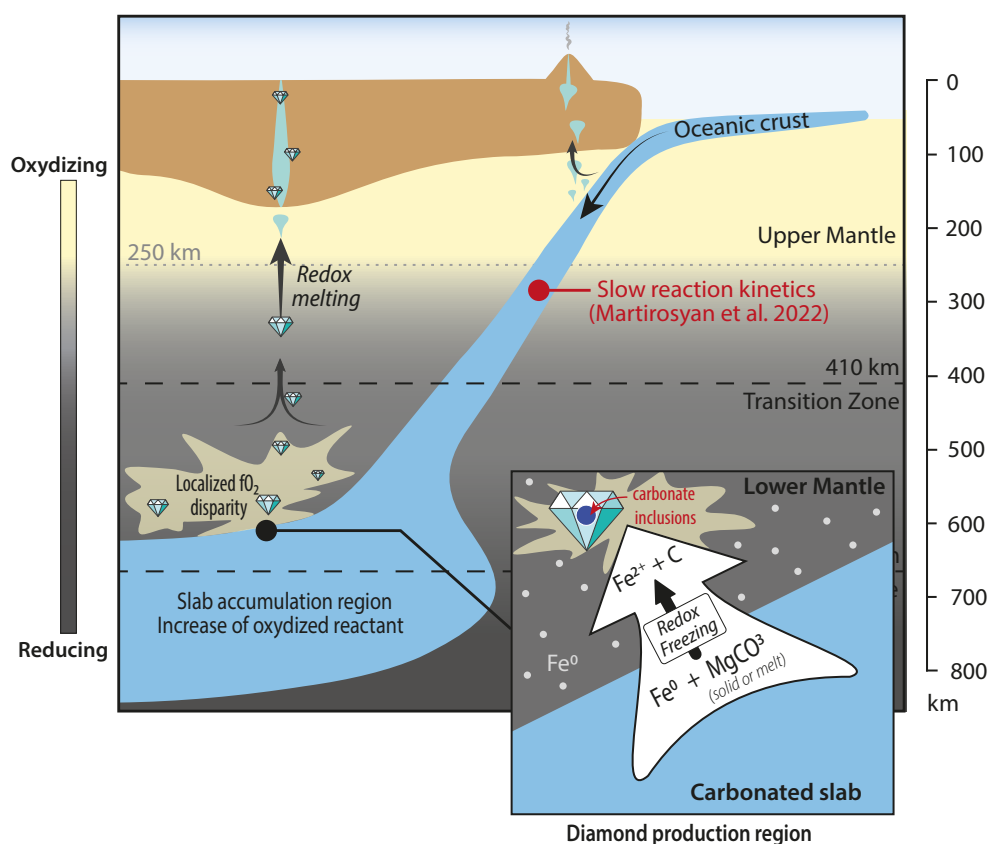


# Graphical Abstract

## Reevaluating the fate of subducted magnesite in the Earth's lower mantle.

Lélia Libon, Georg Spiekermann, Ingrid Blanchard, Johannes M. Kaa, Serena Dominijanni, Melanie J. Sieber, Mirko Förster, Christian Albers, Wolfgang Morgenroth, Catherine McCammon, Anja Schreiber, Vladimir Roddatis, Konstantin Glazyrin, Rachel J. Husband, Louis Hennet, Karen Appel, Max Wilke



## Highlights

### **Reevaluating the fate of subducted magnesite in the Earth's lower mantle.**

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- The stability of magnesite ( $\text{MgCO}_3$ ) was investigated in the presence of iron-bearing bridgmanite at conditions from 25 to 68 GPa and temperatures covering all subduction geotherms (1350 K to 2000 K).
- Magnesite reacts with iron-bearing bridgmanite to form diamonds at conditions relevant to the coldest geotherm.
- Subduction of magnesite, and more generally carbonates, is limited to the top of the lower mantle ( $\sim 700$  km depths), even along cold slabs geotherm.

# Reevaluating the fate of subducted magnesite in the Earth's lower mantle.

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## Abstract

The role that subducted carbonates play in sourcing and storing carbon in the deep Earth's interior is uncertain, primarily due to poor constraints on the stability of carbonate minerals when interacting with mantle phases. Magnesite ( $\text{MgCO}_3$ ) is the most prominent carbonate phase to be present at all mantle pressure-temperature conditions. In this study, we combined

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multi-anvil apparatus and laser-heated diamond anvil cell experiments to investigate the stability of magnesite in contact with iron-bearing bridgmanite. We examined the presence of melt, decarbonation, and diamond formation at shallow to mid-lower mantle conditions (25 to 68 GPa; 1350 to 2000 K). Our main observation indicates that magnesite is not stable at shallow lower mantle conditions. At 25 GPa and under oxidizing conditions, melting of magnesite is observed in multi-anvil experiments at temperatures corresponding to all geotherms except the coldest ones. Whereas, at higher pressures and under reducing conditions, in our laser-heated diamond-anvil cell experiments, diamond nucleation is observed as a sub-solidus process even at temperatures relevant to the coldest slab geotherms. Our results indicate that magnesite was reduced and formed diamonds when in contact with the ambient peridotite mantle at depths corresponding to the shallowest lower mantle (33 GPa). Thus, we establish that solid magnesite decomposes at depths of  $\sim 700$  km as it contacts the ambient mantle. Consequently, the recycling of carbonates will hinder their transport deeper into the lower mantle.

*Keywords:* Deep carbon cycle, Lower mantle, Carbonates, Diamond formation, Decarbonation

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## 1. Introduction

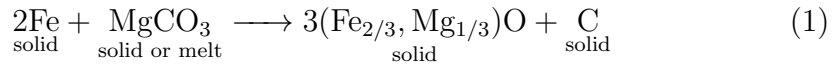
Over geologic time, carbon moved between surface and deeper reservoirs, impacting the atmospheric, oceanic, and crustal  $\text{CO}_2$  budget (Plank and Manning, 2019; Kelemen and Manning, 2015). The carbonates entrapped in subducting slabs have significant potential to transport carbon from the

6 Earth’s surface to its deep interior. The flux of carbon reaching the deep  
7 mantle beyond the volcanic arc remains highly uncertain, with estimates  
8 broadly ranging from 0.0001 to 52 Mt of C per year (Kelemen and Manning,  
9 2015). This uncertainty largely stems from a limited understanding regarding  
10 the survival of carbonate minerals during their transport to deep mantle  
11 conditions. Indeed, carbonates contained within oceanic crust sediments are  
12 expected to be recycled beneath the volcanic arc, with carbon returning to the  
13 surface environment through volcanic degassing and magmatism. Current  
14 constraints suggest that a significant amount of carbonates may survive the  
15 first 150 km of subduction and make it deeper into the Earth’s deep mantle  
16 (Molina and Poli, 2000; Connolly, 2005; Gorman et al., 2006; Kerrick and  
17 Connolly, 2001).

18 Transport of carbonates to at least the transition zone has been pro-  
19 posed based on the presence of carbonate inclusions in super-deep diamonds  
20 (Brenker et al., 2007; Kaminsky et al., 2016; Wirth et al., 2009). Such dia-  
21 monds originate from depths greater than 250 km, and provide direct insight  
22 into the deep carbon reservoir. As subducted carbonates may provide an  
23 appreciable contribution of carbon to the deep mantle, it is imperative to  
24 thoroughly explore the stability of carbonate minerals from upper to lower  
25 mantle conditions.

