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Solidus melting of pyrolite and bridgmanite: implication for the thermochemical state of the Earth's interior

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Abstract

17 Melting properties of the deep mantle remain controversial due to experimental difficulties; e.g., reports 18 of solidus temperatures of mantle-relevant compositions span over ~700K at 2000 km depth. This situation 19 limits our understanding of the thermochemical state of the Earth's interior. Using the laser heated diamond 20 anvil cell (LH-DAC), we performed new experimental determination of the solidus profile of ultra-dry 21 pyrolite and the solidus of two compositions of (Mg,Fe)(Si,Al)O₃ bridgmanite (Bg). Melting was detected (i) 22 from -the correlation between laser power and sample temperature, -changes of sample texture and -the level 23 of visible light absorption, for all samples, (ii) using X-ray diffraction, for the MgSiO₃ composition and (iii) 24 after scanning electron microscope observations, for selected Fe-bearing samples. Special care was given to 25 using ultra-dry experimental chambers and to determination of sample temperature. In particular, we discuss 26 the wavelength-dependent thermal emission of silicate samples, which lowers the solidus by 100 to 300K, 27 compared to the grey-body assumption.

28 The solidus of MgSiO₃-Bg is in good agreement with previous reports using *ab initio* calculations and 29 shock wave experiments. We observe a net decrease in the solid-liquid Clapeyron slope at 60(3) GPa and 30 4400(200) K, which can be related to rapid pressure-induced coordination change of Si in the melt. 31 (Mg_{0.955},Fe_{0.045})(Si_{0.993},Al_{0.007})O₃ Bg melts 600-800 K lower than MgSiO₃-Bg. Its solidus evolves smoothly 32 with pressure, suggesting progressive Si coordination change in the melt. In the pressure range investigated 33 (24-135 GPa) Clapeyron slopes suggest rapid decrease of the volume of fusion, from 14 to 2% for MgSiO₃ 34 and from 9 to 3% for (Fe,Al)-bearing Bg, assuming congruent melting. By comparing the solidii of various 35 silicates, it appears that the higher the number of cations, the less pronounced is the curvature of the solidus. 36 This observation suggests that the relatively ordered structure of simple liquid compositions with a limited 37 number of distinct network-modifying cations frustrates the coexistence of tetrahedrally and octahedrally 38 coordinated Si polyhedral.

39 The solidus of pyrolite presents a smooth evolution from 2200(100) K to 3950(200) K in the same 40 pressure interval. This is very similar to our previous work on chondritic-type mantle. The new solidus is 41 200-300 K lower than that of KLB-1 peridotite, which can be related to more incompatible elements in 42 pyrolite. It remains problematic that our solidus plots several 100 K higher than other recent measurements 43 performed on pyrolite; we discuss the possibility of a higher water content in previous samples, compared to 44 our experiments. Assuming a dry lowermost mantle, our results imply a core-mantle boundary temperature 45 lower than 3950(200) K. Modeling the melting diagram at the core-mantle boundary suggests a pseudo-46 eutectic melt significantly depleted in SiO₂, compared to the composition of the mean mantle.

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49 **Highlights**:

- 50 Mantle solidus evolves from 2200(100) and 3950(200) K with depth in lower mantle 51
 - Solidus of pyrolite suggests core-mantle boundary temperature lower than 3950(200)K
- 52 The initially steep solidus of MgSiO₃ bridgmanite flattens at 60(3) GPa
- 53 Silicate melts with more cations present smooth solidus evolution to CMB pressure
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- 55

56 Introduction

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58 Earth is very hot inside due to the major Moon forming impact that occurred 50-100 million years after 59 its accretion. The impact melted its interior almost entirely (Nakajima and Stevenson, 2015). For this reason, 60 mantle melting contributed largely to the internal dynamics of the Earth during its history. It is believed that 61 partial melting is still occurring today in specific mantle regions such as in the ultra-low velocity zones 62 (ULVZ) atop the core-mantle boundary (CMB; e.g. (Lay et al., 2004)) and the low-velocity layer between 63 350 and 410 km depth (LVL; e.g. (Tauzin et al., 2010)). Knowledge of the melting properties in the deep 64 mantle is key to refine our knowledge of mantle history. In this work, we limit our analysis to the 65 determination of the mantle solidus at lower mantle conditions.

66 There are not many reports on deep mantle melting, due to experimental and theoretical difficulties 67 associated with (i) the very high pressure involved, up to 135 GPa at the core-mantle boundary (CMB), and 68 (ii) the composition of the mantle with includes many elements. Ab initio calculations can be used to 69 estimate the solidii of pure phases, such as MgSiO₃ bridgmanite (Bg) (Stixrude et al., 2009); However, it 70 remains difficult to model the melting properties of more complex geological material. Similar limitation 71 occurs for shock wave experiments, for which it is difficult to investigate a mixture of phases. Another 72 limitation of shock waves is that melting is generally investigated along the Hugoniot; this limitation can be 73 alleviated by sample pre-heating, pre-compression, ramp compression and thermodynamical modeling 74 (Asimow, 2018).

Concerning static experiments, reproducing the P-T conditions typical of deep mantle melting requires today the use of the laser-heated diamond anvil cell (LH-DAC). LH-DAC has been used to determine melting properties for a long time, initially for simple compounds (e.g. (Zerr and Boehler, 1993)) and later for mantle relevant materials (Andrault et al., 2011; Fiquet et al., 2010; Nomura et al., 2014; Zerr et al., 1998). Still, there are major discrepancies between the different works. They can have several origins:

80 (i) Mantle composition: Previous works report the melting properties of either peridotitic, pyrolitic or 81 chondritic-type mantle compositions. They differ in their (Mg.Fe.Ca)/Si ratio, which corresponds to variable 82 fractions of the major minerals of the lower mantle: (Mg,Fe)(Si,Al)O₃ Bg, CaSiO₃ perovskite (very recently 83 named davemaoite, Dvm) and (Mg,Fe)O ferropericlase (Fp). More Fp is expected when going from pyrolite, 84 peridotite to harzburgite model compositions. Still, all these materials contain the same three phases and, 85 therefore, their melting behavior should not be very different. The solidus temperature, in particular, could be 86 very similar if eutectic-type melting prevails (Andrault et al., 2017; de Koker et al., 2013; Liebske and Frost, 87 2012). On the other hand, liquidus temperatures can be significantly different. The second aspect is the 88 content of minor and incompatible elements. The more the material is depleted, from chondritic-type to 89 pyrolite and peridotite, the purer the mineral phases (Bg, Fe and Dvm) must be (Corgne et al., 2005). This 90 can affect the melting properties of each mineral and, in return, modify slightly the mantle solidus. The 91 impact can be major when the mineral phases are saturated in a given incompatible element, which was 92 reported unlikely for typical mantle compositions (Irifune, 1994). Altogether, we are facing small changes of 93 composition. Slight changes of compositions between the materials relevant to the mean-mantle should have 94 a limited impact on the solidus, as long as the concentration of incompatible elements remains below the 95 limit of saturation of the mantle minerals (Irifune, 1994).

