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1 **Diffusion of volatiles in hot stagnant-lid regime planets**

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11 **Key words: stagnant lid; Venus; water; diffusion; exoplanet; volatile**

12

13 **Abstract**

14 Earth is unique within our solar system in having a convective regime dominated by plate
15 tectonic processes. More typical of rocky, 'terrestrial' planets is a "stagnant lid" regime, where
16 the entire lithosphere is a single plate, variably punctured by plume-driven volcanic activity.
17 As such, a significant fraction of 'Earth-like' exoplanets might instead have stagnant lids. For
18 hot stagnant lid planets like Venus, high temperatures towards the base of the lid mean that
19 solid-state diffusion potentially provides a mechanism for redistributing lighter, faster-diffusing
20 volatile elements such as H. To investigate the importance of this mechanism a 1-d model is
21 used to constrain volatile flux from a relatively undegassed planetary interior into a hot stagnant
22 lid. Diffusion only results in significant flux of H through an oxidised lid; diffusion of H in reduced
23 stagnant lids and diffusion of other volatile elements, is inconsequential. For modelled
24 Venusian temperature profiles H diffusion fronts progress a limited distance (10s of km) into
25 the lid over Gyr timescales. However, for a small relative increase in lid temperature (i.e. a
26 slightly hotter than Venus exoplanet), H diffusion into the lid becomes considerable over
27 shorter timescales. H flux upwards into the lid eventually stagnates with decreasing

28 temperature. However, H flux markedly reduces mantle solidus in lower portions of the lid,
29 decreasing lid stability and promoting lid rejuvenation. Given the influence of H on a range of
30 mantle properties from melt relations to rheology, future models of stagnant lid planetary
31 evolution should assess the role of diffusion in redistributing H.

32

33 **1. Introduction**

34 Over the past decade, a marked increase in detection rate of extrasolar planets has led to
35 the identification of numerous “Earth-like” exoplanets (e.g. Coughlin et al., 2016; Dragomir et
36 al., 2019; Gillon et al., 2012), i.e. planets with similar mass and radius to the Earth. This has
37 driven research into issues related to planetary habitability, controls on the initiation of plate
38 tectonics, interplay between geological processes and atmospheric evolution, and the wider
39 issue of what ‘Earth-like’ actually means (Angelo et al., 2017; Barstow et al., 2016; Dittmann
40 et al., 2017; Dorn et al., 2018; Foley, 2018; Foley and Driscoll, 2016; Rushby et al., 2018;
41 Shahar et al., 2019; van Summeren et al., 2011). Within our own solar system Earth is one
42 of 4 ‘rocky’ planets which have iron-rich cores surrounded by shells of silicate. However,
43 among these it is unique in having a geological evolution dominated by plate tectonic
44 processes (O’Rourke and Korenaga, 2012). The lithosphere of Earth is divided into a
45 number of discrete plates. Relative movement of these plates stimulates planet-wide
46 geochemical recycling via subduction, gives rise to magmatism in addition to plume-related
47 mantle melting, and may buffer Earth’s hydrosphere and atmosphere by controlling flux of
48 volatile elements such as H₂O and CO₂. In contrast, Mercury, Venus, Mars and other bodies
49 such as the Moon and Io are ‘single plate’ (Johnson and Hauck II, 2016; Plesa et al., 2018;
50 Smrekar et al., 2018; Veeder et al., 2009; Wieczorek et al., 2006) and have convective
51 regimes in which a thick ‘stagnant lid’ overlies the convecting mantle, at least until the point
52 where heat loss renders bodies geologically inactive. Plume-related upwellings within a
53 stagnant lid regime dominate volcanic activity and interior-to-surface flux of material, and
54 limited recycling of material back into the deep interior is only possible by delamination of the

55 parts of the lid or localised lid melting (Elkins-Tanton et al., 2007), although limited
56 subduction has been proposed on Venus (Schubert and Sandwell, 1995) possibly related to
57 plume upwelling (Davaille et al., 2017). Conditions which result in the development of a
58 global plate tectonic regime remain uncertain, although the fact that they occurred on Earth
59 alone indicates that many 'Earth-like' exoplanets could be 'Venus-like', and although similar
60 to Earth in terms of size and mass, may have stagnant lid convective regimes (Kane et al.,
61 2018; Smrekar et al., 2018).

62

63 Although similar in terms of size and density to the Earth, there is no evidence for global
64 plate tectonic processes on Venus. Instead, a single plate of thick buoyant lithosphere is
65 assumed to inhibit mantle upwelling and active magmatism (Nimmo and McKenzie, 1998;
66 Smrekar et al., 2018). There is ongoing debate as to whether Venus is in a stable stagnant
67 lid regime or a regime punctuated by brief episodes of lid overturn and global resurfacing,
68 although numerical models suggest that even if Venus is within an episodic regime it is likely
69 to have had a stable stagnant lid for >500 Myr (Rolf et al. 2018). A stable stagnant lid is
70 punctured only by volcanic processes related to upwelling plumes (Solomatov and Moresi,
71 1996), resulting in a surface dominated by basaltic magmatism related to plume-driven
72 mantle melting (Ivanov and Head, 2015). In end-member stagnant lid regime planets
73 volcanism provides the main mechanism for transporting volatiles such as H₂O and CO₂ out
74 of the deep interior, i.e. mantle 'degassing'. In the absence of large-scale subduction of
75 lithosphere, flow of volatiles can be considered largely uni-directional.

76

77 The upper atmosphere of Venus is extremely dry (Bertaux et al., 2007). Even accounting for
78 H loss due to photodissociation (Lecuyer et al., 2000), atmospheric water contents are
79 orders of magnitude lower than the amount of surface water on Earth. This observation, and
80 the apparent stiffness of the Venusian crust, have been used to argue that the interior of
81 Venus is largely anhydrous (Elkins-Tanton et al., 2007; Nimmo and McKenzie, 1998). In

82 contrast to the Earth, Venus could have either lost volatiles such as H₂O over the past 4 Gyr
83 by volcanic degassing, or accreted volatile-free. However, Venus Express data indicates that
84 the lower atmosphere of Venus could be variably water-rich (Bezard et al., 2009). Mantle
85 degassing on Venus is also estimated to be an inefficient process at best (e.g. Kaula, 1999;
86 Lecuyer et al., 2000; Mikhail and Heap, 2017). Furthermore, models of planetary accretion
87 demonstrate that Venus and Earth should have similar volatile budgets (Wetherill GW,
88 1986). This is supported by gamma-ray spectroscopic data on lithophile element ratios,
89 which indicate that Venus, Mars and Mercury accreted comparable or greater H than Earth,
90 relative to marked depletions for the Moon and 4 Vesta (Greenwood et al., 2018). Given (1)
91 that that most terrestrial volatiles were delivered during initial accretion of the Earth (Altwegg
92 et al., 2015; Marty et al., 2017) and (2) that even the Moon-forming impact did not drive
93 volatile-loss in the early Earth-Moon system (Saal et al., 2008, 2013), it follows that other
94 inner solar system planets also accreted appreciable volatiles. As such, it appears likely that
95 the interior of Venus was originally volatile-bearing, has remained relatively hydrous and
96 volatile-rich. An H₂O and CO₂-bearing Venusian interior is also supported indirectly by
97 evidence for pyroclastic volcanism (Airey et al. 2015; Campbell et al., 2017), and by
98 geochemical modelling of limited surface composition data from Venera and Vega landers
99 (Filiberto, 2014).

100

101 Regardless of arguments for or against a volatile-bearing Venusian interior, it is probable
102 that a significant fraction of Earth-size/mass stagnant-lid regime exoplanets have volatile-
103 bearing interiors. Recent studies have investigated flux of H₂O and CO₂ in Earth-like
104 stagnant lid exoplanets, largely in terms of implications for planetary habitability (e.g. Foley
105 and Smye, 2018; Noack et al., 2017; Tosi et al., 2017). As well as being of key importance
106 in understanding why Earth or other planets might support life, H₂O (or H) also has a
107 disproportionate influence on a range of terrestrial mantle properties, from rheology to
108 melting behaviour (Peslier, 2010, and references therein). As such, H has a pivotal role in

109 understanding planetary processes more widely. The extent to which volatiles such as H₂O
110 might both influence, and be influenced by processes occurring within stagnant-lid regime
111 planets remains largely unknown, although variable water contents have been used to
112 explain viscosity variations in numerical models (e.g. Rolf et al., 2018). Volatile element
113 redistribution on Venus is typically considered solely in terms of volcanic degassing (e.g.
114 O'Rourke and Korenaga, 2012; Smrekar and Sotin, 2012; Wordsworth, 2016). However, for
115 hot stagnant planets, (1) the inferred stability of stagnant lids over long periods of time (Gyr),
116 (2) high temperatures across the lower portions of the lid (e.g. Ghail, 2015), (3) the
117 possibility that volatile distribution across planetary interiors is heterogenous after planet
118 formation, and (4) fast diffusivities of species such as H, raise the possibility that solid state
119 diffusion provides an additional mechanism for redistributing light, volatile species in
120 undegassed planetary interiors. Solid state diffusion is an inherently slow process and will
121 not influence element redistribution within freely convecting regions of planetary interiors.
122 However, diffusion is highly temperature dependent, and over geological timescales can
123 contribute to redistribution of lighter, more mobile elements, for example, into or out of lower
124 portions of a hot stagnant lid. Although this would likely represent an insignificant
125 mechanism in terms of total volatile element loss from an undegassed planetary interior,
126 progressive flux of elements such as H could have an important influence on lid stability
127 through time. Biased discovery of exoplanets orbiting close to parent stars, and on the inner
128 margin of within stellar habitable zones (Kane et al., 2018) means that consideration of the
129 relative importance of diffusion in Venusian or 'hot Venusian' exoplanets is timely.

