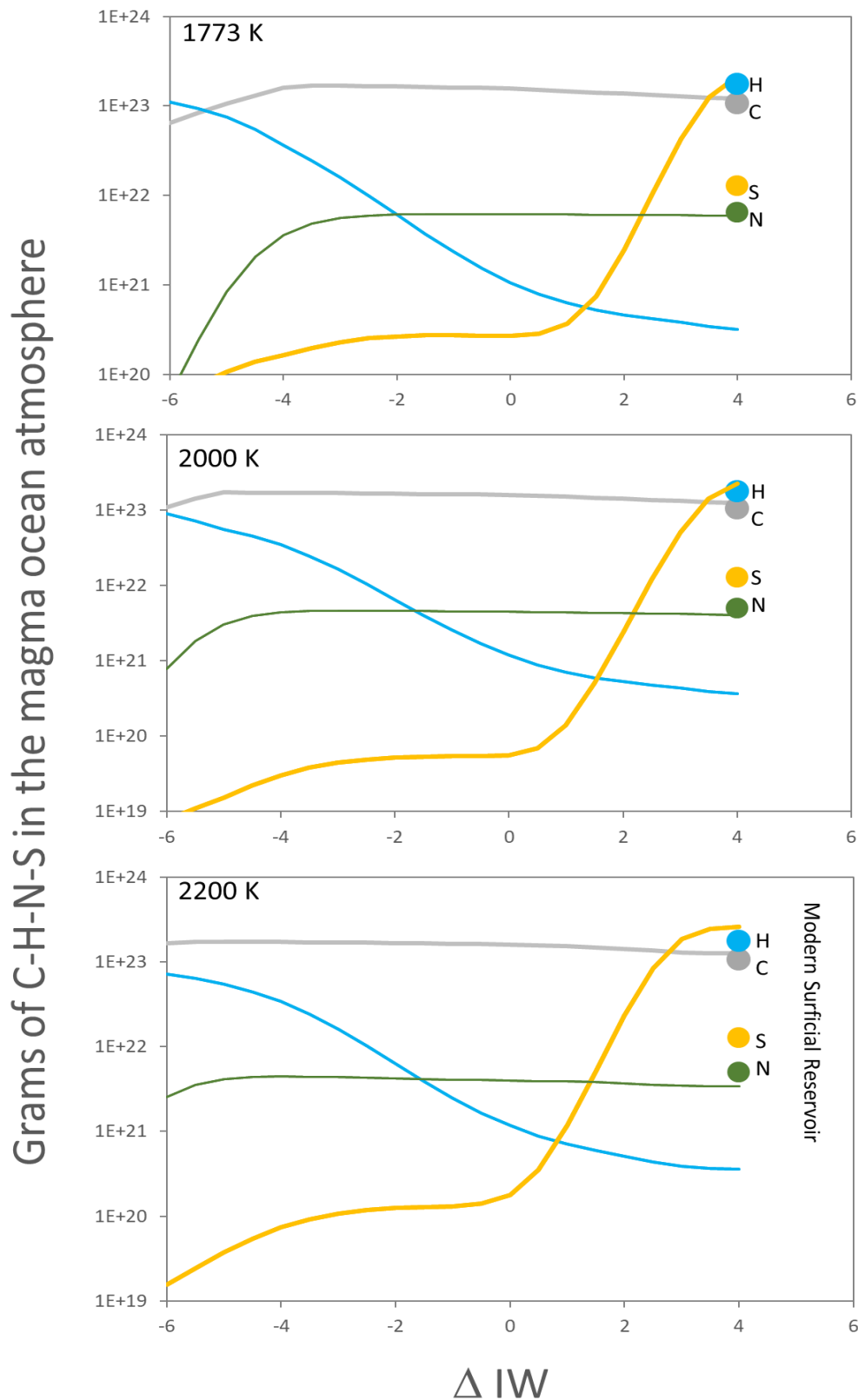
733 It must be clarified that none of these solubility laws has been directly calibrated for a peridotite
734 melt composition and at MO temperatures because of technical challenges for quenching such
735 compositions. This gives room for future improvement of the model and also introduces some
736 unknowns. We consider that the solubility laws for each species (eq. 5, 7-9) may be affected by
737 50% uncertainties due to this bias. This directly translates into 10-50% uncertainties in the
738 calculated concentrations of species in the melt and gas depending on the species considered,
739 which does not affect our conclusion given that solubility laws differ by orders of magnitude.

740 We only considered the stable species at the pressure and temperature prevailing at the MO-
741 atmosphere interface. In the MO atmosphere, however, one expects a thermal gradient from the
742 hot base to the cold upper regions. This must cause a change in the gas speciation with CH_4 and
743 H_2O dominating in the upper (colder) atmosphere while H_2 - CO are stable at the (hot) base;
744 similarly, NH_3 , which is negligible (<0.1% of total N) at high temperature, would be stabilized
745 in the upper (cold) atmosphere. Finally, a variety of CHONS speciations are expected in the
746 melt subject to high pressure in the deep MO (Armstrong et al., 2015; Grewal et al., 2020), but
747 the gas-melt equilibria that interests us occurs at low pressure (eg. tens to hundreds bar) and no
748 speciation data contradicts our assumptions at such conditions.