96 (ii) Melting criteria: several criteria have been used to detect the melting behavior: -change of optical 97 properties, -correlation between laser power and sample temperature, with possible appearance of a 98 temperature plateau and/or sudden temperature increase, -in situ monitoring of the phase content by X-ray 99 diffraction, -density contrasts using nano-tomography, -microstructure of recovered samples using electron 100 microscopy. Previous works generally use several of these criteria and report a good agreement between them in a same study. When using the LH-DAC, the detection of solidus is facilitated by the fact that the 101 102 solid and liquid fractions absorb the laser radiation differently. The change of absorption coefficient of bulk 103 sample upon melting induces a change of heating behavior that is clearly detectable (Geballe and Jeanloz, 104 2012). Consequently, it is unlikely that controversies about the solidus temperature arise from the melting 105 criteria. The situation is much more complicated for the determination of the liquidus temperature, for which 106 a robust criterion should inform on the complete disappearance (melting) of all minerals within the hot 107 sample region, for a locally well-known chemical composition.

(iii) Experimental conditions: Beyond the definition of melting criteria, performing melting experiments
using the LH-DAC remains difficult in many aspects. We emphasize two parameters that can have a major
impact on determination of the solidus: water content and temperature measurements. Concerning the former,
approaching "dry" conditions requires specific procedures. For example, annealing a powder in a vacuum
oven is certainly insufficient to remove the water absorbed at the surface of sample grains. In addition, the

113 sample loading in air inevitably contaminates the sample with atmospheric water. Water can significantly 114 lower the solidus, especially over the saturation limit of the mantle minerals. Concerning the latter: 115 temperature measurements at very high temperature were shown to be more reliable when using reflective 116 objectives, compared to refractive objectives (Giampaoli et al., 2018). In addition, refractive optics change 117 their chromatic response when the optical path is slightly modified, which is common during LH-DAC 118 experiments. The sample emissivity function should also be included in the temperature calculation.

119 In this work, we performed new measurements of the solidus temperature of several mantle materials, 120 using in house optical, in situ X-ray diffraction and post mortem sample characterization techniques, in order 121 to bring additional constraints on the melting behavior of the Earth's lower mantle.

124 Methods

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126 Samples and DAC loading

128 We used a membrane-type DAC mounted with beyeled diamonds and Re gaskets drilled using either 129 spark erosion or laser ablation. Depending on the target pressure, we used beveled diamond anvils of 130 250/300, 150/300, 100/300 or 75/300 µm internal/external diameters, gasket thicknesses from 45 µm to 15 131 µm and hole diameters from 95 µm to 25 µm. One fresh piece of sample was used for each melting point 132 determination. The nominal sample pressure was determined at 300 K from at least one of these methods: 133 fluorescence of a ruby chip positioned in the pressure medium, Raman shift of the diamond anvil at the 134 contact with the pressure medium (Suppl. Fig. 1), cell parameter of the KCl pressure medium determined 135 using X-ray diffraction (Dewaele et al., 2012). Uncertainty in the determination of the nominal pressure at 136 300K is a couple of GPa. Then, some thermal pressure develops in the sample at high temperature, due to 137 partially isochoric heating in the LH-DAC. We apply a pressure correction (ΔP_{corr}) of half the theoretical 138 thermal pressure (ΔP_{Th}), $\Delta P_{corr}=0.5\Delta P_{Th}=0.5(\alpha K_T)_{Bg}(T_{Exp}-300)$ (Andrault et al., 2020), αK_T is the product of 139 thermal expansion and isothermal bulk modulus of Bg (Fiquet et al., 2000), the most abundant phase in our samples, and T_{Exp} is the measured sample temperature. The final value of ΔP_{corr} is about 2.5 10^{-3} GPa per 140 Kelvin above 300 K, with an uncertainty \pm 5 % at the melting temperature. 141

142 As starting materials, we used a natural enstatite and two 143 synthetic glasses; pyrolite and MgSiO₃. To probe the solidus of 144 (Fe,Al)-bearing Bg, we selected a natural enstatite with low Fe and 145 Al, namely $(Mg_{0.955}, Fe_{0.045})(Si_{0.993}, Al_{0.007})O_3$ (Table 1). The reason for this choice is an ambiguous solidus obtained in a previous study for a 146 147 sample with high Fe and Al contents (Andrault et al., 2017), most 148 probably because of incongruent melting and chemical migrations. 149 The low Fe and Al contents in Bg are also relevant to melting 150 conditions in the lower mantle, because of the relatively incompatible 151 character of Fe and Al (Boujibar et al., 2016). On the other hand, the 152 MgSiO₃ glass was synthesized in a classical furnace, while the glass 153 of pyrolite (Table 1; (Ringwood, 1975)) was synthesized using the 154 laser levitation technique. For the latter, the mixture of powders was 155 carefully homogenized in an agate mortar and pre-compressed into a 156 sphere. Levitation above a nozzle is performed by monitoring the flux of Ar with less than 0.05 ppm of oxygen, which yields a $Fe^{3+}/\Sigma Fe$ 157 158 ratio of 7-8 % in the silicate glass. Using infrared spectroscopy, the 159 water content in the glass is found between 18 and 22 ppm, based on 160 the Beer-Lambert law and absorption coefficients given for basaltic

	Tuble 1. Composition of starting						
1	material determined using the						
•	electron microprobe.						
		Орх	Орх	Pyrolite	Pyrolite		
		JF15-67	JF15-67	Synth.	Synth.		
		Wt%	Mole%	Wt%	Mole%		
	SiO2	59.32	50.63	46.53	40.51		
	TiO2	0.00	0.00	0.01	0.01		
	Al2O3	0.33	0.17	4.55	2.34		
	Cr2O3	0.40	0.13	0.01	0.00		
	FeOt	3.10	2.21	8.57	6.24		
	MnO	0.06	0.00	0.02	0.01		
	MgO	36.47	46.40	37.55	48.74		
	CaO	0.35	0.32	2.11	1.97		
	Na2O	0.16	0.13	0.03	0.02		