130

131 **2. Method**

132 A stagnant lid can be envisioned as a complex polycrystalline, multi-phase material. In a
133 material such as this diffusivity of volatiles such as H will vary significantly as a function of
134 temperature, mineralogy, mineral chemistry, oxygen fugacity, grain size and grain boundary
135 width. However, these factors in turn, especially temperature, vary vertically upwards across

136 the stagnant lid. As such, diffusivity across the lid will vary by orders of magnitude in a non-
137 uniform manner. Thermal evolution of the lid will likewise result in progressive changes in
138 diffusivity across the lid.

139

140 In order to provide first constraints on the extent to which diffusion redistributes volatiles
141 across a hot, geologically complex stagnant lid, I develop here a 1D model. The model
142 assumes that the initial distribution of volatiles across the interior of a broadly Venus-like
143 interior is heterogeneous, and that a stagnant lid depleted in volatile elements overlies a
144 relatively undegassed convecting mantle. As such, the model imparts a concentration
145 gradient sufficient to drive flux of volatiles into the lid. A box model is then developed to
146 constrain, using data from experimental studies, how diffusivity varies with depth through the
147 lid as a function of temperature. This model is time-independent, and assumes that the lid
148 and temperature profile remain unchanged. In an evolving planet, the temperature profile
149 across the lid, and lid thickness itself, will vary with time (e.g. Rolf et al., 2018). However,
150 given that solid state diffusion is an inherently slow process only expected to be significant
151 over long timescales (>100 Myr), smaller temperature fluctuations are buffered within the
152 model, and temperature profiles across the lid can be considered as an average set of
153 conditions over time in a mature stagnant-lid regime planet.

154

155 **2.1 Conceptual stagnant lid model**

156 For the model, a simplified stable stagnant lid structure based on that of O'Rourke and
157 Korenaga (2015) was used, based on the internal structure of a Venus. In this model (figure
158 1), a 170km thick stagnant lid consists of 30 km of basaltic crust overlying a mantle
159 lithospheric component. This 2-component lid overlies a convecting mantle. Thickness of the
160 lid, division into crustal and mantle lithospheric components, and a upper surface
161 temperature of 735 K are all based on inferred models for present day Venus (e.g. Nimmo
162 and McKenzie, 1998), although the model is broadly representative of a rocky (i.e. terrestrial)

163 body with a thick, stable stagnant lid. The model used here assumes that the convecting
164 mantle is relatively undegassed, and as such, due to its volume can be considered an infinite
165 reservoir for volatiles. The stagnant lid is assumed to be initially volatile-free (or volatile poor
166 for later models). This is based on the assumption that incompatible volatile elements would
167 partition into primary mantle melts, thereby forming basaltic crust and variably degassing to
168 the atmosphere, with the remainder of the lid comprised of melt residue, and essentially
169 stripped of volatile species. Although an obvious simplification, this model provides a useful
170 system for exploring volatile flux into a hot stagnant lid. The broad concept of a volatile-free
171 lid overlying a progressively more volatile enriched deep interior is, furthermore, in line with
172 experimental studies which demonstrate that 'water', i.e. H₂O, storage capacity is proportional
173 to water fugacity to the power n , $f_{\text{H}_2\text{O}}^n$, and as such, increases markedly with depth (Bolfan-
174 Casanova, 2005; Bromiley et al., 2004; Bromiley and Keppler, 2004; Rauch and Keppler,
175 2002). The model used here can be modified to explore the effect of different initial volatile
176 element distributions, and different stagnant lid compositions and proportions. In the model,
177 the lid mantle component is a 2-mineral mix 60% olivine + 40% orthopyroxene with a 3 mm
178 grain size; this simplified hazburgite composition represents a mantle residue from which 15-
179 25% basaltic liquid has been extracted. However, it is also broadly representative of any
180 ultramafic, peridotitic (olivine-rich) composition. The overlying basaltic crust, which is not
181 expected to contribute to volatile flux but is added here for the sake of completion, is
182 modelled as a 2-mineral mix of 60% pyroxene + 40% plagioclase with a 1 mm grain size.
183 Grain sizes are estimated based on personal observations of gabbroic and hazburgitic units
184 in ophiolitic sequences, and in line with inferred grain sizes in published studies (Demouchy
185 et al. 2010a,b; Bromiley and Hiscock, 2016). Minerals are assumed to be randomly oriented
186 in both lid components, Variation in temperature with depth through the stagnant lid is
187 modelled based on published models of the interior structure of Venus, as discussed below.
188 Variation in temperature, and to a much lesser extent pressure, coupled to changes in
189 mineralogy within the lid results in significant variations in diffusivity of each species with

190 depth. To constrain this variation, the model lid is divided into a series of 10 km thick shells.
191 Bulk temperature within each shell is constrained by the temperature profile, and a
192 representative diffusivity for each species in each phase calculated. For each shell, a
193 weighted bulk diffusivity can then be determined. In this manner, non-trivial variations in
194 diffusivity across a simultaneous concentration gradient can be simulated, which is the key
195 feature of any realistic model for volatile flux into a stagnant lid. A limitation in this approach
196 is that temporal variations such as evolution in the temperature gradient across the stagnant
197 lid or the proportions of the stagnant lid itself, cannot be simulated, although multiple
198 temperature profiles can be used to assess the effects on changes in lid temperature with
199 time. Furthermore, slow diffusion of volatiles over 100 Myr+ durations means that shorter
200 duration temperature variations are buffered over long timescales; as such, temperature
201 profiles used here can be considered as average conditions over the timescales used within
202 the model.

203

204 **2.2 Modelling hydrogen diffusivity**

205 Due to its small mass and incorporation mechanisms in silicates, H is the fastest diffusing
206 volatile species under relevant deep planetary conditions. As such, H will be the volatile
207 most likely to be mobilised within a solid, stagnant lid regime planet. Hydrogen is typically
208 incorporated in nominally anhydrous mantle minerals as interstitial H^+ , charge balanced by
209 metal vacancies or substitutional defects (Bell and Rossman, 1992; Bolfan-Casanova, 2005;
210 Ingrin and Skogby, 2000). Diffusion of H^+ requires coupled diffusion of some other species to
211 maintain charge neutrality, and the nature of this species will influence H^+ diffusivity. H^+
212 diffusion in olivine was modelled here using data from Mackwell and Kohlstedt (1990) who
213 constrained diffusivity of H^+ coupled to counter flux of polarons (i.e. reduction of Fe^{3+} to Fe^{2+}).
214 H flux modelled using this data assumes availability of Fe^{3+} , or in other words, a relatively
215 oxidised stagnant lid. Limited data on the geochemistry of the Venusian lid suggests that this
216 is a reasonable assumption. Wordsworth (2016) proposed that photolysis of H_2O in the early

217 Venusian atmosphere liberated O and H. During subsequent H loss to space, the Venusian
218 mantle would have been progressively oxidised by atmospheric interaction with the
219 remaining O. Wordsworth (2016) calculated that this redox pump mechanism will have
220 oxidised the Venusian mantle to approximately the magnetite-hematite buffer. Similarly,
221 Lecuyer et al. (2000) argued that the simultaneously high D/H and low H₂O content for the
222 Venusian atmosphere compared to Earth is consistent with either significant hydration of the
223 Venusian crust, or photolysis of H₂O, H loss and mantle oxidation. Regardless of this, it is
224 likely that all large (i.e. Earth/Venus sized) rocky planets undergo some degree of self-
225 oxidation during the latter stages of planetary formation. Bodies larger than Mars have a
226 sufficient size to form a substantial silicate perovskite-dominated lower mantle. The
227 perovskite-structured mineral bridgmanite, (Mg,Fe)₂SiO₃, will be the dominant lower mantle
228 mineral over a wide range of compositions, and importantly, has been shown to freely
229 dissociate Fe²⁺ into Fe metal and Fe³⁺ (Frost et al., 2004). Crystallisation of bridgmanite
230 during magma ocean solidification should, therefore, act as a mechanism for self-oxidation in
231 large rocky planets soon after their formation, regardless of later/additional mechanisms for
232 mantle oxidation. A similar mechanism for self-oxidation and iron disproportionation has also
233 been noted in high pressure experiments on garnet and pyroxene-bearing lithologies
234 (Rohrbach et al., 2007). As such, the condition that there is sufficient Fe³⁺ stable in the
235 mantle component of the lid to enable polaron coupled 'fast' diffusion of H⁺ appears
236 reasonable. Most likely, however, H⁺ diffusion will proceed by simultaneous fast diffusion
237 coupled to flux of polarons, and 'slow' diffusion coupled to diffusion of metal cation vacancies
238 within olivine. Therefore, data from Padron-Navarta et al. (2014) on H⁺ diffusivity in Fe-free
239 forsterite, coupled to slower diffusion of metal vacancies, was also used to constrain slow
240 diffusion of H in olivine.

241

242 Diffusion of H⁺ in orthopyroxene can also proceed via a fast mechanism coupled with Fe
243 redox change, and a slower mechanism coupled to diffusion of metal vacancies. To model

244 both processes experimental diffusivity data of Stalder et al. (2007), Stalder and Behrens
245 (2006), and Stalder and Skogby (2003) was used. In contrast to the limited studies on
246 orthopyroxene, there have been numerous, sometimes conflicting studies of H⁺ diffusion in
247 clinopyroxene. Differences between studies are most likely due to the more complex crystal
248 chemistry of clinopyroxene. For fast, redox coupled diffusion, data from Ferriss et al. (2016)
249 for H⁺ diffusivity in clinopyroxene from Nushan was used, which is, according to Ferriss et al.
250 (2016), most comparable to mantle clinopyroxene. Slow diffusion in clinopyroxene was
251 modelled using data on H⁺ diffusivity in Fe-free diopside from Sundvall et al. (2009). In
252 contrast to other phases, H⁺ diffusion in plagioclase is relatively anisotropic, and there is no
253 evidence for fast redox driven diffusion. Diffusion was modelled using data from Johnson
254 and Rossman (2013), who determined H⁺ diffusivity in plagioclase coupled to Na⁺ diffusion.