26 In order to ”survive” subduction to the deep mantle, carbonates must  
27 avoid re-mobilizing processes such as melting and decarbonation. Investiga-  
28 tions on melting temperatures of carbonated oceanic crust have been central  
29 to better understand the behavior of deeply subducted oceanic crust and  
30 surrounding mantle. Deeply subducted carbonates decrease the melting tem-

31 perature of mantle peridotite by several hundreds of degrees (Dasgupta and  
 32 Hirschmann, 2006; Brey et al., 2008; Litasov and Ohtani, 2009; Ghosh et al.,  
 33 2009). Previous experimental studies have constrained the melting tempera-  
 34 ture of carbonated peridotite ( $\sim 1950$  K at 23 GPa) and carbonated MORB  
 35 ( $\sim 1450$  K at 20 GPa) and identified a barrier for carbonate subduction at  
 36 transition zone depths due to melting (Thomson et al., 2016b; Rohrbach and  
 37 Schmidt, 2011; Kiseeva et al., 2013). When oxidized carbonate-rich melts  
 38 are released into the surrounding reduced mantle at depths greater than  
 39 250 km, they are unstable and get reduced to form diamonds (Rohrbach and  
 40 Schmidt, 2011). This is also evidenced by carbon isotope composition of  
 41 sublithospheric diamonds and their mineral inclusions (Walter et al. (2022)  
 42 and references therein). Indeed, the stabilization of a (Fe, Ni)-metal phase  
 43 beyond  $\sim 250$  km depths, due to the disproportionation of FeO into  $\text{Fe}_2\text{O}_3$   
 44 +  $\text{Fe}^{\text{metal}}$  ( $\text{Fe}^0$ ) (Frost et al., 2004; Rohrbach et al., 2007; Frost and McCam-  
 45 mon, 2008), constrains the mantle’s oxygen fugacity ( $f\text{O}_2$ ) at values around  
 46 the iron-wüstite (IW) buffer. Such conditions impose a relative buffering  
 47 capacity within the deep mantle that favors the reduction of carbonates and  
 48 carbonated melts to form diamonds through the ‘redox freezing’ reaction  
 49 (Eq.1) (Rohrbach and Schmidt, 2011; McCammon et al., 2020):



50 Accordingly, ‘redox freezing’ provides an effective mechanism for diamond  
 51 crystallization across the mantle at depths from  $\sim 250$  to  $\sim 700$  km, and  
 52 contributes to the barrier that hinders carbonate transport into the deep  
 53 Earth (Thomson et al., 2016b; Rohrbach and Schmidt, 2011).

54 Despite evidence for a melting barrier that limits the preservation of sub-  
 55 ducted carbonates, it has been proposed that solid carbonates may bypass  
 56 melting and reach the lower mantle if carried in cold subducting slabs (Thom-  
 57 son et al., 2016b, 2014; Kiseeva et al., 2013). Among those carbonates, mag-  
 58 nesite ( $\text{MgCO}_3$ ) is the most likely carbonate phase to be preserved within  
 59 subducted oceanic crust that reaches the lower mantle due to (1) its pro-  
 60 duction during the transformation of major carbonates (dolomite and cal-  
 61 cite/aragonite) at pressure conditions from 3 to 9 GPa (Yaxley and Brey,  
 62 2004; Sato and Katsura, 2001; Luth, 2001) and (2) as a single phase magne-  
 63 site and its high-pressure polymorph ( $\text{MgCO}_3\text{-II}$ ) are stable as solid phases  
 64 throughout all pressure and temperature conditions of the Earth’s mantle  
 65 (Binck et al., 2020; Isshiki et al., 2004; Solopova et al., 2015).

66 Experimental investigations have shown that magnesite is the preferred  
 67 stable carbonate in contact with  $\text{CaSiO}_3$  up to  $\sim 80$  GPa (Biellmann et al.,  
 68 1993; Lv et al., 2021). However, magnesite may become unstable as it reacts  
 69 with  $\text{SiO}_2$  to form diamonds or  $\text{CO}_2 + \text{MgSiO}_3$  even at sub-solidus tem-  
 70 peratures (Drewitt et al., 2019; Maeda et al., 2017; Takafuji et al., 2006;  
 71 Litasov and Shatskiy, 2019; Koziol and Newton, 1995; Kakizawa et al., 2015;  
 72 Seto et al., 2008). Most recently, Drewitt et al. (2019) proposed that the  
 73 deepest plausible carbon survival barrier exists at mid-lower mantle depths  
 74 ( $\sim 60$  GPa) under very cold subduction geotherm conditions. The authors  
 75 observed the decarbonation of magnesite in the absence of melting in laser-  
 76 heated diamond anvil cell (LH-DAC) experiments. However, carbonates en-  
 77 tering the lower mantle ( $\geq 660$  km) will encounter reducing conditions with a  
 78 considerable buffering capacity, as the lower mantle is expected to contain an

79 average of  $\sim 1$  wt% metallic-Fe ( $\text{Fe}^0$ ) (Frost and McCammon, 2008). Whereas  
 80 previous studies have primarily considered simplified iron-free systems with  
 81 magnesite reacting with free  $\text{SiO}_2$ , the role of iron in carbonate-silicate in-  
 82 teractions remains unclear. Even when iron (as  $\text{FeO}$ ) has previously been  
 83 included in the experimental system (e.g., Drewitt et al. (2019)), its po-  
 84 tential to influence redox-sensitive phases such as carbonates, as well as its  
 85 elemental partitioning was not discussed. Subducted carbonates will be in  
 86 contact with metallic iron as they reach the lower mantle. In an effort to  
 87 model such redox interactions, experimental investigations of the  $\text{MgCO}_3$   
 88 +  $\text{Fe}^0$  reaction were conducted at lower mantle conditions, revealing that  
 89 magnesite’s redox-breakdown is a viable sub-solidus mechanism to form dia-  
 90 monds (Dorfman et al., 2018; Martirosyan et al., 2019; Zhu et al., 2019). To  
 91 thoroughly understand the transportation of carbonates in the deep Earth,  
 92 experimental studies of multi-component, natural-like systems are required  
 93 at controlled pressure and temperature and defined redox conditions (Stagno  
 94 et al., 2019).

95 This study further explores the fate of magnesite subducted into the lower  
 96 mantle. We examine the stability of magnesite in co-existence with the most  
 97 abundant lower mantle mineral, bridgmanite  $(\text{Mg, Fe})\text{SiO}_3$ . In particular,  
 98 we assess the processes of decarbonation, melting, and diamond formation  
 99 at lower mantle conditions, in which Fe is likely to play a crucial role. We  
 100 conducted high-pressure experiments with two experimental techniques: (1)  
 101 large-volume press experiments using multi-anvil apparatuses were conducted  
 102 to better assess the presence of melt at the top of the lower mantle (25 GPa  
 103 and 1600 to 2000 K), and (2) LH-DAC experiments were conducted to assess



104 the magnesite-silicate interaction over a wider range of pressures (from top  
105 to mid-lower mantle conditions; 33 to 75 GPa) and temperatures (covering  
106 all subduction geotherms; 1300 to 2000 K). Our system aims to serve as an  
107 analog for reactions that occur between the mantle and carbonated subducted  
108 slabs.

## 109 **2. Material and methods**

### 110 *2.1. Starting materials*

111 All experiments started with natural magnesite ( $\text{Mg}_{0.99}\text{Ca}_{0.01}\text{CO}_3$ ) (<0.5 wt%  
112 of trace elements) (Table 1) mixed with a silicate reactant. Three magnesite-  
113 silicate mixtures were used as starting materials: (1) MG11 = magnesite  
114 + silicate glass in a 1:1 ratio (14 pressure-temperature points) (2) MG13  
115 = magnesite + silicate glass in a 1:3 ratio (2 pressure-temperature points)  
116 and (3) MO11 = magnesite + olivine in a 1:1 ratio (4 pressure-temperature  
117 points). Our synthetic silicate glass used in MG11 and MG13 was synthesized  
118 at ICMN (Orléans, France) by the aerodynamic levitation technique (Hennet  
119 et al., 2002; Auzende et al., 2011). The composition of  $\text{Mg}_{0.8}\text{Fe}_{0.2}\text{SiO}_3$  (Table  
120 1), was purposefully designed for this study to reflect a typical composition  
121 of bridgmanite. Argon (99.999% 2-3 ppm  $\text{O}_2$ ) was used as a levitating gas  
122 to ensure a reducing atmosphere at around  $\log f\text{O}_2 \sim -5.5$  to minimize the  
123 amount of ferric iron in the glass but the content of ferric iron in the synthetic  
124 glass was not analyzed.