Table 1. Composition of starting

FeOt	3.10	2.21	8.57	6.24
MnO	0.06	0.00	0.02	0.01
MgO	36.47	46.40	37.55	48.74
CaO	0.35	0.32	2.11	1.97
Na2O	0.16	0.13	0.03	0.02
K2O	0.02	0.00	0.28	0.15
Total	100.22	99.99	99.66	100.00

Fe/(Mg+Fe)

Al/(Al+Si)

Al/Fe

0.045

0.154

0.007

161 and basanitic glasses. A fragment of the starting material was loaded in the gasket hole between two layers of 162 the KCl pressure medium. KCl is a material of first-choice to study the melting properties of silicates in the 163 LH-DAC: - a very high melting temperature at high pressures, -no chemical reactions with silicates when it is dry, -good thermal insulation between hot-samples and cold-diamonds. The sample thickness was chosen to 164 165 be $\sim 1/3$ of the gasket thickness, in order to limit the axial thermal gradients. These gradients are invisible to 166 optical observations and yet the most critical ones in the LH-DAC.

167 We use special procedures to minimize the amount of water trapped in the pressure chamber: (i) all steps of the sample loading are performed inside a closed glove bag under a flux of dry air or N_2 . All the 168

0.113

0.750

0.104

169 necessary material is dry and inserted in advance in the bag where a numerical water sensor is permanently 170 operational. (ii) Coarse grains of KCl are kept in oven at 130-150 K all the time. (iii) The starting material 171 and a KCl grain are crushed inside the glove bag. We do not crush the sample in fine powder that inevitably 172 adsorb water. Instead, we load a shard of convenient size and shape in the gasket hole. Several criteria are 173 typical of a dry system, like no adhesion between the loaded materials and a needle, except for a weak 174 electrostatic bonding. Presence of humidity can also be detected optically at the surface of the diamond culet. 175 Then, when we would measure a melting temperature lower compared to previous measurements, we reload 176 the cell with new sample and loading tools, to check the melting temperature in another experiment.

177

178 *Optical set-up, laser heating and temperature measurements*179

180 We used two optical set-ups (i) for melting $MgSiO_3$ at ID27 and (ii) for all other experiments in LMV. 181 Both systems follow the basic principles established several years ago (Schultz et al., 2005): in particular, 182 they are both equipped with reflective optics. It was shown that they are superior to refractive optics for 183 determination of very high temperatures in the LH-DAC (Giampaoli et al., 2018). The new laser heating 184 system of LMV (Suppl. Fig. 2) is optimized for simultaneous temperature measurements on both sample 185 sides (using the TRax software (Holtgrewe et al., 2019)). On ID27, temperature was measured on both sample sides prior to performing angle-dispersive X-ray diffraction with monitoring of temperature on one 186 187 sample side only. The MgSiO₃ sample was first heated using a CO₂-laser (10µm radiation) until 188 crystallization of small grains of Bg made the sample slightly opaque to visible light. Then, two fiber lasers 189 (IPG fiber photonic lasers YLR-100-AC producing 1.03µm radiation) could heat the sample up to the 190 melting point. Similarly, fiber lasers were used to study the melting behavior of (Fe,Al)-bearing Bg and pyrolite. The two lasers arrive with an angle of incidence of about 15° with respect to the cell axis and are 191 192 focused on the sample using silica lenses with a focal length of 75 mm, or 50 mm when the pressure exceeds 193 ~80 GPa. The laser paths are remotely controlled using piezoelectric actuators.

194 Temperatures up to 5200 K were measured from the sample thermal emission in the visible range 195 (600 to 1000 nm; Suppl. Figs. 3-5). We dedicated a special care to cross-calibrate the optical response of 196 ID27 and LMV optical systems. For this, we used (i) a platinum heating wire calibrated on the melting points 197 of wollastonite (1817 K) and diopside (1664 K), (ii) a newly acquired commercial lamp calibrated on a 198 formal black body and (iii) an additional tungsten lamp calibrated at LMV and measured at ID27, and vice 199 versa. In addition, we reworked the general assumptions made on the sample emissivity function ($\varepsilon(\lambda)$), 200 which most commonly are (i) a grey-body sample (constant $\varepsilon(\lambda)$) or (ii) same $\varepsilon(\lambda)$ for the sample and the W-201 lamp. We found that the second one is more in agreement with the data available for $\varepsilon(\lambda)$ of silicates (see 202 (Andrault et al., 2022)). For a sample showing a wavelength-dependent (WD) emissivity, using the black 203 body (BB) assumption yields temperature (T_{BB}) overestimated by ~65, ~151, ~280 and ~464 K for a true sample temperature (T_{WD}) of 2000, 3000, 4000 and 5000 K, respectively; the 2nd-order polyhedral relation 204 between T_{BB} and T_{WD} is: $T_{BB}-T_{WD}=2.585 \ 10^{-5*}T_{WD}^2-4.814 \ 10^{-2*}T_{WD}+60.46$. A further argument in favor of 205 206 wavelength-dependent $\varepsilon(\lambda)$ for silicates is the solidii of SiO₂ (Andrault et al., 2022) and MgSiO₃ (see Result 207 section below) falling in very good agreement with shock wave experiments (Akins and Ahrens, 2002) and 208 ab initio calculations (e.g. (Usui and Tsuchiya, 2010)). Following this observation, we will propose a 209 temperature correction to the previous reports of the solidii of peridotite (Figuet et al., 2010) and chondritic-210 type mantle (Andrault et al., 2011).

Another major source of uncertainty comes from temperature gradients: Both optical systems used in this study analyze the thermal emission signal coming from a sample region of 2-3 microns diameter at the center of the laser spot, which minimizes the effect of radial temperature gradient. On the contrary, axial temperature gradients produce superimposition of thermal radiation spectra coming from sample regions at different temperatures, when probing an optically transparent sample. Still, the distortion could remain minor because the hottest region of the sample (i.e. where melting occurs first) provides the strongest contribution to thermal emission.

We note that the sample microstructure becomes heterogeneous after melting, due to melt migration. It affects the laser-absorption as well as the thermal emissivity function, potentially; It can yield distortion of the thermal emission spectrum. For this reason, we always use a fresh piece of sample for each determination of the melting temperature.