255

256 In a polycrystalline material, species can diffuse through crystal structures (bulk, or lattice
257 diffusion), or through grain boundary regions. Diffusivity in grain boundary regions is typically
258 faster, although the low volume fraction of grain boundary regions in most systems means
259 that lattice diffusion typically dominates, except in very fine grained material and/or at lower
260 temperatures. Demouchy (2010a) and Hiscock (2012) demonstrated that H⁺ grain boundary
261 diffusion in olivine may contribute towards total flux of H⁺ in Earth's mantle under certain
262 conditions. In the absence of data on H⁺ grain boundary diffusion for other silicates, we use
263 data from Demouchy (2010a) to model grain boundary H⁺ flux in the stagnant lid. Given
264 mineral proportions within mantle lithologies it is likely that this approach provides a good
265 estimate of the contribution of grain boundary diffusion of H⁺. To model the contributions of
266 both lattice and grain boundary diffusion within the lid we use, in accordance with Demouchy
267 (2010a), the following equation (Balluffi et al., 2005):

268

$$269 \quad D_H^{eff} = D_H^L + \left(\frac{3\delta}{d}\right) \cdot D_H^{gb} \quad [1]$$

270

271 where D_H^{eff} is effective (i.e. total) H diffusivity, D_H^L and D_H^{gb} are lattice and grain boundary H
272 diffusivities, respectively, d is grain size and δ is grain boundary width. Effective H⁺ diffusivity
273 in the lid is, therefore, determined based on a weighted average of diffusivities in crystal
274 lattice and grain boundary regions, without accounting for the likely segregation of H⁺ into
275 grain boundary regions. This, coupled with faster grain boundary diffusivity, might result in
276 slightly higher effective diffusivity. Grain size for [1] is set in the model for both regions of the
277 model stagnant lid. A representative grain boundary width of 0.75 nm, consistent with
278 previous studies (Bromiley and Hiscock, 2016; Demouchy, 2010b, 2010a), is assumed.

279

280 A single value of D_H^L was used for each shell of the model, determined by first calculating an
281 average diffusivity for H in each phase, and then weighting this based on mineral
282 proportions. H diffusivity in most mineral structures is typically highly anisotropic. In olivine,
283 for example, H diffusivity parallel to the crystallographic a axis is approximately one order of
284 magnitude faster than diffusivity parallel to the b and c axes. To test the validity of using an
285 average (i.e. bulk) H diffusivity, I calculated average diffusivity in one direction for a system
286 of 1000 randomly oriented grains, assuming various order of magnitude differences in
287 diffusivity in 2 orthogonal directions. Even in a system where there is a 2 order of magnitude
288 difference in diffusivity in 2 orthogonal directions, average (mean) diffusivity gives, within
289 error, the same result as the actual average diffusivity for 1000 grains (calculated for each
290 individual grain based on actual orientation relative to the 2 orthogonal directions).

291 Therefore, for a sufficient large number of randomly oriented grains, an average diffusivity
292 can be assumed based on the weighted average of diffusivities in different crystallographic
293 orientations.

294

295 Figure 2 shows how bulk D_{eff}^H for each shell changes as a function of depth for 4 model
296 temperature profiles, calculated assuming fast, polaron coupled H diffusion (also see
297 supplementary online material). Temperature profiles are described in detail below, and are

298 based on proposed models for Venus or a Venus-like planet. Modelling demonstrates that
 299 temperature has a dominant influence on D_{eff}^H , which in turn decreases markedly upwards
 300 into the lid as a function of the temperature profile. As diffusivity decreases upwards into the
 301 lid, diffusion will eventually cease to be effective over geological timescales. H flux will
 302 effectively stagnate at some distance into the lid, implying that only the lowermost portions of
 303 the lid can become hydrated. Figure 2 also demonstrates that H diffusivity varies markedly
 304 with small variations in temperature over conditions at the base of the lid.

305

306 To determine the extent of H flux into the lid, diffusion was modelled over discrete time
 307 intervals using a standard infinite source solution to Fick's second law, based on D_H^{eff}
 308 calculated from [1]:

309

$$310 \quad C(x, t) = C_S - (C_S - C_0) \operatorname{erf} \left[\frac{x}{2\sqrt{D_H^{eff} t}} \right] \cdot C_S \quad [2]$$

311

312 where $C(x,t)$ is the concentration of the diffusing species, after time t at a given distance x
 313 from the source. Within the model, each 10 km shell was further divided into 100m slices.
 314 The source for each slice in the model represents the lower boundary of the slice (see
 315 below), and C_S and C_0 are the concentrations of the diffusing species in the source (the
 316 convecting mantle or underlying slice) and the sink (the slice) prior to diffusion.

317

318 **2.3 Diffusivity of other species**

319 Given that there is no evidence for even ppm concentrations of C in mantle minerals,
 320 effectively limiting any influence of lattice diffusion, C flux was modelled solely based on data
 321 from Hayden and Watson (2008) on grain boundary diffusivity of C in polycrystalline olivine,
 322 again using [1] and [2]. Although the data of Hayden and Watson (2008) only allow the total

323 effective diffusivity of C in grain boundary regions to be ascertained, it is assumed that this
324 represents diffusion of atomic C. A similar approach to that outlined for H was used to model
325 diffusion of Ar and He. Data from Thomas et al. (2008) and Cassata et al. (2011) was used
326 to determine Ar diffusivity in olivine and pyroxene, respectively. He diffusivity in olivine and
327 pyroxene was modelled using data from Tolstikhin et al. (2010) and Trull (1981),
328 respectively, and grain boundary diffusion of both noble gases modelled using data from
329 Burnard et al. (2015).

330

331 **2.4 Modelling diffusion through the model stagnant lid**

332 The model stagnant lid used here is constructed of a stacked vertical sequence of 100m
333 thick slices. The bottom surface of the first slice (S_1) corresponds to the base of the stagnant
334 lid (D_1), at a depth of 170km from the surface. The top surface of this first slice is at a depth
335 of D_1-2i , where $i=1000\text{m}$. The next (second) slice in the model then has boundaries at D_1-i
336 and D_1-3i ; as such, there is a 50% overlap between the slices, as shown in figure 3. The
337 remainder of the model consists of an upward sequence of similarly overlapping slices.
338 Average temperature for each slice is set using data shown in figure 2..

339

340 Diffusion through this sequence of overlapping slices was modelled over a series of time
341 steps. The initial conditions for the model have an element concentration at D_1 of X_0 ppm
342 (figure 2A). This corresponds to the element concentration in the underlying convecting
343 mantle (i.e. the infinite source, C_s) which remains constant throughout each subsequent time
344 step. Element concentration at D_1-2i (corresponding to C_0 in [2]) is typically set at 0 ppm for
345 most modelling here, to represent an anhydrous stagnant lid. For time step 1, [2] is then
346 used to model diffusion of the species over a given time interval, at distances of 100 m, to
347 produce a concentration gradient. Representative input and output from this single time step
348 are shown in figure 3A,B.

349

350 The second time step uses the output of time step 1 as input data. For slice one, C_0 is set
351 across the shell, at 100m intervals, based on the output for this slice from time step 1.
352 Element concentration at D_1 remains constant. For slice 2, from D_{1-i} to D_{1-2i} , input from time
353 step 1 gives an initial element concentration. The duration of the time step used throughout
354 the modelling is chosen so that the element concentration at D_{1-2i} approaches C_0 (typically
355 0). Element concentration from D_{1-2i} to D_{1-3i} is then set at C_0 . For slice 2, the initial
356 concentration from D_{1-i} is used for C_s in [2]. Diffusion across both slices is then modelled
357 using [2], and concentration profiles recorded, as shown in figure 2C,D. Output from this time
358 step is then used as the input for time step 3, over which diffusion is modelled for slice 1 to 3
359 (figure 2E). Thus, step wise modelling is used to simulate diffusion with increasing time
360 across the stagnant lid. Using this approach, flux across the entire stagnant lid, where
361 diffusivity changes as a function of distance, can be modelled. The step size (slice size) and
362 time step are chosen to ensure that during each step diffusion of the species can be fully
363 modelled within the shell; as such, progressive diffusion across consecutive slices is
364 modelled step-wise, and flux approximated.

365
366 **3. Fast H diffusion, Nimmo and McKenzie (1998) model.**

367 Diffusivity of H is strongly temperature dependent, and the relative importance of diffusion as
368 a mechanism for mobilising H will depend on the temperature profile across the stagnant lid.
369 Venus potentially provides a useful model for an Earth-like planet with a stagnant lid regime,
370 aside from arguments regarding episodic overturn. However, the geothermal gradient on
371 Venus has not been determined. Here, we use proposed temperature profiles from previous
372 studies to input into the model. Nimmo and McKenzie (1998) proposed a temperature
373 structure for Venus based on a mantle potential temperature similar to that of the Earth,
374 1573K (figure 3A), a 170 km thick stagnant lid, mechanical boundary layer thickness
375 constrained by melt generation and admittance, inferred viscosity and surface temperature
376 of 723 K (figure 2). This temperature profile is close to a geothermal gradient on Venus of 6
377 K/km (figure 2), and would be consistent with a stable mantle structure in which melting

378 could only occur as a result of significant temperature fluctuations (i.e. thermal plumes) or,
379 by analogy to the Earth, by large scale tectonic processes such as rifting and lithospheric
380 thinning. Here, we use the Nimmo and McKenzie (1998) temperature structure to constrain
381 convecting mantle-lid interaction in a system where the deep interior is not degassed. A
382 mantle H content equivalent to 1000 ppm H₂O by weight was used. By comparison, the
383 uppermost terrestrial mantle (the source region for mid-ocean ridge basalts) is estimated to
384 contain up to 200 ppm H₂O based on various geochemical arguments (Peslier, 2010).
385 However, it is likely that the water content of Earth's mantle is highly variable, both due to
386 systematic variations in H storage capacity with depth (Bolfan-Casanova, 2005; Smyth et al.,
387 2006) and as a result of large scale plate movement. The uppermost mantle of Earth has
388 been depleted by both formation of continental crust and large scale mantle melting at
389 divergent plate margins, so likely does not give meaningful insight into the bulk H content of
390 the silicate Earth. The mantle source region for ocean island basalts (i.e. plume related
391 mantle melting) is considerably more H-rich, containing up to 1000 ppm H₂O, for example
392 (Peslier, 2010). The deeper terrestrial mantle may be more H-rich than this due to a marked
393 increase in H storage capacity as a function of pressure and changes in mantle mineralogy
394 (e.g. Bolfan-Casanova, 2005; Bolfan-Casanova et al., 2000).