125 However, using the calibration of O'Neill et al. (2018) and temperature  
126 of 1600 °C a  $\text{Fe}^{3+}/\sum\text{Fe} \leq 0.03$  can be estimated. In MO11 mixture, single  
127 crystals of olivine ( $\text{Mg}_{1.82}\text{Fe}_{0.17}\text{SiO}_4$ ) was used. In addition, for multi-anvil

128 experiments, two silicate glasses were synthesized with the same stoichiomet-  
129 ric composition but doped with either Sr or La ( $\sim 4000$  ppm and  $\sim 5600$  ppm,  
130 respectively, Table 1) and will be referred as MG11:Sr and MG11:La. The  
131 addition of these incompatible elements (Sr and La) served to trace the pres-  
132 ence of melt in our experiments.

wt%	magnesite (15)	glass (25)	Sr:glass (60)	La:glass (17)	olivine (10)
SiO <sub>2</sub>	-	55.51(0.30)	57.47(0.36)	58.55(0.35)	40.87(0.18)
Al <sub>2</sub> O <sub>3</sub>	-	0.42(0.03)	0.45(0.03)	0.45(0.04)	-
FeO	0.05(0.03)	13.71(0.28)	13.48(0.36)	12.04(0.33)	8.23(0.10)
MgO	46.95(0.56)	29.37(0.24)	27.40(0.23)	27.85(0.36)	49.10(0.21)
CaO	0.92(0.32)	-	-	-	0.06(0.004)
MnO	0.01(0.01)	-	-	-	0.12(0.02)
CO <sub>2</sub> <sup>a</sup>	51.97(0.37)	-	-	-	-
SrO	-	-	0.67(0.07)	-	-
La <sub>2</sub> O <sub>3</sub>	-	-	-	0.48(0.07)	-
Total		99.01	99.47	99.37	98.38
Mg#	-	79.3	78.4	80.5	91.4

**Table 1:** Chemical composition of starting materials measured by EPMA (wt%). Numbers in parentheses next to the phase names are the number of analyses averaged. The number in parentheses next to the measurement refers to the standard deviation ( $1\sigma$ ).  
<sup>a</sup>Calculated from the total deficit from the analyses.  $\text{Mg\#} = [\text{Mg}/(\text{Mg}+\text{Fe}+\text{Ca})]\times 100$

133 For LH-DAC experiments, approximately 10 wt.% of Pt-black (platinum  
134 powder) was added to only MO11 as a laser coupler, but not for the other  
135 compositions (MG13 and MG11). All starting materials were powder mix-

136 tures ground in an agate mortar with acetone for 20 minutes to achieve  
137 homogenization and to ensure a grain size  $<5\text{ }\mu\text{m}$ . Each starting material  
138 was checked before mixing by electron microprobe (EPMA) and kept in an  
139 oven ( $\sim 120\text{--}150\text{ }^{\circ}\text{C}$ ) to limit the absorption of atmospheric water over time.

## 140 *2.2. High-pressure and high-temperature experiments and analyses*

141 Two high-pressure devices were used: (1) the multi-anvil apparatus al-  
142 lowed for large sample volume and investigation of quenched run products by  
143 EPMA and scanning electron microscopy (SEM). (2) LH-DAC offered in situ  
144 characterization through the transparent diamond windows, at the expense  
145 of sample size.

### 146 *2.2.1. Multi-anvil apparatus experiments*

147 Experiments were conducted at  $25\pm 1\text{ GPa}$  and  $1600\text{--}2000\pm 100\text{ K}$  for 1 to  
148  $\sim 2$  hours (Table 2) using a Hymag 1000t and a Sumitomo 1200t multi-anvil  
149 apparatus installed at the Bayerisches Geoinstitut (BGI, Germany). Tung-  
150 sten carbide (WC) anvils of 3 mm truncation edge length (TEL) were used  
151 with a 7 mm edge length  $\text{Cr}_2\text{O}_3$ -doped MgO octahedron (OEL), referred to  
152 as 7/3 (OEL/TEL) assembly. The starting materials were either MG11:Sr  
153 (Exp. #4 and #7) or MG11:La (Exp. #4b, #5, #6 and #9) enclosed in  
154  $\sim 1\text{ mm} \times \sim 0.8\text{ mm}$  (length  $\times$  diameter) folded rhenium capsules to prevent  
155 Fe loss. High temperatures were achieved with a cylindrical  $\text{LaCrO}_3$  heater  
156 and kept constant within  $\pm 20\text{ }^{\circ}\text{C}$ . Temperatures were estimated either with  
157 D-type thermocouples ( $\text{W}_{97\%}\text{Re}_{3\%}\text{--}\text{W}_{75\%}\text{Re}_{25\%}$ ) placed horizontally through  
158 the wall of the furnace in direct contact with the capsule, or by the heating  
159 power (W) versus temperature ( $^{\circ}\text{C}$ ) calibration with an accuracy of  $\pm 100\text{ }^{\circ}\text{C}$

160 (Keppler and Frost, 2005). Each experiment contained one capsule except for  
 161 run #4 in which two capsules (#4a and #4b) were placed in one assembly.  
 162 More details on the cell assembly can be found in Fig. S???. The samples  
 163 were quenched by switching off the electrical power and then decompressed  
 164 to ambient pressure overnight ( $\sim 15$  hours). After the experiments, the re-  
 165 covered samples were mounted in epoxy, polished using diamond sprayed  
 166 aluminum pads at BGI, and then, carbon-coated, and examined at the Uni-  
 167 versity of Potsdam for textural features with SEM (Fig. 1A) and for major  
 168 element compositions with an EPMA JEOL JXA-8200. A 15 keV and 15 nA  
 169 beam and a ZAF matrix correction were used. The beam diameter varied  
 170 depending on the phases being analyzed; 2  $\mu\text{m}$  for silicate minerals, 5  $\mu\text{m}$  for  
 171 carbonate minerals, and 5 to 7  $\mu\text{m}$  for average melt composition measured in  
 172 the dendritic quenched-melt (QM) texture. The EPMA standards used for  
 173 silicate phase measurements were either garnet and diopside or clinopyroxene  
 174 and orthopyroxene for Al, Fe, Mg, Ca, and Si, albite for Na, strontianite for  
 175 Sr, and lanthanum-phosphate for La. For the carbonate phase and quenched  
 176 melt measurements, standards were dolomite for Ca and Mg, siderite for Fe,  
 177 strontianite for Sr, lanthanum-phosphate for La, and albite for Na.  $\text{CO}_2$   
 178 concentrations were not quantified but calculated from the deficit of the an-  
 179 alytical totals (Table S??).

### 180 2.2.2. *Laser-heated diamond anvil cell experiments*

181 LH-DAC experiments were performed from 33 to 75 GPa and 1300 to  
 182 2050 K using BX90 diamond anvil cells (Kantor et al., 2012) and diamond  
 183 anvils of 300 or 200  $\mu\text{m}$  culets depending on the target pressure. Rhenium  
 184 gaskets were indented to a thickness of 35 to 45  $\mu\text{m}$  and then drilled to

185 produce sample chambers from 80 to 130  $\mu\text{m}$  in diameter. Compressed 15 to  
186 20  $\mu\text{m}$  thick starting material platelets with a diameter equivalent to the ones  
187 of the sample chambers were loaded between two layers of NaCl to isolate our  
188 sample from the diamond anvils, and to limit C diffusion. One experiment  
189 without magnesite (ON34), containing only a compressed platelet of silicate  
190 glass in between insulating NaCl layers, was carried out at 43 GPa and  
191 1300 K to investigate the run products issued from the glass crystallization  
192 itself. Each cell was placed in an oven at  $\sim 120\text{--}150$   $^{\circ}\text{C}$  overnight prior to  
193 compression to minimize water absorption before closing. The experimental  
194 conditions and run products of each experiment are reported in Table S??.

195 The pressure was determined before and after laser heating using the shift  
196 of the Raman peak of the diamond anvil at the culet (Hanfland et al., 1986)  
197 using the calibration scale of Akahama and Kawamura (2006) with a mea-  
198 surement accuracy of  $\pm 2$  GPa and verified using the equation of state of the  
199 NaCl pressure medium (Fei et al., 2007) after heating. Reported pressures  
200 are those measured from the diamond anvil post-heating, which typically  
201 differed by  $< 4\%$  to the pre-heating pressure. Pressure measured from the  
202 NaCl medium differed by  $\pm 2$  GPa from the diamond anvil post-heating pres-  
203 sure. No corrections were made for thermal pressure during heating, but the  
204 pressure during laser heating may be estimated to be about 10% higher than  
205 the pre-heating pressure at the modest temperatures achieved in this study  
206 (Fiquet et al., 2010).