Finally, we noticed a higher temperature uncertainty when using the lasers at high power (when approaching 100 watts). Reasons for this can be (i) stronger axial temperature gradients in the DAC, yielding less stable temperature at the center of the sample, (ii) convection of air between the diamond cell and the schwarzchild objectives, inducing optical fluctuation, (iii) difficulties to detect the temperature vs laserpower plateau. For this reason, we favor loadings with thick layers of insulating KCl on both sides of a thin sample. Taking all possible precautions, the uncertainty of a given temperature measurement at the highest temperatures is ~50 K (Suppl. Fig. 3).

230 <u>Melting criteria</u>231

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232 To investigate melting of pure MgSiO₃-Bg, we monitored the change of structural properties using X-233 ray diffraction at the ID27 beamline, using the same procedure as in our recent work on SiO₂ (Andrault et al., 234 2020). With increasing temperature, the diffraction rings progressively evolve from coarse and rounded for 235 the compressed glass, continuous and very fine for nano-crystalline Bg, spotty after severe grain growth of 236 Bg grains and, finally, a few diffraction spots, which change positions very fast with time when the sample 237 gets molten. X-ray diffuse scattering of the melt also appears at the melting point (Andrault et al., 2020; 238 Figuet et al., 2010): However, we do not use amplitude of X-ray diffuse scattering and full disappearance of 239 all diffraction peaks as major criteria. The reason is the axial temperature gradient between the two diamonds, 240 which inevitably induce crystallization close to cold diamonds, while the melting temperature is already 241 reached at the center of the sample.

242 For Fe-bearing samples, crystallization was detected by changes in the absorption properties. Next, we 243 performed incremental steps of 0.2 to 0.4 watts during careful monitoring of the temperature, with a special 244 care to detect any anomaly in the sample behavior. An entire experiment generally takes ~30 minutes with a 245 time interval of 30 to 60 seconds between two temperatures. At a sample pressure of e.g. 138 GPa, three distinct sample behaviors can be distinguished (Fig. 1a, see also Suppl. Figs. 4 and 5): (i) a regular increase 246 247 of temperature for laser power between 12 and 32 watts. (ii) a plateau with no significant increase of 248 temperature for laser power between 32 to 52 watts. On the plateau, temperature fluctuations are less than 249 5%. This plateau is interpreted as a progressive increase of the melt fraction in the sample with laser power, 250 with a melt absorbing less the laser radiation than the solid part. This can happen for (Fe,Al)-Bg that contains 251 both Fe^{2+} and Fe^{3+} in large amounts, which implies good absorption of the 1 µm laser radiation. Less Bg implies a higher laser power for maintaining a similar sample temperature. This behavior was well 252 253 established based on the combination of several other melting criteria and modeling of the sample behavior 254 (Andrault et al., 2014; Geballe and Jeanloz, 2012; Thomson et al., 2014). (iii) a larger fluctuation of the 255 sample temperature with further increase of the laser power, before a jump to temperatures 1000 to 2000 K 256 higher than the temperature plateau. This arises when the laser power becomes sufficient to heat the melt 257 above the solidus. Another possible explanation is a low thermal conductivity of the melt, which would 258 induce a higher sample temperature in the sample center (Shen and Lazor, 1995). Altogether, the solidus 259 temperature and its uncertainty, between 50 to 150 K, are determined after averaging the highest 260 temperatures measured on the plateau.

261 After laser shutdown, the sample microstructure provides another criterion for occurrence of melting 262 (Fig. 1b). In particular, the presence of a dark blob at the center of the laser spot is a good indicator of melt 263 migration. The blob is often surrounded by a lighter shell of material, likely Bg depleted in Fe (Nabiei et al., 264 2021). We further characterized the microstructure of selected samples using high-resolution scanning 265 electron microscope (SEM) at CIMAP, following previous works of the same kind (Fiquet et al., 2010; 266 Nomura et al., 2011; Tateno et al., 2014). For this, we prepared thin sections using the focused Ga-ion beam 267 FIB. Cuts were performed perpendicularly to the sample surface across the laser-heated area, which yields an 268 observable sample surface along the paths of the infrared lasers between the two diamonds. Melting induces 269 solid-melt segregation, with a higher Fe-concentration in the melt easily detectable in the SEM (Fig. 1c, 270 (Nabiei et al., 2021)). We note that the microstructure of the molten regions can be complex due to fast 271 recrystallization upon quenching.



273 Figure 1: Melting criteria for LMV experiments: (a) Temperature as a function of increasing laser power 274 for a sample of pyrolite loaded at 138 GPa, yielding a solidus melting temperature of 3950(200) K. "Av" and 275 "Ar" temperatures are measured on each side of the sample. On bottom left, we report the temperature 276 difference between the two sides of the sample (b) Optical microphotograph showing a black spot at the 277 center of the sample after melting at 94 GPa. (c) SEM microphotograph (secondary electrons) of the melted 278 region at 65 GPa. There is central blob of melt enriched in Fe (darker zone; as in (Nabiei, 2017)), surrounded 279 by a first shell of Fe-depleted bridgmanite (lighter zone) and the un-molten pyrolite sample further from the 280 sample. Other examples of the experimental determination of solidii are reported in Suppl. Figs. 4 and 5. 281

283 **Results**

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285 <u>Solidus of MgSiO₃ bridgmanite</u>

287 The solidus of MgSiO₃ was determined from 10 different measurements performed at pressures between 288 35 GPa and 3400K, and 140 GPa and 5200 K (Fig. 2, Table 2). The data plot within the range of melting 289 temperature proposed in previous studies. Up to ~60 GPa, the slope of our solidus is comparable with 290 previous LH-DAC measurements on Al-free Bg (Shen and Lazor, 1995; Zerr and Boehler, 1993), even 291 though our melting temperature plots 200-300 K lower. This corresponds to a steep Clapeyron slope of ~42 292 K/GPa between ~25 and 60 GPa. At high mantle pressures, our MgSiO₃-Bg solidus is in good agreement 293 with previous ab initio calculations (de Koker and Stixrude, 2009) and shock wave experiments 294 (Mosenfelder et al., 2009). Between 60 and 140 GPa, the Clapeyron slope becomes ~10 K/GPa. Due to the 295 change of slope, we modeled the solidus using two different modified Simon and Glatzel equations 296 $[T=T_0(P/a+1)^{1/c}]$ (Simon and Glatzel, 1929): $T_0=274$ K, a=0.2644 GPa and c=1.9575 between 35 and 60 297 GPa, and $T_0 = 403$ K, a = 0.00028 GPa and c = 5.1377 between 60 and 140 GPa (Table 3). We note that while 298 the (T_0, a, b) parameters constrain the melting temperature at a given pressure, the slope and the curvature of 299 the melting curve, each parameter has no formal significance when taken independently of the other two, 300 especially for melting curves restricted to high pressure regions.

