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► **To cite this version:**

Susannah Dorfman, James Badro, Farhang Nabiei, Vitali Prakapenka, Marco Cantoni, et al.. Carbonate stability in the reduced lower mantle. *Earth and Planetary Science Letters*, 2018, 489, pp.84-91. 10.1016/j.epsl.2018.02.035 . hal-02363561

**HAL Id: hal-02363561**

**<https://hal.science/hal-02363561v1>**

Submitted on 31 Mar 2021

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1 **Carbonate stability in the reduced lower mantle**

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16

## 17 **Abstract**

18 Carbonate minerals are important hosts of carbon in the crust and mantle with a key role  
19 in the transport and storage of carbon in Earth's deep interior over the history of the planet.  
20 Whether subducted carbonates efficiently melt and break down due to interactions with reduced  
21 phases or are preserved to great depths and ultimately reach the core-mantle boundary remains  
22 controversial. In this study, experiments in the laser-heated diamond anvil cell (LHDAC) on  
23 layered samples of dolomite (Mg,Ca)CO<sub>3</sub> and iron at pressure and temperature conditions  
24 reaching those of the deep lower mantle show that carbon-iron redox interactions destabilize the  
25 MgCO<sub>3</sub> component, producing a mixture of diamond, Fe<sub>7</sub>C<sub>3</sub>, and (Mg,Fe)O. However, CaCO<sub>3</sub> is  
26 preserved, supporting its relative stability in carbonate-rich lithologies under reducing lower  
27 mantle conditions. These results constrain the thermodynamic stability of redox-driven  
28 breakdown of carbonates and demonstrate progress towards multiphase mantle petrology in the  
29 LHDAC at conditions of the lowermost mantle.

## 30 **1. Introduction**

31 Carbonates are the major minerals responsible for transportation of carbon from the  
32 Earth's surface to its deep interior. Their behavior at depth is critical to the storage capacity and  
33 fluxes of the geologic carbon cycle. Recent estimates of the flux of carbon trapped in carbonate  
34 minerals that reach the deep Earth range from 0.0001 to 52 megatons annually (Dasgupta and  
35 Hirschmann, 2010; Kelemen and Manning, 2015). The uncertainty in this range hinges on poor  
36 constraints on the budget of carbon retained by subducting slabs. Transport of carbon to at least  
37 transition zone depths is demonstrated by carbonate inclusions in diamonds (e.g. Brenker et al.,  
38 2007; Wang et al., 1996), but whether any carbonates remain in the lower mantle is  
39 controversial. Most subducted carbon is expected to melt and/or break down and return to

40 Earth's surface via volcanism (Dasgupta and Hirschmann, 2010; Kelemen and Manning, 2015;  
41 Thomson et al., 2016). However, relatively oxidizing conditions, low temperatures, and resulting  
42 slow kinetics within subducting slabs may result in transportation of carbonates magnesite,  
43 siderite, calcite, and their solid solutions to great depths (Martirosyan et al., 2016). Subducted  
44 carbonates in slabs that reach the base of the lower mantle will undergo multiple phase  
45 transitions and encounter reducing conditions, to be finally buffered by metallic iron at or near  
46 the CMB.