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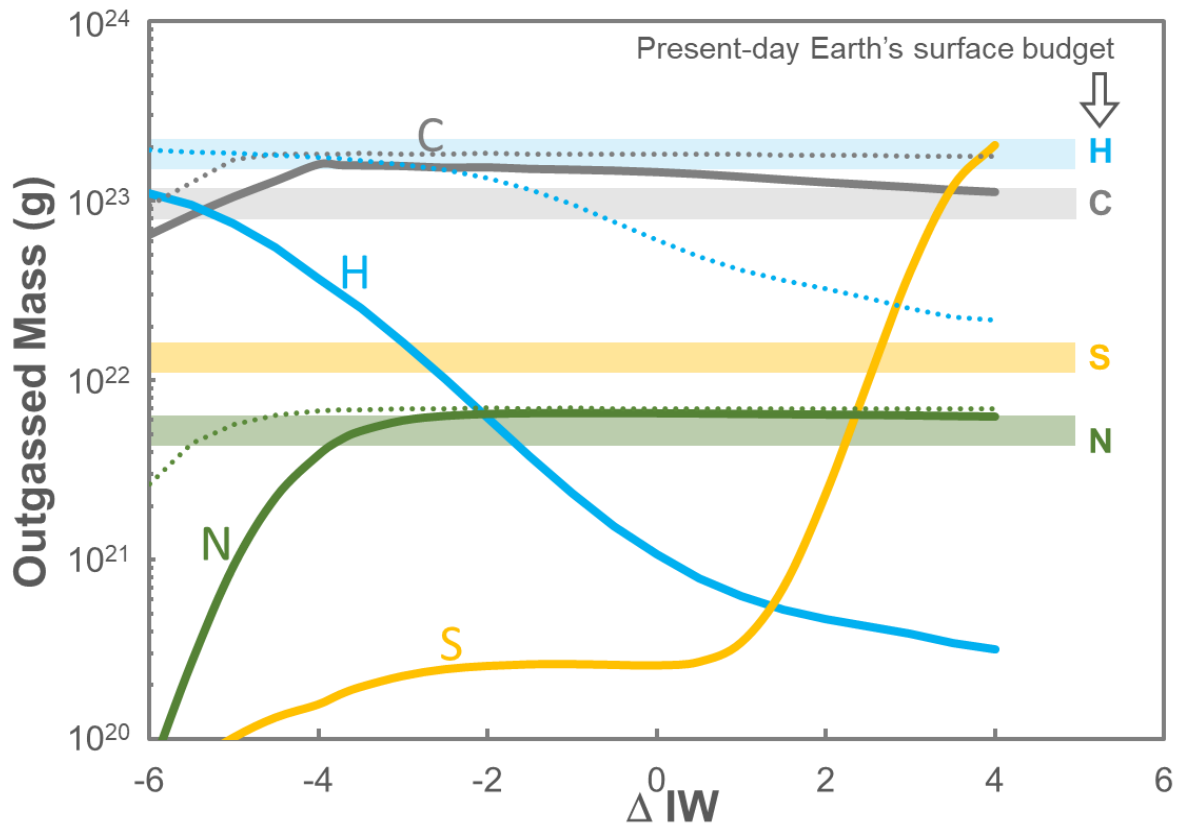
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753 **Figure S1.** The effect of temperature on the mass of outgassed CHNS from the MO. We
 754 illustrate here Case 1 with $\frac{1}{2}$ BSM, (see table 1) at 1500°C - 1927°C . We see that the calculated
 755 effect of T is moderate, which we must essentially attribute to our poor knowledge of the T -
 756 dependence of volatile solubility in basalts. In detail, we see that the low $f\text{O}_2$ domain of graphite
 757 saturation tends to disappear as T increases. This is because C dissolves more in both gas and
 758 silicate melt with increasing T .



759
 760 *Figure S2. The outgassed masses of carbon, hydrogen, sulfur and nitrogen as a function of the*
 761 *oxygen fugacity at the MO surface. The horizontal bands show the present-day mass of C-H-*
 762 *N-S in the Earth's exosphere (atmosphere+ocean+crust). The C-O-H-N-S speciations*
 763 *corresponding to the outgassed masses are shown in Figure 2. The dashed line corresponds to*
 764 *the mass of outgassed elements from a MO crystallized at 90% and in which, H, C and N are*
 765 *treated as completely incompatible elements, which is not the case for sulfur. The water content*
 766 *dissolved in the residual melt of the 90% solidified MO is ca. 5,000-7,000 ppm H₂O at IW>0,*
 767 *yielding little outgassed H (gas phase with <10% H₂O). In contrast to H, the outgassing of the*
 768 *most volatile elements, C and N, is weakly affected by crystallisation of the MO. Our approach*
 769 *here is simple since we treated CHN as incompatible elements. It is, however, likely that the*
 770 *crystallisation of diamond, sulphide, nitrides, carbides, alloys and hydrated silicates made*
 771 *these elements at least moderately compatible, enabling the formation of deep volatile*
 772 *reservoirs. This must consider in future developments.*

773 **Supplementary references.**

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