301 This change of behavior around 60 GPa denotes a marked change in the thermodynamic parameters, 302 most probably a decrease of the volume of fusion (ΔV_m), or a decrease in entropy of fusion, with increasing 303 pressure. Such effect could be due to higher compression rate of the melt, compared to Bg. A major 304 ingredient of melt compaction is the change of Si coordination number from 4 to 6. Our MgSiO₃ solidus 305 suggests a relatively abrupt Si coordination change in the melt at ~60 GPa. Using the Clapeyron relation 306 $(dT/dP = \Delta V_m / \Delta S_m)$ and an entropy change upon melting (ΔS_m) of 63.7 J/molK (Stixrude et al., 2009), we 307 estimate the volume of fusion for MgSiO₃. Based on the Simon and Glatzel equations, we obtain $\Delta V_m/V_{Bg}$ 308 (with V_{Bg} the molar volume of Bg) decreasing from 15% to 2% with increasing pressure from 25 to 135 GPa, 309 respectively (Fig. 3). The abruptness of the ΔV_m change at ~60 GPa is overestimated due to the use of 310 different equations above and below the transition pressure.



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Figure 2: Solidus of bridgmanite: We report our work on MgSiO₃ (blue dots) and (Mg_{0.955},Fe_{0.045})(Si_{0.993},Al_{0.007})O₃ (green dots) bridgmanite together with previous studies: LH-DAC on (Mg_{0.88}Fe_{0.12}SiO₃) (ZB-93, (Zerr and Boehler, 1993)), MgSiO₃ and Mg₃Al₂Si₃O₁₂ (SL-95; (Shen and Lazor, 1995)), shock waves on MgSiO₃ (AK-04; (Akins et al., 2004), M-09; (Mosenfelder et al., 2009)) and *ab initio* calculations for MgSiO₃ (KS; (de Koker and Stixrude, 2009), SK-05; (Stixrude and Karki, 2005)).

318 Solidus of $(Mg_{0.955}, Fe_{0.045})(Si_{0.993}, Al_{0.007})O_3$ bridgmanite

320 Twelve different measurements have been performed to determine the solidus of our (Fe,Al)-bearing Bg 321 compound. We note that this (Fe,Al)-bearing compound may not melt congruently at the solidus, however, 322 our experimental method cannot resolve the finite melting interval between the solidus and the liquidus. The 323 solidus is found between 500 and 1000 K lower than that of MgSiO₃, even though this enstatite sample presents relatively low Fe and Al contents, compared to mantle composition. Still, the several minor 324 325 elements present in this natural phase (Table 1) may also play a role in reducing the melting temperature. 326 The solidus appears more linear in the pressure range investigated, compared to MgSiO₃, which points out a 327 more progressive melt compaction. We acknowledge that our data set presents some scattering between 70 328 and 100 GPa, which may be related to chemical heterogeneities in the starting material. For this reason, we 329 reproduced the measurements several times. Nevertheless, the maximum temperature difference remains 330 within a reasonable range of uncertainties of 200-300 K. The entire solidus can be satisfactorily fitted using a 331 single Simon and Glatzel equation with $T_0= 241$ K, a= 0.03145 GPa and c= 2.8501 (Table 3). Its Clapeyron 332 slope evolves from ~28 to ~12 K/GPa in the pressure range investigated. Finally, we calculate ΔV_m based on 333 the same value of ΔS_m as for MgSiO₃. As expected from the difference in the solidii, ΔV_m decreases more progressively with increasing the pressure, compared to MgSiO₃ (Fig. 3). 334



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Figure 3: Volume of fusion $(\Delta V_m/V_{Bg})$ **for bridgmanite.** We report our data for MgSiO₃ and (Mg_{0.955},Fe_{0.045})(Si_{0.993},Al_{0.007})O₃ bridgmanite phases and MgSiO₃ $\Delta V_m/V_{Bg}$ obtained based on shock-wave experiments (Mosenfelder et al., 2009), ab initio calculations (Stixrude et al., 2009) and glass density measurements (Petitgirard et al., 2015). For MgSiO₃ data, our calculation overestimates the sharpness of the transition at ~60 GPa.

342 <u>Solidus of dry pyrolite</u>343

344 We performed 39 determination of the melting for our pyrolite glass (Table 2). In the lower mantle, 345 pyrolite yields a mineral assemblage made of Bg, Dvm and Fp. As a result, progressive sample melting is 346 expected between the solidus and liquidus temperatures. In this study, we dedicated our experimental efforts 347 to the determination of the solidus profile (Fig 4). It exhibits a smooth evolution from 2200(100) K to 348 3950(200) K for pressures between 24 GPa (the 660 km depth discontinuity) to 140 GPa (close to CMB), 349 respectively. The solidus presents a significant curvature, which corresponds to a Clapeyron slope evolving 350 from 28 to 13 K/GPa in the pressure range investigated, which is very similar to the values obtained for our 351 (Fe,Al)-Bg compound. Still, the solidus of pyrolite plots 500-600 K lower. In addition to 3 phases, instead of 352 one for (Fe,Al)-bearing Bg, pyrolite contains a significantly larger amount of incompatible elements, which 353 can also contribute to lowering the solidus.

354 In the low pressure range, our solidus plots in very good agreement with our recent determination of the 355 solidus at pressures up to 27 GPa, using the multi-anvil apparatus (Pierru et al., 2022). We note that higher 356 melting temperatures were proposed for the melting of mantle-relevant materials in the upper mantle and 357 transition zone (e.g. (Litasov and Ohtani, 2002; Tronnes and Frost, 2002)). The discrepancy may arise from 358 several factors, including a rather high melt fraction reported in previous work. This matter is discussed at 359 length elsewhere (Andrault et al., 2018; Pierru et al., 2022). To provide a convenient model for the pyrolite 360 solidus at all mantle pressures, we coupled the two data sets on the same pyrolitic sample and fitted two 361 Simon and Glatzel equations (Fig. 4). We obtain T_0 = 1609 K, a= 61.1176 GPa and c= 1.1288 for the pressure 362 range between 5 and 24 GPa and T_0 = 235 K, a= 0.0300 GPa and c= 3.0067 between 24 and 138 GPa (Table 363 3).