47 Carbon provides key constraints on the chemical evolution of the deep Earth through its  
48 role as a proxy for mantle redox conditions, as its speciation is largely governed by oxygen  
49 fugacity, or  $f_{O_2}$  (Frost and McCammon, 2008). Evidence of deep mantle chemistry (Walter et al.,  
50 2011) and redox state (Ryabchikov and Kaminsky, 2013; Smith et al., 2016) in local  
51 environments of diamond formation can likely be inferred from diamond inclusions. Diamonds  
52 and their inclusions indicate widely varying local  $f_{O_2}$  (Brenker et al., 2007; Walter et al., 2011;  
53 Ryabchikov and Kaminsky, 2013; Smith et al., 2016; Kaminsky, 2012), though  $f_{O_2}$  is expected to  
54 generally decrease with mantle depth (Frost and McCammon, 2008; Rohrbach and Schmidt,  
55 2011). Both isotopic evidence (e.g. Harte, 2010; Tappert et al., 2005) and carbonate inclusions in  
56 diamonds (e.g. Wang et al., 1996) suggest that diamonds are (at least in part) formed by  
57 reduction of subducted carbonate minerals or carbonate melts. Reduction of carbonates to  
58 diamond takes place by interactions with mantle silicates (Pal'yanov et al., 2002; Stagno et al.,  
59 2011, 2013, 2015) or metal (Arima et al., 2002; Siebert et al., 2005; Rouquette et al., 2008;  
60 Pal'yanov et al., 2013). These redox reactions contribute to the barrier to carbonate transport to  
61 the deep Earth (Rohrbach and Schmidt, 2011; Thomson et al., 2016). The key to determining the

62 amount of oxidized carbon in the deep Earth is the dependence of both the thermodynamics and  
63 the kinetics of redox reactions in carbonates on temperature, pressure, and  $f_{O_2}$ .

64 Petrologic observations, experiments and computational studies on stability and  
65 breakdown kinetics of carbonates have determined that magnesite is the most stable carbonate  
66 phase throughout most of the mantle (e.g. Dasgupta and Hirschmann, 2010; Rohrbach and  
67 Schmidt, 2011), but calcite and siderite polymorphs have also attracted interest. Relative to  
68 aragonite (Spivak et al., 2011) or siderite (Tao et al., 2013), magnesite is more likely to subduct  
69 to the deep mantle due to its higher melting temperature (Isshiki et al., 2004; Katsura and Ito,  
70 1990; Martinez et al., 1998; Solopova et al., 2014). Melting experiments on carbonated peridotite  
71 (Dasgupta and Hirschmann, 2010; Ghosh et al., 2014; Rohrbach and Schmidt, 2011) and eclogite  
72 (Thomson et al., 2016) systems confirm that calcium and iron carbonate components are more  
73 likely to enter a melt phase than magnesium carbonate in silicate lithologies. At sub-solidus  
74 temperatures,  $MgCO_3$  is also favored in carbonate-silicate mixtures by the reaction  $CaCO_3 +$   
75  $MgSiO_3 \rightarrow MgCO_3 + CaSiO_3$  at lower-mantle pressures up to 80 GPa (Biellmann et al., 1993;  
76 Seto et al., 2008). Due to its broad solid solution with siderite (Lin et al., 2012; Liu et al., 2015),  
77 magnesite in the mantle will host iron. An (Mg,Fe)-carbonate in the lowermost mantle may have  
78 mixed redox state and coexist with diamond (Boulard et al., 2012). However, both  $(Mg,Fe)CO_3$   
79 (Brenker et al., 2007; Kaminsky et al., 2016; Phillips and Harris, 1995; Ryabchikov and  
80 Kaminsky, 2013) and  $CaCO_3$  (Brenker et al., 2007; Meyer and McCallum, 1986) have been  
81 observed in inclusions in diamonds, including ultra-deep diamonds from the transition zone or  
82 possibly the lower mantle (Brenker et al., 2007). These inclusions demonstrate that both  
83  $(Mg,Fe)CO_3$  and  $CaCO_3$  may be preserved by kinetic effects within carbonate-rich sediment in  
84 cold subducting slabs, consistent with slow breakdown kinetics observed in experiments at

85 transition zone conditions (Martirosyan et al., 2016). The relative stability of (Mg,Fe)CO<sub>3</sub> and  
86 CaCO<sub>3</sub> may also change at depth due to polymorphism. If (Mg,Fe)CO<sub>3</sub> or CaCO<sub>3</sub> reaches the  
87 base of the lower mantle, density functional theory calculations (Oganov et al., 2008; Pickard  
88 and Needs, 2015) and experiments (Boulard et al., 2011; Ono et al., 2007) suggest these  
89 carbonates will transform to tetrahedrally-coordinated structures. If the transition in CaCO<sub>3</sub>  
90 occurs at a shallower depth than the analogous transition in MgCO<sub>3</sub>, as predicted by Pickard and  
91 Needs (2015), CaCO<sub>3</sub> would be the denser and more energetically-favored carbonate in the deep  
92 lower mantle.