395

396 Figure 4 shows the results of modelling H diffusion based on the Nimmo and McKenzie
397 (1998) profile, with H concentration gradients shown after $t = 100$ Myr, 200 Myr, 500 Myr, 1
398 Gyr and 2 Gyr, from right to left. Concentration profiles arising due to H diffusion through the
399 model lid have a characteristic S-shaped form. From left to right in figure 4, with increasing
400 depth, the first change in gradient in each profile represents the maximum distance to which
401 H can diffuse after a given period of time, or the diffusive front (D_F). Each profile then has a
402 relatively constant gradient, the steepness of which is a function of how quickly bulk
403 modelled diffusivity changes with depth/temperature. The concentration gradient then rapidly
404 decreases as the profile levels out to approach the H content of the convecting mantle. This

405 distance can be defined as the saturation front (S_F) as it represents the distance at which a
406 given portion of the lid, after time t , attains the maximum volatile content possible via
407 diffusion.

408

409 The extent of H diffusion using this temperature profile is limited. After 2 Gyr, S_F extends
410 only 5.5 km into the base of the lid, with D_F extending to around 35 km. H concentration
411 profiles are relatively steep as temperature, and thus diffusivity, drops markedly with
412 distance upwards into the lid (Figure 2). The water storage capacity of the lid, or the
413 maximum solubility of H_2O in the 2 phase olivine + orthopyroxene mix, indicated on figure 4
414 is based on pressure/temperature dependence of H solubility summarised in Bolfan-
415 Casanova (2005). Water storage capacity of the base of the lid is >1700 ppmw H_2O , and
416 decreases with increasing distance into the lid due to a decrease in H solubility in both
417 olivine and orthopyroxene with decreasing pressure. Water storage capacity only
418 approaches 1000 ppmw H_2O around 50 km into the lid; as such, all H diffusing into the lid
419 can be fully incorporated as interstitial defects within olivine and orthopyroxene, with no
420 additional hydrous phase present. This would also be the case for a more complex stagnant
421 lid mineralogy containing additional clinopyroxene \pm garnet (i.e. more lherzolithic
422 composition).

423

424 For comparison with the model presented here, the light grey line in Figure 4 shows a
425 concentration gradient calculated for a single 'infinite source' solution to Fick's second law,
426 for a comparable time period of 2 Gyr. This is calculated assuming a convecting mantle
427 water content of 1000 ppmw H_2O , a fixed boundary between convecting mantle and
428 anhydrous lid, and a single D_H^{eff} across the entire lid, based on the value for the lowermost
429 shell. As expected, there is a marked difference in gradient compared to outputs from the
430 model where D_H^{eff} decreases markedly upwards through the lid. H diffuses a much greater
431 distance into the lid, which is only effectively saturated at the boundary with the convecting

432 mantle. As a consequence, distribution of H across the lowermost lid varies considerably,
433 and in marked contrast to the model presented here. However, a simple calculated
434 characteristic diffusion distance, $L_D = \sqrt{D_H^{eff} \cdot t}$ does give a reasonable insight into the extent
435 of H flux in the model. For example, a constant $D_H^{eff} \approx 10^{-8} \text{ m}^2 \cdot \text{s}^{-1}$ (Figure 2) implies $L_D \approx 18 \text{ km}$
436 after 1 Gyr, and $\approx 25 \text{ km}$ after 2 Gyr, which compares reasonably well with the extent of
437 migration of concentration profiles over the same time intervals.

438

439 The thin grey line in figure 4 marks the solidus for hazburgite determined by Maaloe (2004).
440 Hazburgite is, terrestrially, a melt residue formed by large degree (typically 15-25%) melting
441 of garnet lherzolite. As such, it is not surprising that the solidus for hazburgite greatly
442 exceeds temperatures across the lid. Hazburgite composition was used for diffusion
443 modelling in this study as it represents a simple mantle composition from which basaltic melt
444 has been extracted. However, it is also broadly representative of any ultramafic (i.e. olivine
445 dominate) peridotitic composition. Exact mineralogy of any stagnant lid will depend on the
446 complexity of geological processes which it has been subjected to, and the bulk silicate
447 composition of the planet. A more generic peridotitic composition, under conditions of the
448 lower portion of the stagnant lid, would likely additionally comprise garnet and clinopyroxene.
449 The presence of these decreases the mantle solidus markedly, although would have only a
450 very minor influence on bulk H diffusivity. Dashed lines on figure 4 mark positions of a dry
451 (i.e. H-free) peridotite solidus, and solidi for peridotite with 200 ppmw and 1000 ppmw H_2O ,
452 respectively, as determined by thermodynamic modelling of the effect of H incorporation on
453 depression of the mantle solidus (Hirschmann, 2006). A nominal 'wet' mantle solidus lies
454 $>200 \text{ K}$ lower than the harzburgite solidus, depending on the exact water content. However,
455 from figure 4 it is apparent that all mantle solidi are substantially ($>100\text{K}$) higher than lid
456 temperatures across the model. As such, diffusion of H into the lid in this model is unable to
457 induce partial melting. For a constant temperature profile across a stable lid over Gyr
458 timescales diffusion will, however, depress the solidus of the lower 10-20 km portion of the

459 lid by approximately 50-100K, due to the presence of 200 ppm-1000 ppmw H₂O. This will
460 significantly increase the likelihood of 'wet' melting of the base of the lid due to thermal
461 anomalies such as upwelling plumes. The extent of wet melting will be a function of the
462 lifetime of the stagnant lid, and the H content of the convecting mantle. However, in the
463 general case where a less degassed interior is overlain by a relatively anhydrous stagnant
464 lid, diffusion of H increases the possibility that upwelling plumes promote melting, and
465 rejuvenation, of the lowermost portion of the lid in Venus, and exo-Venus planets.

466

467 In terms of loss of water from the convecting mantle to the stagnant lid, diffusion modelling
468 indicates that 4×10^{18} kg are transferred to the stagnant lid after 10 Myr, increasing to 2×10^{19}
469 kg after 1 Gyr and 3×10^{19} after 2 Gyr. If we assume, in crude comparison to the Earth, that
470 water in the mantle of Venus is distributed over the upper mantle and mantle transition zone,
471 this equates to a loss of mantle water content to the lid of between 0.0005 and 0.0034%. As
472 such, loss of water from the mantle to the lid by diffusion is inconsequential. Any diffusive
473 loss of H will have no impact on mantle properties, and make no effective contribution to
474 mantle degassing. In this regard, the lid acts as a relatively impermeable barrier to volatile
475 loss and interior/atmospheric exchange.

476

477 **4. Slow H diffusion and flux of other species, Nimmo and McKenzie (1998) model**

478 Figure 5 shows a comparison of concentration profiles for different species after 2 Gyr using
479 the same Venusian temperature profile from Nimmo and McKenzie (1998). Even after a
480 protracted period of 2 Gyr, slow diffusion of H, i.e. coupled to metal vacancies as opposed to
481 Fe redox changes, only results in a D_F extending under 2 km into the lid. As expected,
482 therefore, diffusion mechanism has a significant control on the effectiveness of diffusive loss
483 of H to the stagnant lid. For reduced stagnant lids, H diffusion will be largely coupled to
484 slower metal vacancy diffusion, and the extent of H mobility is limited, even over Gyr
485 timescales. However, in larger stagnant lid regime planets, mantle self-oxidation during

486 magma ocean crystallisation should occur as a consequence of mantle crystallisation (Frost
487 et al., 2004; Frost and McCammon, 2008). Furthermore, operation of redox pump type
488 mechanisms, as inferred for Venus, might also further promote mantle oxidation. This will
489 promote fast H diffusion due to the presence of Fe^{3+} in olivine and pyroxene within NAMs in
490 the lid, and much greater flux of H.

491

492 Diffusion of other volatiles is also extremely limited. As shown in figure 5, D_F for He and Ar
493 are approximately 2 km and <0.5 km, respectively. Little effective diffusion of C occurs in the
494 model as flux is only possible through grain boundaries. The limited data available on volatile
495 diffusivities for these species in the various mantle phases, and within grain boundaries, and
496 large potential variability in the proportion of grain boundaries within the model lid (which is a
497 function of grain size and grain boundary width) mean that modelled concentration gradients
498 in Figure 5 have a significant error on them. However, they are broadly illustrative, and imply
499 that diffusion of all volatile species other than H, when not coupled to flux of metal
500 vacancies, is inconsequential. As expected, solid state diffusion can only result in effective
501 mobilisation of H in stagnant lid regime planets, unless mantle temperatures greatly exceed
502 those expected in Venus-like planets.