Figure 4: Solidus of pyrolite: Data sets from multi-anvil press ((Pierru et al., 2022), blue dots) and diamond anvil cell from this work (orange dots) are combined to determine the solidus of pyrolite at all mantlerelevant pressures.

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374	Table 2: Experimental data: Summary of
375	all experimental measurements of solidii
376	reported in this work
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MgSiO3		(Fe,Al)-bea	ring Bg	Pyrolite			
P(GPa)	Т(К)	P(GPa)	Т(К)	P(GPa)	Т(К)	(continued	d)
58.1	4321	33.2	2780	24.1	2184	69.0	3080
65.5	4479	36.5	2800	29.4	2230	69.8	3039
96.2	4790	33.2	2780	31.5	2364	71.9	3072
113.6	4942	36.5	2800	40.6	2579	82.2	3175
122.8	5018	45.1	3152	43.0	2638	84.3	3225
137.2	5167	47.0	3100	43.1	2670	84.3	3230
40.0	3504	71.5	3700	45.0	2775	88.3	3385
69.5	4479	73.4	3900	46.7	2721	88.9	3378
36.4	3462	79.9	3850	46.7	2738	90.1	3373
48.2	3959	91.2	3986	50.4	2867	90.4	3357
		95.9	3850	56.1	2955	91.7	3366
		99.2	3966	56.3	3021	102.2	3579
		108.7	4171	59.0	2906	104.6	3530
		145.0	4691	62.8	3023	104.7	3565
				63.2	3016	105.9	3450
				63.4	3118	111.2	3575
				63.6	3163	117.4	3664
				65.4	3116	121.5	3715
				65.9	3041	133.0	3900
						138.3	4000

Table 3: Melting equations: Summary of the parameters
refined for Simon&Glatzel melting equations through
data points of MgSiO₃ and our (Fe,Al)-bearing Bg, and
pyrolite.

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Simon et Glatze			
Compound	MgSiO3	(Fe,Al)-Bg	Pyrolite
P-range (GPa)	35-60	32-145	5-24.
T0 (K)	274	241	1609
a (GPa)	0.2644	0.03145	61.118
C	1.9575	2.8501	1.1288
P-range (GPa)	60-140		24-138
T0 (K)	403		235
a (GPa)	0.00028		0.0300
C	5.1377		3.0067

393 Discussion

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395 <u>Mantle solidus: Comparison between different studies</u>

397 We compare our pyrolite solidus with other recent determinations of the solidus for various mantle 398 relevant compositions (Fig. 5). We make the following observations: (i) Our solidus plots 300-400 K lower 399 than that reported for peridotite (F-10; (Fiquet et al., 2010)). (ii) It is very compatible with many studies 400 between 20 and 50 GPa; however the different studies diverge at higher mantle pressures to become (iii) 401 100-150 K lower than that reported for chondritic-type mantle (A-11; (Andrault et al., 2011)) and (iv) 300-500 K higher than other reports for pyrolite by (N-14; (Nomura et al., 2014)) and (K-20; (Kim et al., 2020)) 402 403 at the CMB conditions. At this point, we note that F-10, A-11 and our new study were performed in very 404 similar conditions, in particular with same type of synthetic starting material and similar optical systems 405 mounted with reflective objectives. A major difference, however, is how the sample emissivity $\varepsilon(\lambda)$ was 406 considered to calculate temperatures from thermal emission. F-10 and A-11 assume a grey-body function (i.e. 407 $\varepsilon(\lambda)$ =constant), while this method could induce artifacts (Deng et al., 2017). Unfortunately, $\varepsilon(\lambda)$ is not 408 known for silicates at the high P-T investigated in this study. So far, the most appropriated assumption could 409 be same $\varepsilon(\lambda)$ as the W-lamp (see (Andrault et al., 2022)). We calculate a temperature correction, of a couple 410 100 K, that would account for wavelength-dependent thermal emission of peridotite and chondritic-type 411 mantle in previous studies (light orange and purple bands in Fig. 5). For A-11, we also include in the 412 calculation the solidus data points reported for the same sample based on multi-anvil press work (Andrault et 413 al., 2018). Interestingly, the corrected chondritic-type solidus falls in perfect agreement with our pyrolite 414 solidus. This result is coherent with the small difference between these two compositions, which have a 415 similar fertility (amount of minor incompatible elements) and for which the main differences are the Bg, 416 Dvm and Fp phase fractions. Concerning F-10 data, the corrected values plot 200-300 K above ours, which 417 could be due to a more depleted peridotite composition. The three data sets (F-10, A-11 and our pyrolite data) 418 converge to a solidus temperature of 3950(200) K at the 135 GPa of the CMB. 419



Figure 5: Solidus temperatures of various mantle materials. We plot the new pyrolite solidus (P-22) together with previous reports (F-10, (Fiquet et al., 2010); A-11, (Andrault et al., 2011); N-14, (Nomura et al., 2014); K-20, (Kim et al., 2020)). For F-10 and A-11, we report both the original solidii (thin orange and purple lines) and the corrected solidii (light but thicker lines indicated by black arrows) for which temperatures have been recalculated taking take into account the wavelength-dependent thermal emission (see text).

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427 The N-14 and K-20 data sets that plot significantly lower than ours, for which the most likely 428 explanation is the presence of some water in these experiments. Noticeably, the K-20 data set plots at lower 429 temperatures than N-14, for which the reported water content in the sample is 400 ppm. In K-20 work, 430 vacuum oven was used to dry powders before loading and then to dry the entire DAC after loading. In our 431 previous experience on melting of chondritic-type mantle (Andrault et al., 2011), we did not succeeded to 432 reproduce the solidus using starting materials made of powders, and always found much lower temperatures. 433 Our explanation is that annealing temperatures much higher than e.g. 150°C (i.e. oven) are needed to remove 434 the water adsorbed at the surface of the grains. Fine powders can adsorb a significant amount of water in a 435 few minutes. For this reason, we use chips of glass for the loading in the DAC and all loadings are performed 436 in a glove bag flushed with inert atmosphere.