93 This study examines a Mg-Fe-Ca carbonate system in the petrologic context of a  
94 subducted carbonate assemblage in contact with metallic iron. Metallic iron may be present at  
95 the percent level throughout the mantle (Frost et al., 2004), and the outer core provides an  
96 unlimited reservoir of iron. Subducted carbonates may contact reduced core-mantle mixing  
97 regions if they reach depths within ~10s km from the base of the mantle (Frost and McCammon,  
98 2008; Otsuka and Karato, 2012). Previous studies of carbonates at lower mantle pressures have  
99 investigated mineralogical stability of single phases as a function of pressure and temperature  
100 alone (Isshiki et al., 2004; Solopova et al., 2014; Boulard et al., 2011; Ono et al., 2005), or used  
101 mixtures of carbonates and silicates which complicate textural analysis of run products  
102 (Biellmann et al., 1993; Thomson et al., 2014). In contrast, we examine reaction interfaces  
103 between multiple carbonates and iron; similar previous studies have been limited to transition  
104 zone conditions (Martirosyan et al., 2016; Pal'yanov et al., 2013). We determine the relative  
105 stability and metastability of Mg-, Fe-, and Ca-carbonates as host phases for oxidized carbon  
106 storage in the lower mantle.

107        **2. Methods**

108            To bring experimental petrology of carbonates to the Mbar pressures and 1000s K  
109 temperatures of the core-mantle boundary, experiments must be miniaturized: sample geometry  
110 must be controlled within the ~50x50x10-micron chamber of the laser-heated diamond anvil cell,  
111 and analysis must be performed with ~100-nm-scale spatial resolution of typical grain sizes of  
112 run products. Dolomite, a major constituent of subducted marble, provides a unique advantage as  
113 a starting material as it has a mixed Mg-Fe-Ca carbonate composition homogeneous to <nm  
114 scale. Natural dolomite crystals with composition determined to be  $(\text{Mg}_{0.38}\text{Ca}_{0.59}\text{Fe}_{0.03})\text{CO}_3$  by X-  
115 ray fluorescence spectroscopy and structure confirmed by X-ray diffraction were used as starting  
116 materials. Single dolomite crystals were polished to ~10-micron thickness and dried in a 120°C  
117 oven overnight before loading. 3-micron thick 99.85% iron foil was machined into discs with a  
118 ps-pulsed 532-nm laser or cut with a razor blade. Iron foils were loaded sandwiched between  
119 dolomite crystals in symmetric diamond anvil cells. No other pressure standard or medium was  
120 loaded in order to prevent reactions with other components and contamination of the chemical  
121 system. Sample sandwiches were loaded within chambers cut in Re gaskets in diamond anvil  
122 cells. Diamond anvils with flat culets of 200 micron diameter or beveled culets of 150 micron  
123 diameter were chosen to generate pressures corresponding to the lower mantle.

124            Samples were compressed to pressures of 51, 66, 77, and 113 GPa, as determined by the  
125 equation of state of the iron foil (Mao et al., 1990) before laser heating (Table 1). Pressures were  
126 not measured during heating due to chemical reaction of the iron foil with the dolomite, but were  
127 likely ~7-10 GPa higher than those reported here due to thermal pressure. Laser heating was  
128 performed with *in situ* X-ray diffraction at the GSECARS sector of the Advanced Photon Source

129 (Prakapenka et al., 2008). The laser spot was focused to a diameter of ~10 microns with a flat-  
130 top beam shape. Each sample was heated for 10-20 min at 1800-2500 K.