503

504 **5. *Fast H diffusion, Ghail (2015) model***

505 Ghail (2015) proposed a model for Venus where the presence of CO_2 in the mantle results in
506 minor melting and the formation of an asthenosphere. In this model, plume activity results in
507 lid rejuvenation, which significantly contributes to heat loss and allows Venus to maintain a
508 stable tectonic regime. Ghail (2015) suggested that the 12 mWm^{-2} geotherm shown in Figure
509 2 can be used to approximate the temperature profile through a region of old, stable lid on
510 Venus, i.e. a cool lid unaffected by plume activity. Over the lowermost lid this temperature
511 profile is somewhat similar to a 5 K/km geothermal gradient (figure 2). The 18 mWm^{-2}
512 geotherm approximates, according to Ghail (2015) the thermal structure of a region of the lid

513 heated by a mature plume, but at a distance from the plume tail. He further proposed that a
514 36 mWm^{-2} geotherm approximates the thermal structure of a region of the lid directly heated
515 by an impinging plume head. Therefore, these proposed geotherms provide an alternative
516 thermal structure for Venus which can be used to assess the extent of volatile flux through
517 an old, stable lid, and also a hotter lid heated by plume activity. Figure 6 shows these
518 modelled Venusian geotherms and melt relations from Falloon and Green (1989) for the
519 corresponding carbonated peridotite mantle composition. Ghail (2015) suggested that
520 intersection of 18 and 36 mWm^{-2} geotherms with 'minor' and 'major' melting curves (i.e.
521 mantle solidi) results in small to large degrees of melting towards the base of a CO_2 -bearing
522 peridotitic Venusian stagnant lid heated by upwelling plumes.

523

524 H concentration profiles shown in Figure 6 are based on temperature profiles consistent with
525 18 and 12 mWm^{-2} geotherms, for the same 5 times steps shown in Figure 4. A 12 mWm^{-2}
526 geotherm infers temperatures $<1600\text{K}$ across the lowermost stagnant lid. This reduces the
527 extent of H diffusion, and concentration profiles in figure 6B show that D_F progresses $<30\text{km}$
528 into the lid after 2 Gyr, and just over 20 km after 1 Gyr. Once again, temperatures across
529 hydrated regions of the lid are sufficiently below than the lid solidus for H to have any
530 influence on lid stability. This temperature profile, similar to that derived from Nimmo and
531 McKenzie (1998) again suggests that H flux into an old stagnant lid is relatively minor, only
532 partially hydrated the lowermost portions of the lid.

533

534 The 18 mWm^{-2} geotherm can be used to approximate temperature profile through a region
535 of the lid heated by plume activity, but not directly involved in plume upwelling and mantle
536 melting. Figure 6A demonstrates that higher temperatures across the lowermost lid, and a
537 flatter temperature profile greatly enhance H flux and change the shape of H concentration
538 gradients. A difference in the shape of H concentration gradients between figures 6B and 6A
539 and figure 4 highlight the effect that a drop in temperature upwards through the lid has in

540 stalling H diffusion. For flatter temperature profiles, H concentration profiles have a lower
541 gradient, and the difference between D_F and S_F remains large. For typical sloping
542 temperature profiles, where diffusivity drops markedly with distance into the lid, H
543 concentration profile gradients are steeper, and H flux reduces with time/distance. This
544 means that, regardless of the increasing effects of evolution in lid temperature with time or
545 lid stability, forward modelling H diffusion for periods of time exceeding 2 Gyr is of limited
546 value for most geotherms: the extent of additional migration of both the S_F and D_F will be
547 limited. For the Ghail (2015) 18 mWm^{-2} geotherm, there is a greater separation of the S_F and
548 D_F even at considerable distance into the lid. After 2 Gyr, D_F extends to nearly 50 km
549 upwards into the lid, with S_F extending upwards approximately 25 km. However, a change in
550 the 2 Gyr H concentration profile around 125 km depth indicates that the continual, small
551 drop in temperature and concurrent drop in diffusivity, as shown in Figure 2, start to result in
552 stagnation in H flux, which would with time result in steepening of the H concentration
553 gradient. Importantly, this stagnant occurs over the range of depths where there is only a
554 small decrease in temperature, highlighting the fact that small changes in inferred
555 temperature control whether solid state diffusion is relevant.

556

557 Timescales used for the modelling shown in figure 6A obviously exceed the duration of
558 localised heating from a plume, which is presumably stable on 100 Myr time scales at most,
559 and ignore any localised lid instability due to plume activity (Davaille et al., 2017). Lid
560 temperature would be expected to slowly drop after cessation of adjacent upwelling.

561 Similarly, for a slowly heating stagnant lid regime planet (Venus, or Venus analogue, hybrid
562 stagnant lid regime), 1 Gyr probably approaches or exceeds the time period of temperature
563 fluctuations between episodes of large scale melting and resurfacing (Rolf et al., 2017).

564 Comparison of profiles in figures 6A and 6B can, however, be used to assess the effect of
565 temperature changes on H flux into the lid. The grey shaded region shown in Figure 6B is
566 delimited by H concentration profiles after 2 Gyr for both 12 and 18 mWm^{-2} geotherms. This

567 depth-concentration space provides constraints on the effect of temporal heating of the base
568 on the stagnant lid within the Ghail (2015) model.

569

570 The difference between calculated water-depressed mantle solidi and the carbonated
571 peridotite melting relations shown in figure 6 is due to phase stability and total volatile
572 content contrast in the two systems: i.e. trace amounts of water for peridotitic solidii vs 2.4
573 wt% CO₂ in a carbonated peridotite. The 18 and 36 mWm⁻² geotherms intersect the
574 +1000ppm H₂O mantle solidus at around 125 km depth, and the +200 ppmw H₂O solidus
575 around 95 km depth. As such, diffusion is unable to deliver H far enough into the lid to
576 induce lid melting. For example, the maximum distance into the lid to which 200 ppmw H₂O
577 can diffuse in the model corresponds to a depth just over 125 km, even after 2 Gyr for a lid
578 continually heated by plume activity. However, in a Ghail (2015) type model, where plume
579 activity promotes melting and lid rejuvenation, diffusion does result in significant transport of
580 H into lower portions of the lid. Melt relations under these conditions for carbonated
581 peridotite are poorly constrained. However, a period of 100 Myr is sufficient, with an elevated
582 mantle geotherm, to promote diffusion of around 200 ppmw H₂O 5 km into the lid. This
583 distance exceeds 15 km after 500 Myr, 25 km after 1 Gyr, and 43 km after 2 Gyr. As such,
584 for a stable planet within the stagnant lid regime, diffusion will result in a hydrated lowermost
585 lid. In a regime where melting is promoted by the presence of CO₂, the presence of water
586 would increase the degree of melting, modify melt relations and melt chemistry, and further
587 enhance lid rejuvenation.

588

589 The Ghail (2015) model assumes that the mantle component of the lid contains CO₂ in
590 significant enough proportions to considerably depress the solidus. In contrast, the starting
591 point for diffusion modelling here is an anhydrous lid. The effect of an H-bearing lid can be
592 readily simulated by setting C₀ in [2] to any given value. In figure 6C, concentration profiles
593 based on a Ghail 18mWm⁻² geotherm are shown for an anhydrous lid, and convecting

594 mantle with 1000 ppmw H₂O, and a lid with a uniform 200 ppmw H₂O. By definition, varying
595 C_S has no influence on D_F or S_F except where C₀ approaches C_S. However, for any given
596 time, the distance to which water concentrations intermediate between C₀ and C_S extend into
597 the lid is increased slightly, increasing the possibility of water-induced partial melting.

598

599

600 **6. Fast diffusion in a hot stagnant lid: assessing the importance of H diffusion**

601 From concentration profiles shown in figures 6A it is clear that slightly higher temperatures at
602 the base of the lid using a Ghail 18 mWm⁻² geotherm, and a relatively flat geotherm over the
603 lower portions of the lid, result in significantly enhanced H flux. To fully explore the extent of
604 H diffusion, a 'hot exo-Venus' temperature profile was used assuming (1) a wet (1000 ppmw
605 H₂O), broadly peridotitic convecting mantle and olivine-rich lid, (2) a temperature at the top
606 of the convecting mantle just below the 1000 ppmw H₂O solidus, and (3) a surface T of 723
607 K. Within the bounds of the model this profile represents the hottest the base of the stagnant
608 lid can be before the onset of partial melting, for an approximately terrestrial mantle
609 composition. As shown in Figure 2, it lies between 6 and 7 K/km geothermal gradients.

610

611 The continual temperature reduction upwards through the stagnant lid with this profile results
612 in a sharp decrease in H diffusivity (Figure 2), ultimately producing steeper H concentration
613 gradients, as shown in figure 7. However, the effect of elevated temperatures relative to
614 other profiles is to increase H flux significantly. After 2 Gyr, D_F moves ~45 km into the lid
615 (~15, 25, 33, and 40 km after 100 Myr, 250 Myr, 500 Myr and 1 Gyr, respectively). More
616 importantly, S_F also progresses significantly into the lid, resulting in H₂O contents of around
617 1000 ppmw ~30 km into the lid after 2 Gyr, ~20 km after 1 Gyr and ~10 km after 500 Myr.
618 Due to starting conditions in this model the geotherm never intersects the 1000 ppmw H₂O,
619 and because water contents remain below the storage capacity, diffusion cannot induce
620 melting or stabilise a free fluid phase. For this to occur H would need to diffuse 60 km or

621 more into the lid, which, given that diffusivity is reduced markedly upwards, cannot feasibly
622 occur due to stagnation in H flux. Within this static model, therefore, regardless of the T
623 profile across the lid, diffusion of H will never induce lid melting on its own. The effect of any
624 progressive increase in temperature, i.e. for a stagnant lid regime planet slowly heating prior
625 to eventual lid overturn and a planetary resurfacing event, will instead be to initially induce
626 melting in the deeper convecting mantle. However, H diffusion can play an important role in
627 terms of H redistribution across the convecting mantle and lid. From figure 7 it is evident that
628 a slightly increased ambient mantle temperature results in hydration of the lowermost lid;
629 comparison with figure 4 highlights the dominant influence that temperatures across the
630 bottom of the lid have on the extent of S_F and D_F migration. For Venus, temperature profiles
631 remain, due to a lack of primary data, very poorly unconstrained. For other stagnant lid
632 planets, temperature profiles through the lid and the uppermost convecting mantle will define
633 the importance of H diffusion into the lid. If we assume that stagnant lid regimes are stable
634 up to 0.5 Gyr or longer, in between or in the absence of periods of global resurfacing, Venus
635 sized or larger hot exoplanets can be envisaged as having slightly 'leaky' stagnant lids.
636 Diffusion results in equilibration of H contents across the convecting mantle and lowermost
637 lid to distances of 10s of km or greater. Whilst this does not promote melting within the lid, it
638 does have the effect of significantly lowering the lid solidus, such that any thermal
639 perturbations, for example upwelling plumes, are much more likely to result in localised lid
640 melting.