207 Synchrotron in situ X-ray diffraction (XRD) measurements were car-  
208 ried out at the Extreme Conditions Beamline (ECB, P02.2) at PETRA III,  
209 in Hamburg (Germany) (Liermann et al., 2015). High-temperature condi-

210 tions were achieved by using a double-sided YAG fiber laser emitting at  
 211 1072 nm with a Gaussian shape and a spot size of 20  $\mu\text{m}$  (FWHM) which  
 212 was co-aligned to a micro-focused X-ray beam of  $1.5 \times 1.5 \mu\text{m}^2$  (FWHM)  
 213 (Konôpková et al., 2021). Two beam shapers are equipped on each side of the  
 214 laser heating system, which enables independent shaping of the focal spot and  
 215 are intended to ensure a flat-top intensity distribution of the laser-focused  
 216 beam. The high temperature was held stable for 5 to 36 minutes, after which  
 217 the sample was quenched by turning off the laser emission. The temperature  
 218 was measured radiospectrometrically during heating in the center of the hot  
 219 spot by fitting a grey body distribution to the measured thermal radiation  
 220 spectra in the spectral range between 640 to 850 nm. The temperature error  
 221 is 10% of the temperature value at ECB, which includes temperature gradi-  
 222 ents, heating instabilities due to fast changes in optical properties from the  
 223 sample, and signal sensitivity (Konôpková et al., 2021). The reported tem-  
 224 peratures are the temporal average of the temperature measurements series  
 225 over the heating duration (Fig. S??). Between one and three heating spots  
 226 were made in a single cell. Diffraction patterns were collected at 42.7 keV  
 227 using a Perkin Elmer (XRD1621) detector before and after heating but still  
 228 at high pressure by performing 2D scanning maps over the heated area. The  
 229 position and distance between the detector and the sample were calibrated  
 230 using a  $\text{CeO}_2$  standard. The diffraction patterns were analyzed using the  
 231 DIOPTAS software by Prescher and Prakapenka (2015) for phase identifica-  
 232 tion, pressure estimation, image integration, and background correction.

233 After the release of the pressure to ambient conditions, LH-DAC samples  
 234 were recovered and further analyzed. Raman spectroscopy was performed

235 on the raw samples to assure no contamination of carbon from later sample  
 236 preparation and, to detect diamonds in the experiments, as described in  
 237 Drewitt et al. (2019). A HORIBA Jobin Yvon Confocal LabRAM HR 800  
 238 available at the University of Potsdam. Maps covering the entire area of the  
 239 sample chamber were made using a grid of  $2 \times 2 \mu\text{m}^2$  or  $4 \times 4 \mu\text{m}^2$  steps, with  
 240 10 to 20 sec acquisition per spectrum. Spectra for diamond detection were  
 241 acquired with a 532 nm laser and an 1800 gr/mm grating in 1300 to 1400  $\text{cm}^{-1}$   
 242 spectral range. The processing of the Raman 2D maps was designed to search  
 243 for the first-order diamond band at 1332  $\text{cm}^{-1}$ . For each point of the maps,  
 244 the diamond band integral was calculated using the spectral range between  
 245 1320 to 1340  $\text{cm}^{-1}$ , and a baseline correction was applied by subtracting the  
 246 background intensity obtained from 1360 to 1380  $\text{cm}^{-1}$  spectral range (Fig  
 247 2A).

248 Samples were prepared for scanning transmission electron microscopy  
 249 (STEM) analyses at the PISA facility at the Helmholtz-Zentrum Potsdam  
 250 Deutsches GeoForschungsZentrum (GFZ), Potsdam (Germany) by drilling  
 251 them out of the gaskets using the highly energetic  $\text{Ga}^+$  ion beam of a Focused  
 252 Ion Beam (FIB) FEI Helios G4 UC (Dual Beam). Discs of approximately  
 253 150-170  $\mu\text{m}$  in diameter were glued onto an SEM holder and coated with  
 254 amorphous carbon and then sectioned parallel to the compressional axis to  
 255 access the laser-heated region. When the center of the heated region was  
 256 revealed, a 2  $\mu\text{m}$  thick Pt layer was deposited to protect the sample surface  
 257 from the  $\text{Ga}^+$  ion beam during the foil preparation. FIB lamellae were ex-  
 258 tracted and fixed on a copper grid and then thinned to a thickness of 3  $\mu\text{m}$ .  
 259 Samples were analyzed by energy dispersive X-ray (EDX) maps using an FEI

Quanta 3D (Dual Beam). Afterwards, several foils were thinned to electron transparency ( $\sim 100$  nm thickness) and analyzed by STEM, EDX spectra mapping, electron diffraction (ED), and electron energy loss spectroscopy (EELS) using a Thermo Fisher Scientific Themis Z transmission electron microscope. The instrument is equipped with an aberration corrector at the probe side, a SuperX EDX 4 quadrant detector, and a Gatan Imaging Filter (GIF) Continuum 1065. The microscope was operated at 300 kV. All EDX maps were collected using a 50 pA electron beam and averaged multiple frame acquisition. The experimental conditions and run products of each experiment are reported in Table S??.

### 3. Results

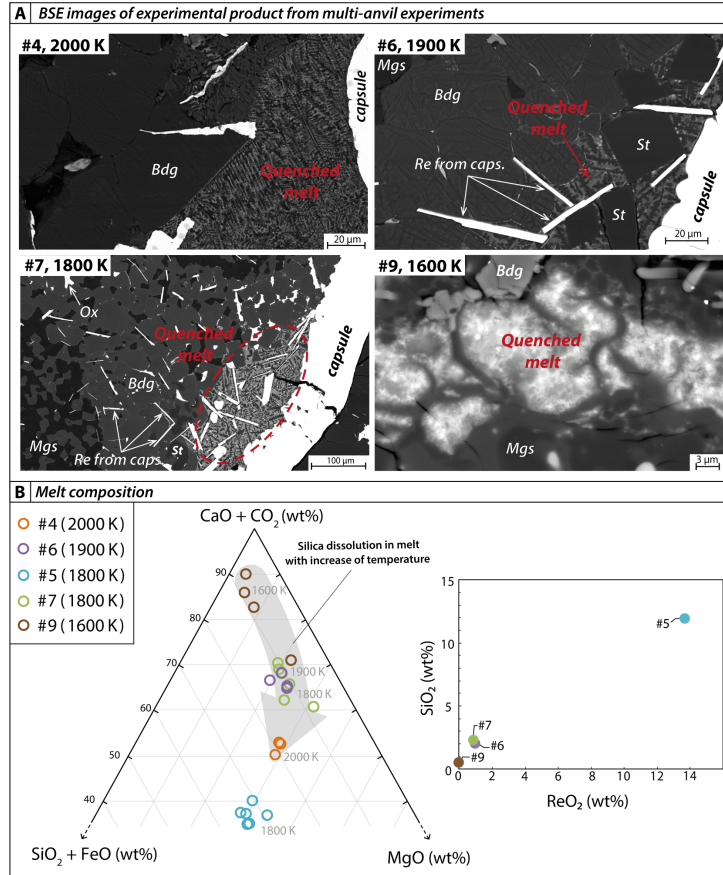
The first set of the five multi-anvil experiments revealed the occurrence of melt at 25 GPa and between 1600 to 2000 K (Table 2). Despite modest temperatures, all runs performed were above the solidus and contained an assemblage of ferromagnesite  $[(\text{Mg}_{0.88-0.95}\text{Fe}_{0.04-0.06})\text{CO}_3]$ , bridgmanite  $[(\text{Mg}_{0.86-0.92}\text{Fe}_{0.10-0.13})\text{SiO}_3]$ , stishovite ( $\text{SiO}_2$ ) and quenched melt (QM) (Fig.1, Table S??). Rhenium shards are observed in all capsules. In two experiments (#6 and #7, Table S??),  $\text{ReO}_2$  and (Re,Fe,Mg)-oxide were found in the vicinity of the melt pockets, likely from an interaction between the rhenium capsules and the carbon-rich melt produced.  $\text{Re-ReO}_2$  is a solid state metal-oxide buffer, and may therefore have influenced the oxygen fugacity in the multi-anvil experiments at around +5 log units relative to iron-wüstite (IW) (Rohrbach and Schmidt, 2011).