131 After recovery to ambient conditions, each heated spot was sectioned using a Zeiss NVision  
132 40 dual-beam scanning electron microscope and focused Ga<sup>+</sup> ion beam (Centre Interdisciplinaire  
133 Microscopie de Electronique (CIME), EPFL). Each sample was coated with 15 nm Au to reduce  
134 charging in the scanning electron microscope. To protect the samples from damage by the Ga<sup>+</sup>  
135 ion beam, an additional ~1-2 micron thick layer of Pt or C was deposited across the centers of  
136 heated spots. Thin sections of each heated spot were extracted and polished to electron  
137 transparency (~100 nm thickness).

138 Imaging of recovered thin sections was performed with scanning transmission electron  
139 microscopy (S/TEM) and energy-dispersive X-ray spectroscopy (EDX) in a FEI Tecnai Osiris  
140 analytical TEM (CIME, EPFL). Accelerating voltage for these measurements was 200 kV. The  
141 Osiris TEM is equipped with four wide-solid-angle detectors for high-speed chemical  
142 measurements by EDX spectroscopy. EDX maps were scanned over 1024x1024 pixel areas with  
143 pixel dwell time of 50 microseconds. Typical count rates were ~40,000-50,000 counts per  
144 second. Chemical mapping prevents migration of elements due to damage by the electron beam.  
145 Uncertainties in compositions were determined from standard deviations of EDX measurements  
146 obtained from selected regions within multiple grains.

### 147 **3. Results**

148 Laser-heating dolomite-iron sandwiches from both sides produces a lens-shaped heated  
149 zone (Figure 1), as predicted by models (Kiefer and Duffy, 2005; Rainey et al., 2013) and  
150 measurements (Campbell, 2008) of thermal diffusion in the diamond anvil cell. Laser absorption



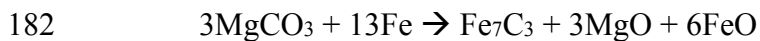
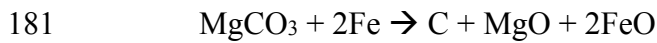
151 and diffraction indicate that the sample reaches a steady state within a few minutes. The hottest  
152 region of the sample is the laser-absorbing central iron layer. The insulating dolomite layers  
153 experience both axial and radial temperature gradients, with highest temperatures at the contacts  
154 with the iron foil and lowest temperatures at the diamond anvil surface. High-resolution TEM  
155 inspection of recovered thin sections indicates that grain sizes decrease away from the surface of  
156 the iron foil, consistent with this thermal gradient (Figure 1). At the cool upper and lower edges  
157 of the heated spot, ribbons of magnesium and calcium carbonate exsolve from the dolomite  
158 (Figure 2), as has been observed at lower pressures (Sato and Katsura, 2001; Shirasaka et al.,  
159 2002).

160 Both EDX analysis of recovered thin sections in the TEM (Figure 3) and diffraction  
161 patterns obtained during and after sub-solidus laser heating (Figure 4b) show that the metallic  
162 iron at the sample center reacts completely with the dolomite to generate a mixture of FeO and  
163 Fe<sub>7</sub>C<sub>3</sub>. The iron layer thus exhibits oxidation which must be compensated by reduction of the  
164 carbonate. Within the carbonate layer near the hot interface with the iron foil, three phases are  
165 found in all samples: diamond, Mg-bearing ferropericlase, and CaCO<sub>3</sub> (Figure 3). The diffusion  
166 of iron from the sample center propagates breakdown of the magnesium carbonate to diamond  
167 and ferropericlase. Due to diffusion, this ferropericlase has much more MgO than the FeO at the  
168 sample center (Figures 5-6). Unlike MgCO<sub>3</sub>, CaCO<sub>3</sub> exsolves from the dolomite but is never  
169 observed to break down. EDX composition analysis confirms that the CaCO<sub>3</sub> phase retains both  
170 O and C within measurement error and there is no evidence for measurable Ca in any other phase  
171 (Figure 5). At the pressures examined here, the stable polymorph of CaCO<sub>3</sub> is the post-aragonite  
172 phase (Ono et al., 2005). Post-aragonite-type CaCO<sub>3</sub> is observed in diffraction patterns after  
173 heating (Figure 4b), along with unreacted dolomite. These experiments show that a carbonate-

174 rich rock such as subducted marble subjected to reducing conditions in contact with metallic  
175 iron, post-aragonite-type  $\text{CaCO}_3$  is a more stable form of carbonate than  $\text{MgCO}_3$  throughout the  
176 lower mantle pressure range.