437438 Comparison of the curvatures of solidii

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440 We plot together the solidii of various silicate phases. To strengthen the comparison, we selected the 441 works performed using the same methodology (Fig. 6); in addition to compositions discussed above, we include SiO₂ (see (Andrault et al., 2020) and its "comment" taking into account its wavelength-dependent 442 443 behavior (Andrault et al., 2022)) and mid-ocean ridge basalt (MORB; (Andrault et al., 2014), also corrected 444 here for its $\varepsilon(\lambda)$). As logically expected, the larger the amount of cations entering in the sample composition 445 $[N_{Cat}]$, from 1 to 6 between pure SiO₂ and our pyrolite sample, the lower is the solidus. Another interesting 446 observation is the curvature of the melting slope, which (i) is significantly less pronounced and (ii) appears at 447 higher pressure, with increasing N_{Cat}. A sharp change of the Clapeyron slope is found around 40 GPa for 448 SiO₂, it is also clear at 60 GPa for MgSiO₃, one could argue for a deviation in the 60-80 GPa range for 449 (Mg_{0.955},Fe_{0.045})(Si_{0.993},Al_{0.007})O₃ Bg, and the solidi present a progressive change between ~40 and ~100 GPa 450 for mantle-relevant peridotitic, chondritic-type, or pyrolitic compositions. Since this curvature denotes a 451 change of the volume of fusion with increasing pressure, the observed trend is consistent with a more abrupt 452 change in the cation coordination number when N_{Cat} is smaller. The major structural change at mantle depth 453 being the Si coordination change from 4 to 6, it suggests that the coexistence in the melt of the two structural 454 entities, SiO₄ and SiO₆, is facilitated for a larger number of cations. Interestingly, the MORB solidus is 455 significantly more curved than the mean-mantle relevant compositions. This effect could arise from a higher 456 SiO₂ content in this material.



Figure 6: Solidii of various silicates. To improve the strength of the comparison, we only report the solidii
of silicate phases determined using the same experimental techniques, in particular (i) reflective objectives
that offer a best temperature measurement at high temperature (Giampaoli et al., 2018) and (ii) dry glasses
loaded using a glove bag flowed by inert atmosphere. SiO₂ (Andrault et al., 2020; Andrault et al., 2022),
peridotite (Fiquet et al., 2000), chondritic-type mantle (Andrault et al., 2011), MORB (Andrault et al., 2014)
and MgSiO₃, (Mg_{0.955},Fe_{0.045})(Si_{0.993},Al_{0.007})O₃, and pyrolite (this work).

464 465 *Building the melting diagram at mantle depth: example of the core-mantle boundary*

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467 Several approaches have been developed to discuss the thermodynamics of mantle melting in the lower 468 mantle. One of them consists in refining the thermodynamical properties of silicate melts with end-member 469 compositions, such as MgSiO₃, MgO, SiO₂, etc., using either first-principles molecular dynamics simulations 470 or shock-wave experiments (Asimow, 2018; de Koker et al., 2013; Mosenfelder et al., 2009; Stixrude et al., 471 2009; Stixrude and Karki, 2005). Then, melting properties of mantle-relevant compositions can be modeled 472 based on well-defined mixing properties between the end-members. In this work, we provide directly the 473 solidii, which unfortunately does not help to constrain the basic thermodynamic parameters, but which can 474 help constraining the melting diagrams.

475 If we leave to further works the goal to solve the controversy about the solidus of pyrolite, there is an 476 overall good coherence on the solidii of the different silicate compositions (Fig. 6). If we focus on the CMB, 477 data sets (F-10, A-11 and this work) converge to a solidus mantle temperature of 3950(200) K (Fig. 5). In 478 these conditions, the melt composition is not well constrained and it anyway depends on the degree of partial 479 melting. Nevertheless, previous studies performed at less extreme pressures suggest a pseudo-eutectic melt 480 composition close to peridotite, based on multi-anvil press (Ito et al., 2004) and LH-DAC experiments (e.g. 481 (Tateno et al., 2014)). Based on this, we draw a pseudo-binary phase diagram between MgSiO₃-Bg and a 482 mixture of the other oxides (Fig. 7; see details of the strategy in (Andrault et al., 2017)). We model a linear 483 solidus profile from the melting temperature of MgSiO₃-Bg and our (Fe,Al)-bearing Bg. Similarly, a linear liquidus profile is drawn from melting point of MgSiO₃-Bg to the liquidus temperature of the chondritic-type 484 485 mantle (Andrault et al., 2011). The linear extrapolation of the liquidus to a pseudo-eutectic temperature of 486 3950 K yields an estimated composition of the pseudo-eutectic melt. Here, we do not consider the liquidus 487 temperature of ~5400 K proposed for peridotite at the CMB (Figuet et al., 2010), because such experimental 488 temperature corresponds more likely to the melting temperature of pure Bg. 489



Figure 7: Melting diagram of silicate mantle at the CMB pressure of 135 GPa: A pseudo binary diagram is presented in which one pole is MgSiO₃ bridgmanite and a second one regroups all other elements (FeO, CaO, Al₂O₃ and MgO). The left blue vertical line corresponds to the composition of bridgmanite investigated in this study. The second vertical line corresponds to typical mantle compositions. We compare our estimate of the melt composition at the pseudo-eutectic temperature (purple ellipse) with previous reports in the MgO-MgSiO₃ system (de Koker et al., 2013; Ohnishi et al., 2017; Ozawa et al., 2018; Usui and Tsuchiya, 2010).

497 The melting diagram (Fig. 7) yields important information: -the higher the Bg content, the closer the 498 solidus temperature is to that of the MgSiO₃-Bg end-member. -The Bg grains in equilibrium with mantle melts should be significantly enriched in Fe and Al with decreasing temperature below the liquidus. -The 499 500 pseudo-eutectic melt composition at the CMB should be significantly depleted in SiO₂ (i.e. enriched in FeO, 501 CaO, MgO and/or Al₂O₃), compared to classical models of mean mantle composition. Our estimated value 502 plots within the interval of values reported for the simplified MgO-MgSiO₃ composition at the CMB (de Koker et al., 2013; Ohnishi et al., 2017; Ozawa et al., 2018; Usui and Tsuchiya, 2010) -Finally, the 503 504 difference between solidus and liquidus reaches a maximum of ~700 K for a mantle composition with ~90% 505 of MgSiO₃ and it decreases progressively with increasing the Fp and Dvm contents up to the pseudo-eutectic 506 composition (where solidus and liquidus temperatures are equal).