Quenched melt is identified in all MAP experiments by its dendritic tex-



Run n°	P (GPa)	Temp. (K)	Dur. (min)	Starting mat.	Run products
<b>Multi-anvil experiments</b>					
#4a <sup>1</sup>	25	2000	60	MG11:Sr	Bdg, Mgs, Sti, Fp, QM
#4b <sup>1</sup>	25	2000	60	MG11:La	Bdg, Mgs, Sti, Fp, QM
#5	25	1800	135	MG11:La	Bdg, Mgs, Sti, QM
#6	25	1900	135	MG11:La	Bdg, Mgs, Sti, QM, Re-Ox
#7	25	1800	135	MG11:Sr	Bdg, Mgs, Sti, QM, Re-Ox
#9	25	1600	120	MG11:La	Bdg, Mgs, Sti, QM, La-Si
<b>LH-DAC experiments</b>					
ON01	41	1750	23	MG11	Bdg, Mgs, Sti, Dia, Fp
ON02	41	1450	36	MG11	Bdg, Mgs, Sti, Dia, Fp
ON03	41	1600	26	MG11	Bdg, Mgs, St, Fp*
ON06	68	1850	33	MO13 + Pt	Ol, Bdg, Sti, Dia
ON07	68	2000	27	MO13 + Pt	Ol, Bdg, Sti, Dia
ON08	44	1900	30	MG11	Bdg, Sti, Dia, Fp*
ON11	40	2050	36	MO13 + Pt	Ol, Bdg, Dia, Fp, Mgs
ON13	40	2000	22	MO13 + Pt	Ol, Bdg, Dia, Fp*
ON19	51	1700	21	MG11	Bdg, Mgs, Sti, Dia
ON20	51	1400	14	MG11	Bdg, Mgs, Sti, Fp*
ON21	33	1650	14	MG13	Bdg, Mgs, Dia, Fp
ON22	33	1350	12	MG13	Bdg, Mgs, Dia, Fp
ON25	62	1650	13	MG11	Bdg, Mgs, Sti, Dia, Fp
ON26	62	1700	18	MG11	Bdg, Mgs, Sti, Fp*
ON27	62	1350	5	MG11	Bdg, Mgs, Sti, Dia, Fp
ON28	56	1400	11	MG11	Bdg, Mgs, Sti, Fp*
ON29	56	1900	8	MG11	Bdg, Mgs, Sti, Dia, Fp, Wus
ON31	66	1400	14	MG11	Bdg, Mgs, Sti, Dia, Fp*
ON32	66	1650	17	MG11	Bdg, Mgs, Sti, Dia
ON33	66	1500	16	MG11	Bdg, Mgs, Sti, Fp*
ON34	43	1300	14	(Mg, Fe)SiO <sub>3</sub> glass	Bdg, Sti, Fe-metal

**Table 2:** Compilation of observed phases from all analytical methods in multi-anvil and LH-DAC experiments presented in this work. <sup>1</sup> two capsules were placed inside a single experiment. Phases: Bdg - Bridgmanite, Sti - Stishovite, Mgs - Magnesite, Dia - Diamond, Fp - Ferropicrlase; Fp\* was not observed directly but assumed, Ol - Olivine, Wus - Wüstite, QM - Quenched melt, Re-Ox - Rhenium oxide, La-Si - Lanthanum-Silicate, Pt - Black platinum. Details of major element composition for multi-anvil experiment can be found in Table S?? and analytical investigations used for each run of LH-DAC experiments are provided in Table S??. 15



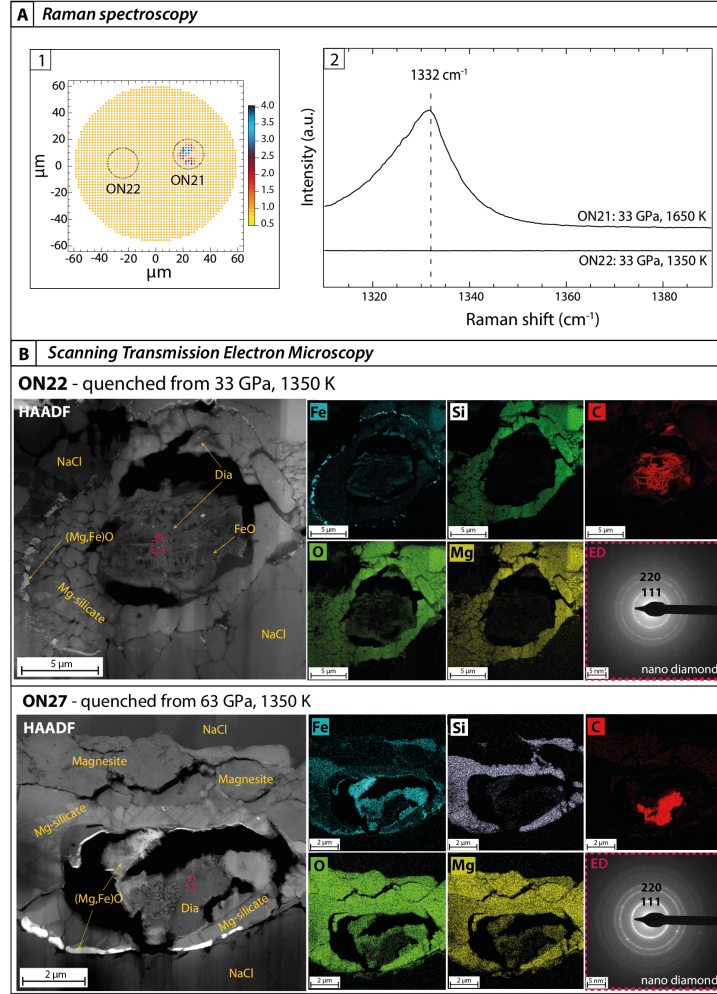
**Figure 1: Results from the multi-anvil experiments.** A) Back-scatter electron images of experimental products from multi-anvil quench experiments. Melt pockets (in red) are located in the hottest area of the capsules. Bdg: bridgmanite, Mgs: magnesite, St: stishovite, capsules are made of rhenium. B) Composition of melts from EPMA analyses.

284 ture (Fig.1A) and confirmed by the presence of the incompatible Sr and La  
 285 dopants (Table S??). Therefore, these experiments indicate that the solidus  
 286 line must be lower than the lowest temperature achieved in this study (#9,  
 287 1600 K at 25 GPa). Silicate mineral grains were found to be larger in the  
 288 proximity of the melt pockets than elsewhere in the capsule (Fig.1A). This is  
 289 particularly evident in the case of stishovite grains, indicating that stishovite  
 290 growth is enhanced by melt. No bubbles were observed, suggesting that no  
 291 CO<sub>2</sub>-fluid was produced. The composition of the quenched melt evolves with  
 292 increasing temperature (Fig.1B) from essentially silica-free and carbon-rich  
 293 at 1600 K to 11 wt.% SiO<sub>2</sub> at 2000 K (Table S??). Run #5 is an exception  
 294 to this trend, with an even higher enrichment of SiO<sub>2</sub>, and ReO<sub>2</sub> reaching  
 295 13.7 wt.% (Fig. 1B). This systematic trend observed in the quenched melt  
 296 composition (Fig.1B) indicates that a thorough chemical exchange between  
 297 solids and melt was established in our multi-anvil experiments. The textures  
 298 of the samples after the experiment revealed that significant temperature gra-  
 299 dients were present and that the quenched melt is located at the hottest part  
 300 of the capsules (center). The enrichment of La or Sr in the quenched melt  
 301 further supports thorough chemical exchange that likely involved transport  
 302 along T-gradients. Previous time series on the carbonate-peridotite system  
 303 have shown that equilibrium was reached within ~10 hours at 1500 °C and  
 304 6 GPa at an overall carbonate content of only 10% of the starting mate-  
 305 rial (Brey et al., 2008). However, due to the high proportion of carbonate  
 306 in our experiments chemical transport within the capsule is facilitated, as in  
 307 the pure carbonate (CaCO<sub>3</sub>–MgCO<sub>3</sub>) system equilibrium was reached within  
 308 1 h 18 min at 1700 °C (Sieber et al., 2022). Representative major element

309 compositions obtained by EPMA are reported in Table S??.