#### 177 **4. Discussion**

178 The mixture of  $(\text{Mg,Fe})\text{O}$ , diamond,  $\text{Fe}_7\text{C}_3$  and  $\text{CaCO}_3$  is produced by redox coupling  
179 between the iron and carbon and breakdown of the  $\text{MgCO}_3$  component. The following reactions  
180 explain these observations:



183 In the center of the sample, the system is saturated in iron, leading to a mixture  
184 dominated by  $\text{Fe}_7\text{C}_3$  and  $\text{FeO}$ . In the region where the carbonate breaks down, the carbon/iron  
185 ratio is higher, and reduced carbon is found in diamonds rather than carbides. The breakdown of  
186  $\text{MgCO}_3$  is favorable in all heated regions in the presence of iron. The stable host phase for  
187 carbon is controlled by the  $\text{Fe}/\text{MgCO}_3$  ratio of reactants. Recent studies have largely focused on  
188  $(\text{Mg,Fe})\text{CO}_3$  as a host phase for oxidized carbon in the deep Earth, as the melting point of  
189 magnesite or ferromagnesite is higher than that of  $\text{CaCO}_3$  in the transition zone. However,  
190  $(\text{Mg,Fe})\text{CO}_3$  is much more susceptible to redox breakdown than  $\text{CaCO}_3$ .

191 Redox breakdown will promote diamond formation from  $(\text{Mg,Fe})\text{CO}_3$  in carbonated  
192 eclogite and peridotite. This study and others have shown that diamonds nucleate and grow  
193 directly from carbonates at subsolidus, reducing conditions, and inclusion-bearing diamonds  
194 used as evidence that carbonates are stable to great depths in the mantle record incomplete redox  
195 breakdown (e.g. Wang et al., 1996). Reducing agents relevant to carbonate stability at different

196 stages of Earth's chemical evolution include graphite (Pal'yanov et al., 1999), H<sub>2</sub> (Pal'yanov et  
197 al., 2002), Si metal (Siebert et al., 2005), and Fe metal. In a mixture of carbonate and Fe-Si alloy,  
198 Si and C were oxidized, producing a mixture in which diamonds coexist with metallic iron  
199 (Siebert et al., 2005). Other studies have suggested either that pure iron and pure carbon should  
200 not coexist in equilibrium (Rouquette et al., 2008; Scott et al., 2001) or that iron carbides and  
201 diamond compete as hosts of reduced carbon (Iizuka et al., 1996). In this study, metallic iron  
202 reacts completely to carbide and oxide, indicating that the system is oversaturated in carbon.  
203 Because the mantle has been suggested to be a highly reducing environment, saturated in  
204 metallic iron (Frost et al., 2004; Frost and McCammon, 2008; Rohrbach et al., 2007; Rohrbach  
205 and Schmidt, 2011), carbonate in this system will be susceptible to redox breakdown at  
206 subsolidus temperatures. Reduction of subducted carbonates by interaction with metallic iron  
207 was previously explored at relatively modest depths (Martin and Hammouda, 2011; Martirosyan  
208 et al., 2015a, 2015b; Stagno et al., 2011). Most previous studies were conducted at pressures  
209 reaching ~6 GPa (Martin and Hammouda, 2011; Martirosyan et al., 2015a, 2015b), too low to  
210 model the depths at which metallic iron becomes available to react with subducted carbonate.  
211 Metallic iron may also be present in the lower mantle due to charge disproportionation in  
212 silicates (Frost et al., 2004; Rohrbach et al., 2007), mixing at the CMB (Knittle and Jeanloz,  
213 1989; Otsuka and Karato, 2012), or residue of magma ocean solidification (Zhang et al., 2016).  
214 Recently, iron-magnesite mixtures were examined at 16-45 GPa and 1500-1700 °C,  
215 corresponding to transition zone to lower mantle depths (Stagno et al., 2011). At these  
216 conditions, diamonds are observed to coexist with magnesite, ferropericlase and carbon-free  
217 iron-iridium alloy. The Ir alloy was used to determine that  $f_{O_2}$  was ~3 log units above the iron-  
218 wüstite buffer. The breakdown of magnesite observed here may imply lower  $f_{O_2}$  conditions,