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Thermal state of the core-mantle boundary

510 Extrapolation of the mantle geotherm along an adiabatic gradient to the 135 GPa yields a value of 511 ~2630 K(60) at the CMB, based on the elastic parameters of the mantle constituent minerals (Katsura et al., 512 2010). This does not take into account a possible super-adiabatic temperature gradient in the lower mantle. 513 By performing global inversion of seismic radial profiles based on compressional and shear properties of the 514 minerals, the lowermost mantle temperature was refined between 2800 and 3400 K (Matas et al., 2007). 515 Such type of modeling is poorly sensitive to the rapid change of temperature occurring in the thermal 516 boundary layer extending a few 100 km above the CMB. It was proposed that the Bg to post-Bg transition, 517 which is sharp for MgSiO₃ composition, provides a constraint for the temperature in this region (Hernlund, 518 2010). Supposing that the loop-shaped low-velocity regions of the lowermost mantle correspond to a double 519 crossing between the mantle temperature profile and the Clapeyron slope of this transition, the CMB 520 temperature is estimated at ~3700 K (Tateno et al., 2009). Unfortunately, the Bg to post-Bg transition is 521 progressive and occurs at too high pressures for a relevant (Fe,Al)-bearing mantle compositions (Andrault et 522 al., 2010; Catalli et al., 2009), which shed doubts on this method. From core properties, the CMB 523 temperature is estimated to ~4050 K, based on the melting point of a relevant Fe-alloy at the inner-core 524 boundary (Anzellini et al., 2013).

A CMB temperature of 4050 K would be similar or higher than the mantle solidus, which we refine at 525 526 3950(200) K for 135 GPa in this study (Fig. 5). It would induce global mantle melting at the contact of the 527 core, which is incompatible with seismic observations of ULVZ (e.g. (Yu and Garnero, 2018)). Instead, the 528 CMB temperature should be lower than ~3950 K. Uncertainties remain regarding the fertility of the mantle 529 located above the CMB, which could range from undepleted primitive to recycled peridotite compositions. 530 The more the material is depleted, the higher its solidus and the higher could be the CMB temperature. The 531 material that lies on the CMB could also be of a different nature, which we discuss below. Anyhow, it is very 532 possible that the mantle geotherm reaches ~3950 K at the CMB, given the strong temperature increase when 533 approaching the CMB. Then, a local enrichment in incompatible and/or volatile elements could depress the 534 mantle solidus by several 100 K and induce melting in specific regions, producing the ultra-low velocity 535 zones (Yu and Garnero, 2018). The nature of the chemical heterogeneities remains uncertain. Many of the 536 incompatible elements, such as Na and K, may have a moderate effect on the solidus temperature, as they 537 can be incorporated into the structure of Dvm (Corgne et al., 2005; Irifune, 1994). In contrast, H₂O could 538 depress the mantle solidus significantly, possibly down to 3400-3500 K if we assume that water explains the 539 difference between our study and the previous experimental works (Kim et al., 2020; Nomura et al., 2014). 540 Finally, the melting of basalt was reported at a temperature of 3600 K (corrected from (Andrault et al., 2014) 541 for wavelength-dependent $\varepsilon(\lambda)$), which is slightly lower than the melting point of the mantle. Altogether, this brackets the CMB temperature between 3600 and 3950 K, or between 3400-3500 and 3950 K, if melting of 542 543 e.g. pyrolitic in ULVZ is triggered by a high concentration of incompatible elements, or water, respectively. 544

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Solidus melting of pyrolite and bridgmanite: implication for the thermochemical state of the Earth's interior

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<u>Supplementary material caption</u>: The supplementary material contains several figures:

- Suppl. Fig. 1: Pressure measurement using Raman spectroscopy
- Suppl. Fig. 2: LH-DAC experimental set-up developed at the LMV
- Suppl. Fig. 3: Investigation of the uncertainty of temperature measurement
- Suppl. Fig. 4: Series of thermal emission spectra recorded up to the solidus temperature
 - Suppl. Fig. 5: Typical laser power vs temperature plateaus

21 Supplementary Figures

Suppl. Fig. 1: Pressure measurement using Raman spectroscopy. Pressure is calculated from the shift of the inflection point (blue lines) of Raman spectrum recorded at room (red) and high (black) pressure. Raman spectra are recorded on the surface of the diamond culet as close as possible from the sample. In this example, the inflection point shifts from 1310.8 +/-0.5 cm⁻¹ and 1524.5 +/-2.0 cm⁻¹ yielding a nominal pressure (at 300K) of 108.7 +/- 2.5 GPa.



36 37 Suppl. Fig. 2: LH-DAC experimental set-up 38 developed at the LMV. Main components are 39 the water-cooled diamond anvil cell, two fiber 40 lasers focused on the compressed sample with an 41 degrees. angle of ~15 two reflective 42 Schwarzschild objectives, a camera to visualize 43 the laser spots on both sample sides and a 44 spectrometer to determine the sample pressure 45 and temperature on both sides simultaneously.

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Spectrometer: double grating CCD: camera MP : Mirror with Pinholes S : External Shutter L : Convex Lens: f=50 or 75mm FO : Clean-up Filter SF : Short range pass Filter NF : Notch Filter ND : Neutral Density Filter Camera : with Zoom



55 Suppl. Fig. 3: Investigation of the 56 uncertainty of temperature 57 measurement. A same thermal emission 58 spectrum recorded at the solidus of 59 pyrolite at ~138 GPa is fitted using 4 60 different ranges of wavelengths: from 640, 61 660, 680 or 700 nm to ~990 nm. The 4 62 adjustments yield temperatures between 4017 and 4080 K. The best fit is obtained 63 64 when using the narrowest range of 65 wavelengths; however, the fit quality may 66 be misleading. When using a wider range of wavelengths, the quality of the fit is 67 68 degraded due to a lower signal intensity at 69 wavelengths shorter than ~700 nm. This 70 effect could arise from a stronger 71 interaction between light and electrons at



high light energies, inducing a relatively low sample emissivity (i.e. high sample absorption). Still, this type
of effects are not known well and could also affect other regions of the recorded thermal emission spectra.
As a compromise, it arises that a sample temperature of 4040 +/- 25 K is compatible with the fits performed
over a wide range of wavelengths.

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79 Suppl. Fig. 4: Series of thermal emission spectra recorded up to the solidus temperature: (a)
80 Bridgmanite at 45 GPa (b) Pyrolite at 138 GPa.





84 Suppl. Fig. 5: Typical laser power vs 85 temperature plateaus: Evolution of the sample temperature with increasing laser power for 86 87 bridgmanite at 45 GPa and 109 GPa (upper and 88 middle frames) and pyrolite at 138 GPa (lower 89 frame). Temperature remains below the solidus 90 on the plateau; we therefore determine the 91 solidus temperature by averaging the highest 92 temperatures. 93