641

642 **7. The importance of H diffusion and limitations in the model**

643 Whether H diffusion and lid hydration is important depends both on the temperature profile
644 across the lowermost lid in stagnant-lid regime planets, and lid stability. The temperature
645 profile across the Venusian mantle remains poorly constrained, and given the paucity of
646 data, a slightly hotter Venusian mantle is certainly not impossible. Higher mantle
647 temperatures will certainly occur in a given proportion of exo-Venus planets. It is also likely

648 that the interior of Venus was hotter earlier in the history of the planet and/or that Venus
649 undergoes periods of periodical heating and eventual global melting. As noted by Ghail
650 (2015), mechanisms which promote lid rejuvenation are of use in explaining heat flow in
651 stagnant lid regimes, which is otherwise much less efficient than with plate tectonics. It is
652 important to note, however, that modelling here is based on a number of simplified
653 assumptions. The lid is modelled as having a hazburgitic composition. This gives a
654 reasonable assessment of bulk H mobility in various systems, as H diffusivities in peridotitic
655 mineral assemblages, which are similarly olivine-dominant, will not be significantly different.
656 Much less certain remains mantle melt relations which are highly composition dependent,
657 and vary significantly with major element and volatile content. For a truly hazburgitic mantle
658 lid, melting is not expected to occur even in the presence of considerable H₂O. However,
659 such a lid composition is unrealistic; the solidus for more peridotitic compositions is
660 considerably lower, implying that H can have a variable influence on lid stability, but only
661 after geotherms are locally elevated by upwelling plumes. Likewise, for other bulk silicate
662 planetary compositions, mantle potential temperatures, and the extent of H flux, could be
663 significantly higher whilst lids remain stable. However, temperature gradients across the
664 mantle will also control thickness of the stagnant lid, so any assessment of H flux in hot
665 stagnant lid planets would require a detailed modelling of planetary evolution.

666

667 The starting distribution of volatiles in the model used is based on extreme convecting
668 mantle-lid fractionation, with a volatile-rich interior and anhydrous lid. More likely, lowermost
669 portions of the lid would incorporate some H, unless they represented true melt residue from
670 which volatiles were stripped, or regions of the mantle affected by previous melt processes.
671 However, the presence of pre-existing H in the lid does not influence H diffusion significantly,
672 as the effect of decreasing T upwards into the lid means that H flux stagnates, and the
673 maximum H content of the lid is always limited by H content in the convecting mantle.
674 Importantly, for the model presented here, regardless of lid H content and T profile, H

675 diffusion can never result in overstepping of a realistic 'wet' or 'damp' solidus, and melting
676 will always be initiated in the underlying convecting mantle.

677

678 The model developed here is static and assumes that the temperature profile through the lid
679 does not vary with time. It also assumes that the lid is stable and does not vary in thickness
680 or become altered by any geological process. This simplification allows varying diffusivity
681 across a complex geomaterial to be modelled, and importantly, the considerable influence of
682 varying temperature of volatile mobility to be assessed. Thermal structures of planets,
683 however, obviously vary significantly with time. The stagnant lid is itself the result of thermal
684 evolution of the entire planet, and represents a thermal boundary layer across which heat is
685 conducted from the convecting mantle to the surface. A more accurate assessment of H flux
686 would require a time-dependent model of the lid, including evolution of convecting mantle
687 temperature, of lid temperature and thickness, and also of crust thickness (Rolf et al., 2018).
688 However, the fact that diffusivities vary considerably with even small changes in temperature
689 would greatly add to the complexity of such a model, as would the fact that the presence of
690 H, and variations in H concentration, in turn have a disproportionate influence on physical
691 properties, notably both rheology and thermal stability (e.g. Peslier, 2010). Furthermore, a
692 more accurate assessment of the extent of H diffusion would require a more accurate initial
693 H distribution across the model. This distribution is dependent on factors such as magma
694 ocean crystallisation, which remain poorly constrained.

695

696 Results here suggest, within the limitations of a static model with simple imposed H
697 concentration gradient, that conditions towards the base of a model Venusian stagnant lid
698 are transitional between solid state diffusion effectively redistributing H and having no
699 meaningful effect. Aside from considerable uncertainties regarding the internal structure of
700 Venus and temperature profile through the lid it should also be noted that H diffusivities over
701 temperatures expected at the base of the lid are based on experimental data at considerably

702 lower temperatures (typically <1473 K for data used here). Diffusion laws for H in mantle
703 minerals are also variably constrained, adding to uncertainties in extrapolated H diffusivities.
704 Any appreciable H flux is insignificant in terms of volatile flux from the convecting mantle,
705 although its effect of mantle solidus would be to promote lid rejuvenation, for example during
706 plume heating. For exoplanets with higher temperatures across the stagnant lid, H diffusivity
707 is markedly increased, resulting in considerable H flux over 100 Myr timescales. Mature
708 stagnant lids in hotter, exoVenus planets can be envisioned as 'slightly leaky' in terms of H,
709 with diffusion destabilising the lowermost lid by reducing the mantle solidus. Given the
710 importance of H in terms of mantle properties ranging from melting behaviour to rheology,
711 future models of such planets should assess the effects of solid state diffusion of H.

712

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716

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969

970 **Figure 1. Simplified stagnant-lid regime model used in this study. Text denotes**
971 **composition of each part of the stagnant lid. Convecting mantle is assumed to be an**
972 **infinite reservoir for each volatile species (direction of flux shown by arrow).**

973

974 **Figure 2. Top: 4 model Venusian temperature profiles used to constrain variations in**
975 **temperature with depth across the model stagnant lid. See text for detailed**
976 **descriptions of each. Dashed grey lines are 5, 6 and 7 K/km geothermal gradients**
977 **based on a Venusian surface temperature of 735 K. Bottom: calculated effective**
978 **diffusivity for H for each modelled temperature profile, assuming fast lattice diffusion**
979 **in an oxidised stagnant lid.**

980

981 **Figure 3. Graphical representation of box modelling procedure used. A) depth (D),**
982 **temperature (T) and concentration of species (X) data used as the input to the first**
983 **time step in the model. B) shows a representative concentration (i.e. diffusion) profile**
984 **after time t. This concentration profile is then used as the input into the second time**
985 **step C), over which concentration changes in two shells are then modelled. D) The**
986 **output from the second time step is then used as the input into the next time step E).**
987 **This procedure is repeated upwards through the model.**

988

989 **Figure 4. H concentration profiles through the model stagnant lid after $t=100, 250, 500,$**
990 **1000 and 2000 Myr (from right to left) based on the Nimmo and McKenzie (1998)**
991 **temperature profile for Venus (black line). For comparison, the light grey line shows a**
992 **concentration profile based on an ‘infinite source’ solution to Fick’s second law after**
993 **2 Gyr (see text for details). Grey solid line marks the H₂O storage capacity of the lid,**
994 **based on solubility of H₂O in orthopyroxene and olivine (Bolfan-Casanova, 2005). At**
995 **water contents exceeding this value a free fluid phase or hydrous melt will be present.**
996 **Thin black line marks the hazburgite solidus (Maaloe, 2004), and dashed black lines**

997 denote the dry mantle (peridotite) solidus, and calculated effect of H₂O on depression
998 of the mantle solidus from Hirschmann (2006).

999

1000 **Figure 5. Comparison of concentration profiles for H₂O (both fast and slow H**
1001 **diffusion), C diffusion (by grain boundary diffusion only), He diffusion and Ar**
1002 **diffusion after 2 Gyr calculated based on a Nimmo and McKenzie (1998) Venusian**
1003 **tempearture profile.**

1004

1005 **Figure 6. Fast H concentration profiles through the model stagnant lid based on**
1006 **Venusian geotherms from Ghail et al. (2015). A. Black lines are model geotherms**
1007 **(Ghail, 2015) for an ambient stagnant lid (12 mWm⁻²) and a lid heated by thermal**
1008 **plumes (36 mWm⁻² for the centre of plume head; 18 mWm⁻² for a region adjacent to a**
1009 **mature plume). H concentration profiles for same time steps as Fig. 4 are based on a**
1010 **18 mWm⁻² geotherm. Grey lines and shaded fields mark melt relations in carbonated**
1011 **peridotite from Ghail (2015). B. H concentration profiles for a 12 mWm⁻² geotherm. C.**
1012 **H concentration profiles for a Ghail (2015) 18 mWm⁻² geotherm for initial stagnant lid**
1013 **water contents of 200 ppm.**

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1015 **Figure 7. H₂O concentration profiles based on a hypothetical 'hot Venusian' geotherm,**
1016 **or hot stagnant lid. Key same as figure 4.**