310 The second set of experiments was performed using LH-DAC, including  
311 one reference LH-DAC experiment (ON34, see Table 2 and S??), containing  
312 only the synthetic silicate glass used in MG11 and MG13 without magnesite  
313 in order to investigate the phase assemblage that forms from the crystalliza-  
314 tion of the silicate glass in the absence of magnesite. Results obtained from  
315 the diffraction patterns of our LH-DAC experiments exhibited peaks corre-  
316 sponding to bridgmanite, stishovite, NaCl (pressure medium), and in some  
317 cases magnesite (Fig. S ??). Bridgmanite was observed in all runs including  
318 the reference experiment that did not contain magnesite in the starting mate-  
319 rial (ON34, Fig. S ??). Consequently, bridgmanite formed from our silicate  
320 starting material. In addition, no decarbonation products, i.e., diamond or  
321 CO<sub>2</sub>, were identified with in situ XRD, mainly due to peaks overlapping in  
322 multi-phase systems, which complicates the analyses of run products analy-  
323 ses. Furthermore, the X-ray focus size, the small volume of material being  
324 probed, and the relatively low scattering power of carbon and oxygen cre-  
325 ate an extremely challenging environment to detect carbon-bearing phases,  
326 as also stated in previous studies (Drewitt et al., 2019; Mao and Boulard,  
327 2013).

328 Fig. 2A1 shows a representative example of a processed 2D map ob-  
329 tained by Raman spectroscopy revealing the presence of diamond in run  
330 ON21 (33 GPa and 1650 K), which was later confirmed during FIB prepa-  
331 ration Fig. S??. In contrast, no diamond peaks were detected in run ON22  
332 (33 GPa and 1350 K) in the same Raman 2D map, but STEM analyses con-  
333 firmed later the presence of nanometer-sized diamonds in this run (ON22,



**Figure 2: Results from ex situ analyses of recovered LH-DAC samples.** A) (1) Example of Raman spectra illustrating the process of diamond detection, by investigating the presence of the first-order diamond peak at  $1332 \text{ cm}^{-1}$ , with (2) the examples of two experimental points (ON21 and ON22) confirming either the presence (ON21) or the absence (ON22) of diamond within the sensitivity of the equipment. B) HAADF-STEM images, EDX maps, and electron diffraction (ED) from nano-diamonds of selected recovered samples (ON22 and ON27) with red dashed rectangles on the HAADF images indicate the localization of the ED measurements. Reaction zones (hottest area) display in their center nano-sized diamond, that for ON22 was undetected by Raman spectroscopy. Around the nano-diamond center, the presence of Mg-silicate and a ring of ferropericlase delimit the reaction zone. The presence of wüstite (FeO) was found in a couple of experiments next to nano-diamond. The ON27 Raman 2D map is provided in supplementary material in Fig. S??, and close-up view of the nano-diamond area of ON22 and ON27 in Fig. S??

334 Fig. 2B). Therefore, STEM analyses have been shown to be the preferred  
335 analytical tool for identifying the presence of nanometer-sized diamonds. In  
336 contrast, Raman spectroscopy is more susceptible to being affected by non-  
337 perfect sample properties such as the unpolished sample surface, and the  
338 dark heated area, which reduces the penetration thickness and scattering  
339 efficiency of the Raman laser (see Table S??). Accordingly, unsuccessful  
340 STEM sample preparation by FIB milling directly caused an incapacity to  
341 confirm diamond presence for some runs, as well as expected reaction phases  
342 such as ferropericlase, that were undetectable by XRD. However, from our  
343 lowest temperature observation, it can be assumed that diamond formation  
344 happened under all conditions.

345 Textural and chemical features observed by STEM (Fig. 2B) are similar  
346 in all investigated experiments. The location of the laser-heated reaction  
347 center was easily identified as a round-shaped area, with a concentric distri-  
348 bution of phases (Fig. 2B). Within the center, a mixture of nanometer-sized  
349 diamonds, and ferropericlase, or wüstite (FeO), was observed. Crystal struc-  
350 tures were confirmed using ED and EELS (Fig. 2B and Fig. S?? for FeO  
351 in ON29). An iron-depleted amorphous silicate phase, interpreted as bridg-  
352 manite before quenching, surrounds the 'diamond-ferropericlase' center. The  
353 amorphization of the bridgmanite may have been caused by the  $\text{Ga}^+$  beam  
354 during FIB milling (Marquardt and Marquardt, 2012). A ring of ferroper-  
355 iclase encloses and marks the border of the heated area. The surrounding  
356 volume consists of NaCl and unheated starting materials, which explains the  
357 presence of magnesite peaks in the diffraction patterns after heating since  
358 the XRD probed the entire thickness of the sample. The ferropericlase ring

likely results from chemical migration during laser heating, which is a distinct effect of a radial temperature gradient in LH-DAC experiments. The quench textures of the reaction zones are very heterogeneous, with different phases that crystallize. If a melt was present during the quench, we could have identified a homogeneous region (e.g. a melt pool) in the center of the heated area. Solid state experiments (Sinmyo and Hirose, 2010) as well as partial melting experiments (Baron et al., 2022) describe similar quenched textures emphasizing that the described texture is not sufficient to distinguish between sub-solidus and supra-solidus conditions. Further, the XRD settings did not allow the recording of diffuse signals from a weakly scattering carbonate melt. If partial melting occurred the melt may have undergone immediate redox freezing to diamond and ferropericlase, both occurring within the reaction zone (Fig. 2B).

Our starting material was placed within two layers of NaCl acting as a pressure-transmitting medium, an insulator from the diamond anvil as well as to limit element segregation during laser heating. No reaction products such as Na-carbonates were found, neither by XRD nor during STEM analyses, that could have affected the system compositions. This is also supported by the sharp contact observed between NaCl and other phases, in Fig. 2B and Fig. S??.

In the reference experiment (ON34), the STEM investigation revealed that heating of the starting glass results in the crystallization of a phase mixture of bridgmanite, stishovite, and metallic iron. Stishovite was identified from pure SiO<sub>2</sub> regions in EDX maps and confirmed by ED (Fig. S??). Metallic iron was identified in elemental maps as oxygen-depleted versus iron-

rich regions. Chemical analyses revealed high iron concentration and an oxygen K-edge peak too low to be an iron-oxide. Previous studies have reported the occurrence of metallic iron grains in lower mantle phase assemblages due to the Fe disproportionation reaction (Dorfman et al., 2021; Auzende et al., 2011; Frost et al., 2004). Additionally, the presence of metallic iron suggests that the redox conditions are at  $\Delta\log fO_2$  around 0 to -1.5 relative to the IW buffer (Rohrbach and Schmidt, 2011). Although observed in ON34, metallic iron was not found in any run loaded with magnesite indicating that it reacted completely to form oxides (Fig. S??).

Here, we assume that stishovite is produced by exsolution as a result of low Fe solubility in bridgmanite that cannot accommodate all Fe available and that ferropericlase is a reaction product of the decarbonation reaction of magnesite to diamond. However, no diffraction peaks of ferropericlase and/or metallic iron could be identified, even in ON34. Therefore, ferropericlase is assumed to be present, although not observed (Table 2), in experiments in which stishovite or diamond was observed. However, given the Fe-content of the bridgmanite-glass, the enhanced solubility of Fe in bridgmanite for pressures exceeding  $\sim 20$  GPa (Dorfman et al., 2021, 2013) should lead to the incorporation of all provided Fe in bridgmanite. In contrast, we report crystallization to a mixture of metallic Fe, stishovite, and bridgmanite up to 43 GPa at 1300 K (run ON34). It could also be possible that a slight non-stoichiometric excess of  $SiO_2$  in our starting material could lead to the exsolution of stishovite during the crystallization of the glass. Additionally, iron could also dissolve in the melt at high pressure and temperature and eventually quench to nano-crystalline ferropericlase or wüstite in the quenched



409 silicate melt, which was observed by SEM. This highlights the need to inves-  
410 tigate further the Fe-solubility in bridgmanite as a function of temperature  
411 and oxygen fugacity. Our results do not provide conclusive information in  
412 this regard.