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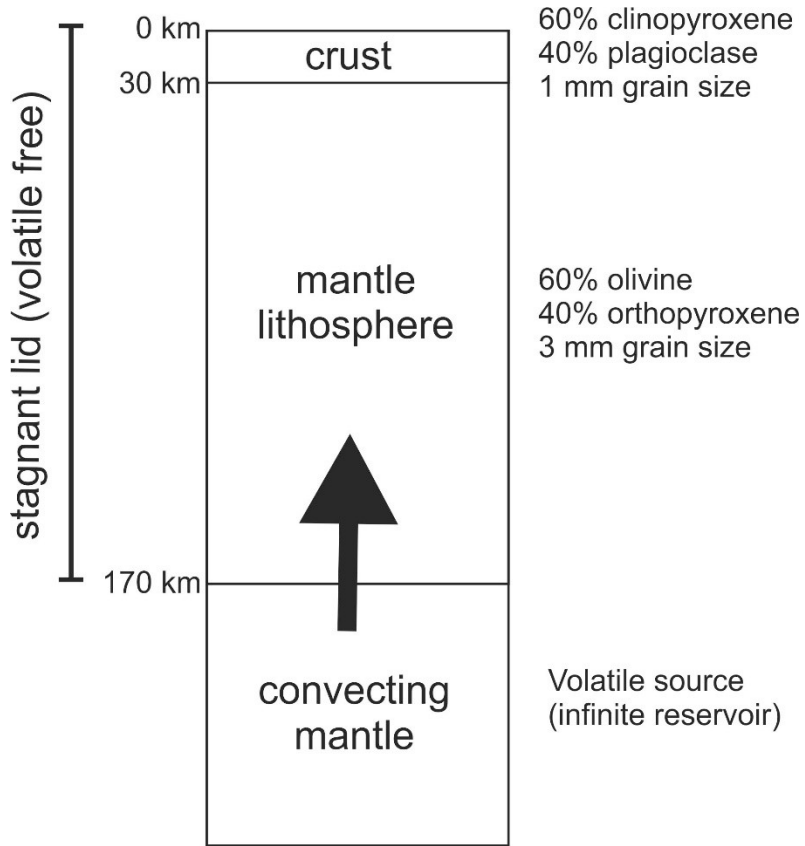
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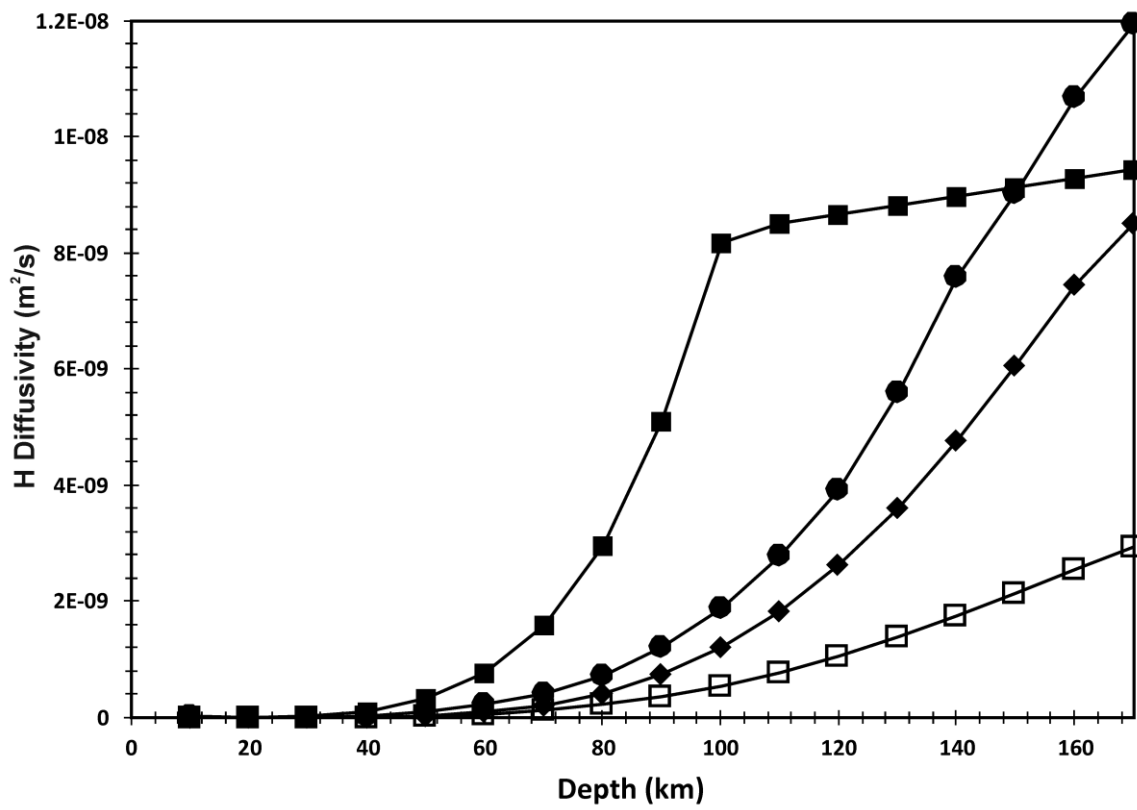
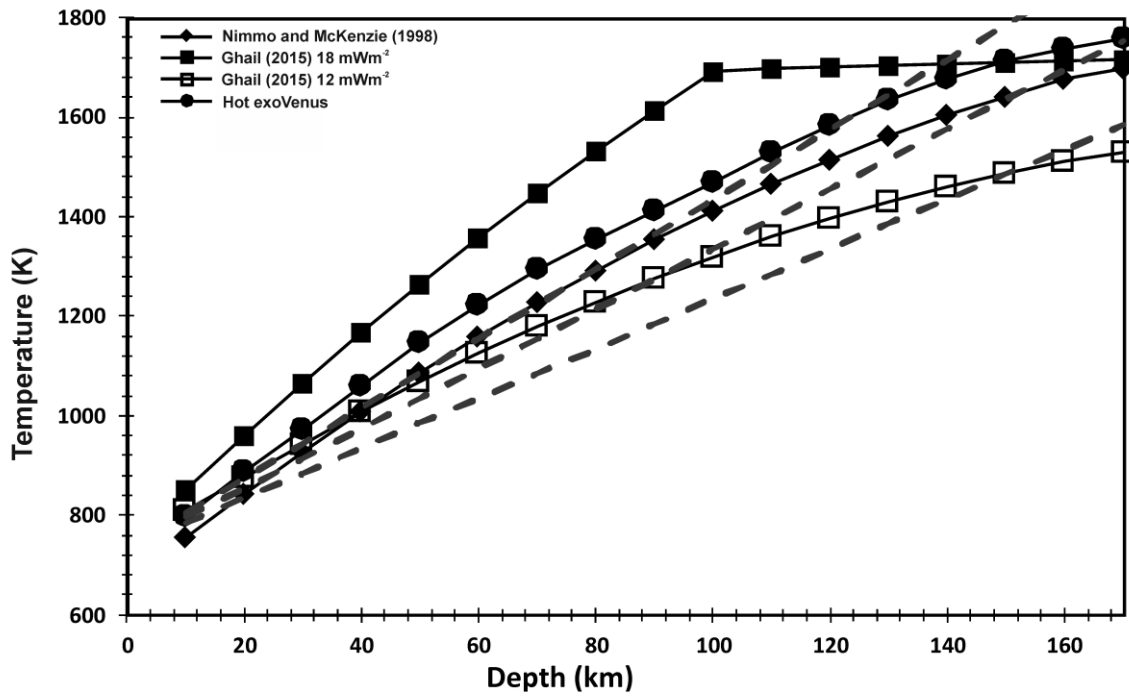
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1024 **Figure 1**
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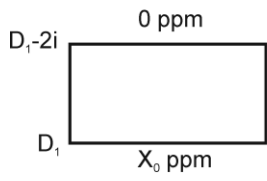
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1035 **Figure 2**
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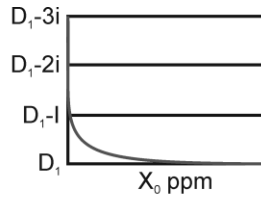


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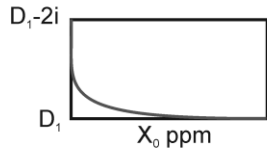
1039 **Figure 3**
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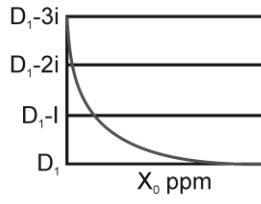
A) Initial Model Input