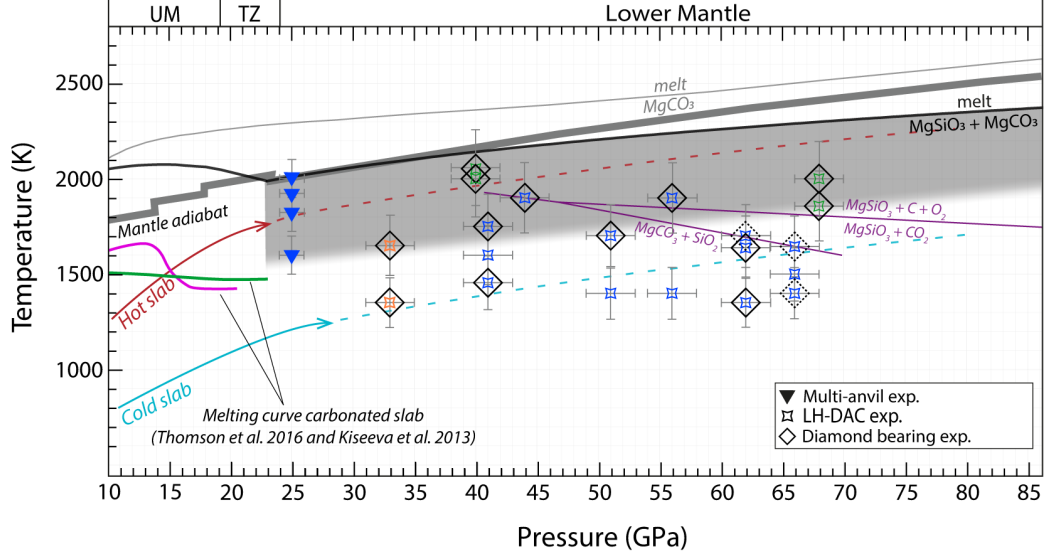
413 Four pressure-temperature points (ON06, ON07, ON11, and ON13) were  
414 investigated with the MO11 starting material containing Pt (as a laser cou-  
415 pler). Despite the difference in the starting composition, XRD revealed the  
416 same phase assemblage as in other runs (Table S??). However, none of these  
417 samples were recovered successfully for STEM investigation, and only Ra-  
418 man spectroscopy identified the presence of diamonds in the 4 experiments.  
419 Therefore, no additional data could be collected to evaluate the potential  
420 effects of (1) the change of starting composition in the reaction and (2) Pt  
421 on the Fe contained in the sample

422 Most STEM foils show void areas that are associated with cracks formed  
423 during decompression, manipulation, and thinning during FIB milling. Most  
424 damages were caused by the beam used during EDX mapping at the FIB-  
425 SEM and failed attempts of field emission gun electron microprobe (FEG-  
426 EMP) mapping, performed before STEM analyses. All experimental con-  
427 ditions, run products, and analytical investigations used for each run are  
428 provided in Table 2 and in detail in Table S??.

## 429 4. Discussion

### 430 4.1. *The fate of deeply subducted magnesite*

431 Our results provide new insights into the stability field of magnesite in the  
432 presence of Fe-bearing lower mantle assemblages (Fig. 3). Our experiments



**Figure 3: Pressure-temperature diagram of carbonates stability within subducted oceanic crust through Earth's mantle.** Top grey line is the melting curve of  $\text{MgCO}_3$  constrained by Solopova et al. (2015) and black line is the melting curve of  $\text{MgCO}_3 + \text{MgSiO}_3$  according to Thomson et al. (2014). Purple lines indicate decarbonation reaction of  $\text{MgCO}_3 + \text{SiO}_2$  from Drewitt et al. (2019). The bold grey line is the mantle adiabat after Katsura et al. (2010). Typical slab geotherms (hot slab in red and very cold slab in sky blue) are modified from Maeda et al. (2017). The colors of symbols refer to the starting composition used in our experiments: blue = MG11; orange = MG13 and green = MO11. Symbols correspond to the experimental technique used, triangle for multi-anvil and stars for LH-DAC experiments. Grey-shaded zone indicates the area where melting is expected in our system. Symbols encased in a diamond shape indicate the presence of diamonds that were confirmed by Raman spectroscopy and/or STEM, the dashed diamond shape was only confirmed by EDX during FIB milling. The absence of the diamond shape indicates experiments in which diamonds were not detected during Raman measurements and could not be investigated by STEM because of preparation failure during FIB milling. UM: Upper mantle and TZ: Transition Zone.

433 reveal the breakdown of magnesite by (1) the presence of a carbonate-melt in  
 434 multi-anvil experiments by melting at 25 GPa and 1600–2000 K (downward  
 435 triangle in Fig.3), and (2) the presence of diamond in LH-DAC experiments  
 436 via a 'decarbonation reaction' at 33–75 GPa and 1300–2000 K (diamond  
 437 shape around star symbols in Fig.3). These results notably differ from previ-  
 438 ous investigations utilizing simplified iron-free systems (Maeda et al., 2017;  
 439 Kakizawa et al., 2015; Litasov and Shatskiy, 2019), indicating that the pres-  
 440 ence of iron plays a major role in magnesite stability, as previously suggested  
 441 by experimental investigations (Dorfman et al., 2018).

442 The previously determined melting curve of the iron-free  $\text{MgCO}_3 + \text{MgSiO}_3$   
 443 system at lower mantle depths (constrained by LH-DAC experiments) indi-  
 444 cates eutectic melting at 25 GPa and  $\sim 2000$  K (Thomson et al., 2014). In  
 445 contrast, our results on the Fe-containing—plus a minor amount of either Sr or  
 446 La—system reveal that melting occurs at temperatures 400 K lower (1600 K  
 447 at 25 GPa). The lower melting temperature may be explained by the addi-  
 448 tion of Fe, which should lower the temperature of the eutectic as found for  
 449 other Fe-Mg silicate systems (Agee et al., 1995). Generally, the addition of  
 450 components that do not induce immiscibility in the melt phase should lead  
 451 to lowering of the melting temperature. This is exemplified in carbonated-  
 452 MORB systems such as in Kiseeva et al. (2013) and Thomson et al. (2016b),  
 453 with compositions containing respectively 3.54 to 3.78 wt% and 2.58 wt%  
 454 of  $\text{Na}_2\text{O} + \text{K}_2\text{O}$  in total in their starting material, an even lower melting  
 455 temperature is obtained reaching  $\sim 1400$  K, if extrapolated up to 25 GPa.  
 456 Our data, coupled with published data sets, support that at more oxidizing  
 457 conditions, around the Re-ReO<sub>2</sub> buffer, melting may be an important mech-

458 anism for the elimination and recycling of carbonates from the subducted  
459 oceanic lithosphere, along all subduction geotherms except for the very cold  
460 ones (Drewitt et al., 2019; Maeda et al., 2017).

461 Experimental investigations have shown that if carbonate melts infiltrate  
462 the reduced ambient mantle at depths  $\geq 250$  km, the melt will become un-  
463 stable and will be reduced to diamond via redox freezing (Rohrbach and  
464 Schmidt, 2011). The presence of Re/ReO<sub>2</sub> in our multi-anvil experiments  
465 suggests that the experimental redox conditions might have been too oxi-  
466 dized (around IW +4 to +5) (Rohrbach and Schmidt, 2011) when compared  
467 to expected deep mantle conditions (around IW to IW -1.5) (Frost and Mc-  
468 Cammon, 2008), thus may have prevented diamond nucleation. However,  
469 diamond formation was observed in our LH-DAC experiments at tempera-  
470 tures as low as, and even lower than, the coldest subduction geotherm at  
471 33 GPa (1350 K) and at 62 GPa (1350 K), respectively (Fig. 3). The ex-  
472 perimental conditions in which diamonds are observed differ noticeably from  
473 the ones reported in Drewitt et al. (2019) (purple lines in Fig. 3). These dif-  
474 ferences can result from the differences between starting bulk compositions,  
475 highlighting the necessity to couple several analytical techniques such as in  
476 situ or ex situ XRD, Raman and/or STEM in multi-phases run products in  
477 LH-DAC experiments (see Results).

478 The breakdown of magnesite into diamond in LH-DAC experiments im-  
479 plies the presence of a reducing agent. Previous studies have shown that  
480 metallic iron is a relevant reducing agent for magnesite (Dorfman et al.,  
481 2018; Martirosyan et al., 2019; Zhu et al., 2019), but these studies do not  
482 account for the presence of silicates. The results of our magnesite-free refer-

483 ence experiments (ON34, see methods and results) show that metallic iron  
484 is produced during the crystallization of our starting silicate glass. Neither  
485 metallic iron nor Fe-carbides were observed to co-exist with diamond, indi-  
486 cating that the metallic iron may have formed as an intermediate phase and  
487 then was completely consumed by reacting with  $\text{MgCO}_3$  to form diamond  
488 via redox freezing (see Eq. 1). Whereas the remaining  $\text{Fe}^{2+}$  is partitioned  
489 into ferropericlase and/or wüstite and the  $\text{Fe}^{3+}$  into bridgmanite.