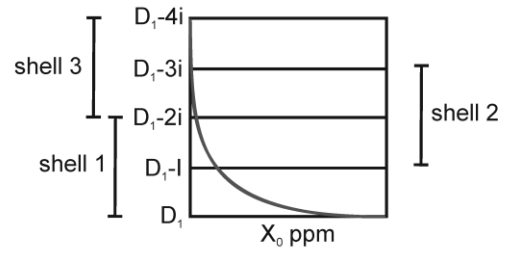
C) Input to time-step 2



B) Output after time-step 1



D) Output after time-step 2

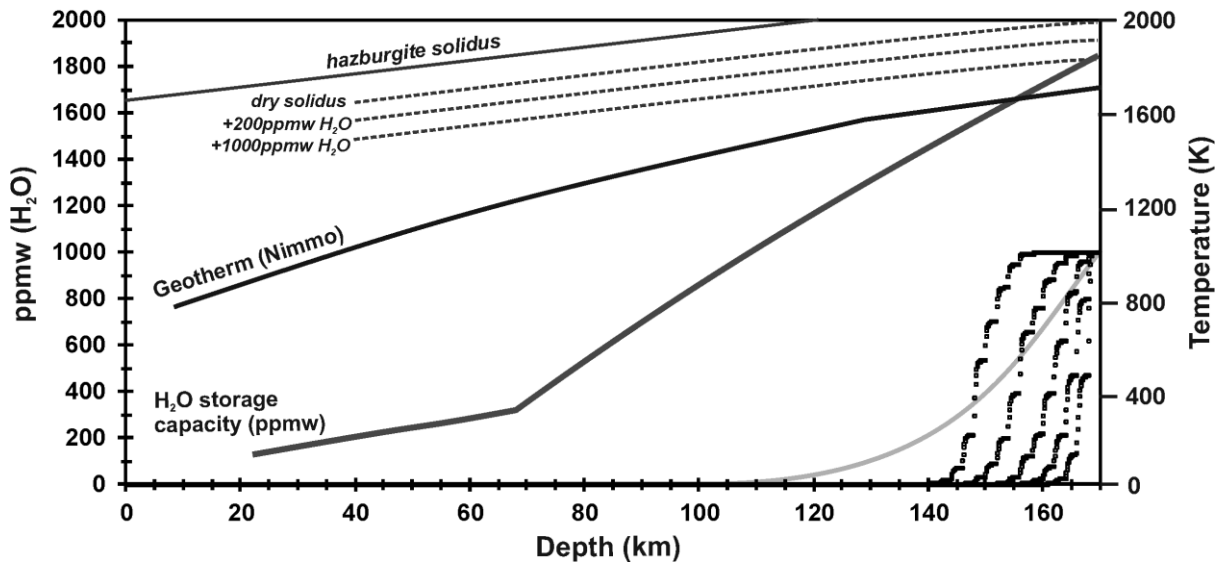


E) Input to time-step 3

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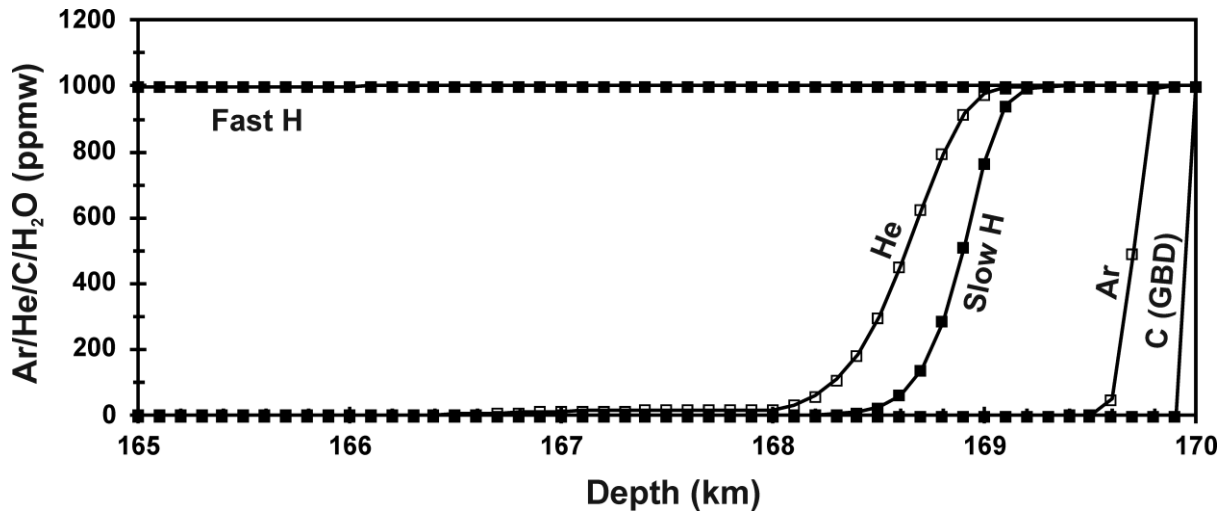
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1044 **Figure 4**
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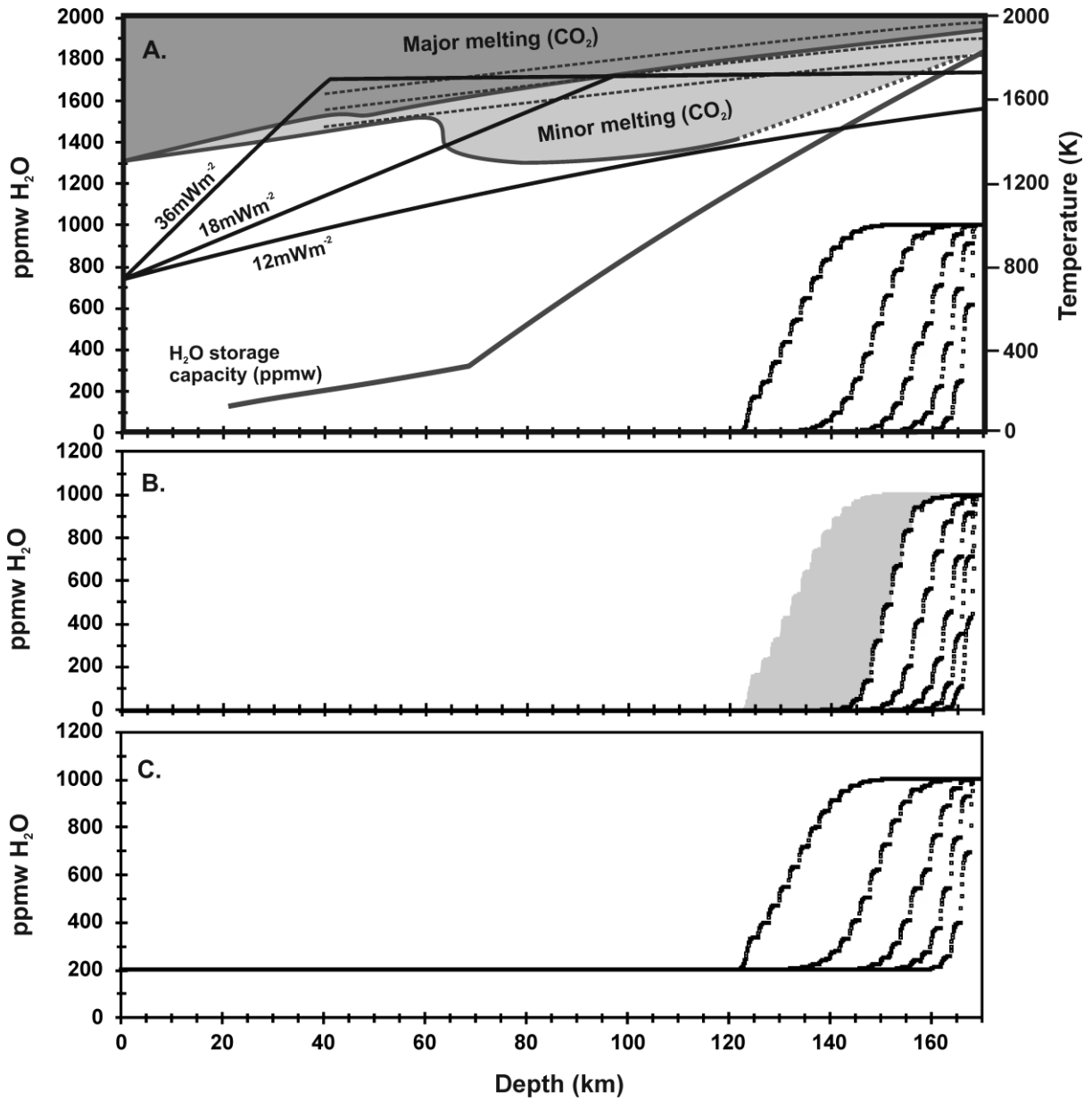
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1051 **Figure 5**
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1056 **Figure 6**
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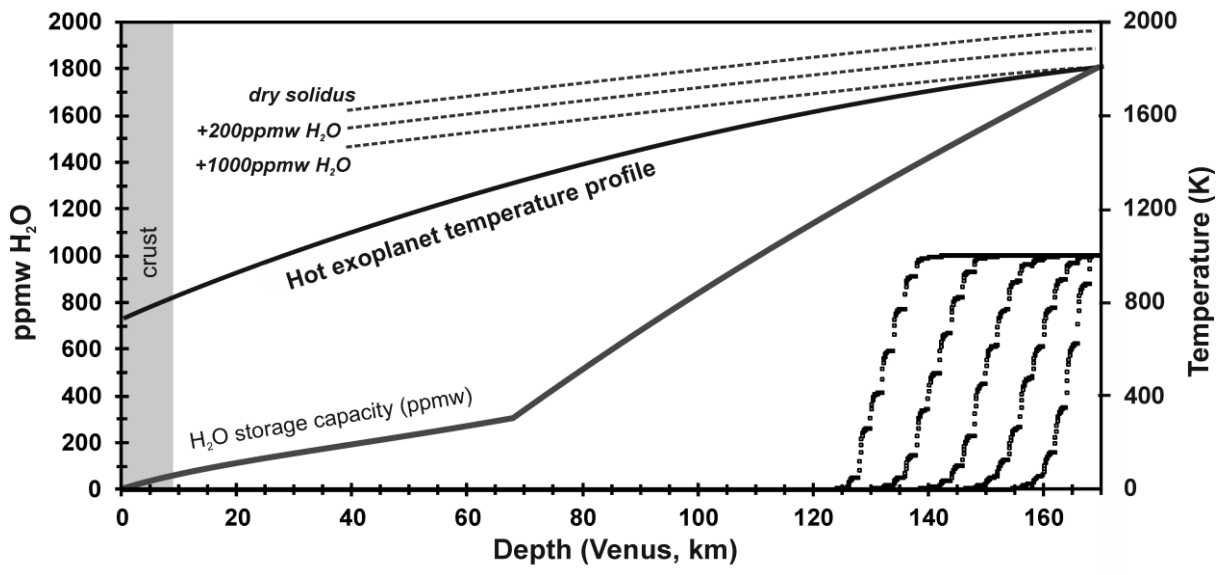


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Figure 7



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