490 We do not have a similar experiment to ON34, with only olivine as the  
491 starting material. However, previous studies have investigated lower man-  
492 tle assemblages using olivine with a similar composition to the one of this  
493 study (Auzende et al., 2008). They reported a mixture of bridgmanite, fer-  
494 ropericlase, and iron metal as run products attributed to disproportionation  
495 in bridgmanite (Frost et al., 2004). With the increase in pressure, the iron's  
496 solubility in bridgmanite increases too, and can reach up to  $\sim 75$  mol% at deep  
497 lower mantle conditions ( $\sim 90$  GPa) (Dorfman et al., 2013). This indicates,  
498 that at higher pressure, the olivine starting material does not crystallize in a  
499 mixture of phases but only as single-phase bridgmanite, since it can accom-  
500 modate the iron completely. However, in the highest pressure explored in this  
501 study (e.g. ON07 at 68 GPa and ON31/32/33 at 66 GPa), stishovite was  
502 observed in the in situ XRD, meaning that it is likely that the iron was not  
503 fully incorporated in the bridgmanite and that a mixture of bridgmanite +  
504 stishovite + ferropericlase and probably metallic iron were produced. While,  
505 without direct observations, we cannot fully rule out the presence of metallic  
506 iron, we consider that some might have formed in these experiments.

507 The temperatures of diamond formation reported here are lower than the

508 melting temperatures reported from our multi-anvil experiments, whereas no  
 509 satisfactory evidence of melting was observed in our LH-DAC experiments  
 510 such as diffuse scattering during heating in our XRD spectra. Nonetheless,  
 511 we expect that the shape of our iron-bearing melting curve will be parallel  
 512 to the iron-free curve by Thomson et al. (2014), adjusted to considerably  
 513 lower temperatures. The newly derived iron-bearing melting area (grey area  
 514 in Fig. 3) indicates that melting may occur at similar temperatures (but  
 515 higher pressures) at which diamond crystallization is observed. This su-  
 516 perimposition highlights a possible dynamic relationship between diamond  
 517 crystallization and melting. Indeed, super-deep diamonds originating from  
 518 depths from  $\geq 250$  km to the transition zone appear to have crystallized from  
 519 low-degrees of partial melting of subducted carbonate-rich oceanic crust, as  
 520 indicated by the elevated trace elements content within super-deep diamond  
 521 mineral inclusions (Walter et al., 2008; Bulanova et al., 2010; Thomson et al.,  
 522 2016a; Walter et al., 2022). In addition, oxygen ( $^{18}\text{O}$ ) isotopic compositions  
 523 from mineral inclusions in super-deep diamonds, coupled with carbon ( $^{13}\text{C}$ )  
 524 and nitrogen ( $^{15}\text{N}$ ) isotopic compositions from the diamond hosts, reveal that  
 525 the carbon source for diamond formation is depth-dependent. Whereas sub-  
 526 lithospheric diamonds that crystallize at depths  $\leq 700$  km (up to the shallow  
 527 lower mantle) indicate a source from recycled oceanic crust, diamonds formed  
 528 at depths  $\geq 700$  km lack evidence of such a source, supporting the barrier for  
 529 carbon subduction at the top of the lower mantle (Regier et al., 2020).

530 Our study is not sufficient to respond on whether or not diamond forma-  
 531 tion necessarily involves redox freezing of a carbon-rich melt or happens as a  
 532 sub-solidus reaction but rather serve to look for fundamental chemical inter-

actions in multiphase systems in which carbonates and lower mantle silicate interact. Therefore, further experiments are needed to localize the solidus in the investigated system. Nevertheless, the presence of diamond in our data clearly demonstrates that magnesite is not stable when in contact with (Mg, Fe)-silicates at depths reflecting the shallow lower mantle (25 to 60 GPa) and suggests that magnesite will unlikely be preserved throughout the lower mantle, even if transported in the coldest slab. Accordingly, the recycling of magnesite within the shallow lower mantle ( $\leq 40$  GPa) inhibits the transport of carbonates to Earth’s deeper interior.

#### 4.2. *Implications for the genesis of super-deep diamonds*

One persisting uncertainty is whether or not subducted carbonates will survive within slabs to depths of at least 660 km without being reduced to diamonds at shallower depths since Fe-metal is already stable at 250 km (Frost et al., 2004). The recent study of Martirosyan et al. (2022) assessed the complexities of carbonate + silicates + Fe redox interactions and evaluated their reaction kinetics at upper-mantle and hot subduction geotherm conditions (6 GPa and  $\sim 1400$  K). Their results indicate that the presence of silicates in an anhydrous and melt-free environment will slow down the redox reaction due to the barrier that silicates constitute on Fe and O diffusion. In such a scenario, carbonates may persist and reach the lower mantle and provide the carbon source for super-deep diamonds. Seismic imaging indicates that slabs can stagnate at the shallow lower mantle due to an increase of mantle viscosity (Fukao and Obayashi, 2013; Marquardt and Miyagi, 2015). This stagnation may promote an environment where carbonated slabs accumulate, increasing the amount of oxidized reactant over time to reduce and

558 form super-deep diamonds, even in the coldest subduction as shown by our  
 559 data. As a result, a diamond production region (Zhu et al., 2019) is expected  
 560 at the transition zone/lower mantle boundary. The rate of subduction will  
 561 have a great influence on the supply of oxidized carbon necessary to produce  
 562 diamonds over geological time since the concentration of carbonates present  
 563 in slabs is limited to  $\sim 0.3$  wt.% (Dasgupta and Hirschmann, 2010). The  
 564 influx of oxidized carbon in the form of solid carbonates or carbonate-melt  
 565 in this mantle region is expected to buffer the fugacity locally (Stagno et al.,  
 566 2019, 2011) by the consumption of metallic iron nearby, as seen in our LH-  
 567 DAC experiments. A metal-free mantle region may result if the supply of  
 568 oxidized phases surpasses the redox metallic iron capacity locally. Such lo-  
 569 calized  $f\text{O}_2$  disparities are revealed from carbonate inclusions in diamonds  
 570 (Brenker et al., 2007; Kaminsky, 2012; Bulanova et al., 2010), reflecting a  
 571 higher oxidation state within the diamond production region, around IW +2  
 572 to +3 (at  $\sim 25$  GPa) where magnesite and diamond co-exist (Stagno et al.,  
 573 2011).

574 The re-mobilization of such diamonds by mantle upwelling to lower depths  
 575  $\leq 250$  km (where the ambient mantle ceases to be metal saturated) will form  
 576 carbonate-melt via the redox melting, the inverse process of redox freezing  
 577 (Rohrbach and Schmidt, 2011). Those melts may then transport carbon back  
 578 to the surface in a rising mantle plume, such as within ocean-island basalts  
 579 (OIB) or carbonatites (Hammouda and Keshav, 2015; McCammon et al.,  
 580 2020; Dasgupta and Hirschmann, 2010).



## 581 **5. Conclusion**

582 We conducted a multi-experimental and analytical study using multi-  
583 anvil apparatus and laser-heated diamond anvil cells to investigate the re-  
584 action between magnesite and iron-bearing bridgmanite. This reaction is  
585 used as an experimental proxy to investigate the interactions of carbonate  
586 minerals contained within the oceanic crust subducting into the lower man-  
587 tle. Our data demonstrate that magnesite is not stable in the Fe-bearing  
588 system at cold slab temperatures (1350 K) and shallow lower mantle condi-  
589 tions (33 GPa). Magnesite is thus unlikely to carry oxidized carbon deeper  
590 into the reduced lower mantle to depths greater than 700 km. Carbon will  
591 instead be present in its immobile and reduced form, diamond, and stored  
592 over long timescales in the deep mantle where it could be re-mobilized by  
593 mantle upwelling. Furthermore, we can speculate that the reduction of car-  
594 bonate minerals contained in stagnating slabs will consume the metallic iron  
595 and produce a locally oxidized mantle, creating regions where oxidized and  
596 reduced carbon phases may co-exist.

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## 617 **Appendix A. Supplementary materials**

618 Supplementary materials can be found in the document “Supplementary  
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