219 perhaps due to the sample environment in the diamond anvil cell or higher pressures. For  
220 subducted marble or carbonated silicate lithologies that reach a reduced zone near the core-  
221 mantle boundary,  $(\text{Mg,Fe})\text{CO}_3$  cannot be preserved.

222 Spin transitions in ferromagnesite have recently been studied for their potential to affect  
223 carbonate stability (Lin et al., 2012; Liu et al., 2015). The spin transition results in a ~8% unit  
224 cell volume collapse for  $(\text{Mg}_{0.35}\text{Fe}_{0.65})\text{CO}_3$  (Lin et al., 2012) and would thus be expected to have  
225 a significant effect on phase equilibria. As the minimum pressure examined in these experiments  
226 is above the spin transition pressure, we are unable to evaluate whether the spin transition is  
227 related to the observed breakdown of  $(\text{Mg,Fe})\text{CO}_3$ . The susceptibility of  $(\text{Mg,Fe})\text{CO}_3$  to  
228 disproportionation at low  $f_{\text{O}_2}$  suggests that low-spin iron-bearing carbonates are unlikely to be  
229 stable in Earth's mantle.

230  $\text{CaCO}_3$  is less sensitive than  $(\text{Mg,Fe})\text{CO}_3$  to redox breakdown, but melting, reaction with  
231 silicates, and buoyancy remain challenging barriers to its transport to the deep mantle. Although  
232 the melting point of  $\text{CaCO}_3$  (Bayarjargal et al., 2010; Thomson et al., 2014) is well above a 1600  
233 K adiabatic geotherm (Brown and Shankland, 1981), the eutectic melting point for carbonate  
234 mixtures is substantially lower and comparable to the geotherm (Thomson et al., 2014). Eutectic  
235 melting has been argued to effectively block carbonate transport to the lower mantle (Thomson  
236 et al., 2016). However, no evidence is observed for melting of the dolomite carbonate in this  
237 work. Moreover, geotherms both for the average mantle (e.g. Brown and Shankland, 1981;  
238 Andrault et al., 2011; Nomura et al., 2014) and subducting slabs (e.g. Andrault et al., 2014)  
239 remain highly uncertain. The key question is whether, for realistic subducted carbonates, the  
240 melting point of the mixture is high enough relative to the temperature in the slab to prevent  
241 diamond formation. With temperature uncertainties of at least 100s K, in addition to potential

242 kinetic effects on the efficiency of carbonate reduction and melting (Martirosyan et al., 2016),  
243 preservation of carbonates in the lower mantle cannot yet be ruled out.  $\text{CaCO}_3$  is also expected to  
244 be destabilized in the mantle by reaction with  $(\text{Mg,Fe})\text{SiO}_3$  in peridotite or eclogite to produce  
245  $\text{CaSiO}_3$  and  $(\text{Mg,Fe})\text{CO}_3$  (Biellmann et al., 1993; Seto et al., 2008). This reaction suggests  
246  $\text{CaCO}_3$  is most likely to be preserved in silicate-poor, dolomite-rich marble entrained with  
247 subducting slabs. Because metasediment is likely to be as much as ~5-15% less dense than  
248 surrounding peridotite, ~100 m packages of marble would likely rise to the surface through  
249 diapirism (Kelemen and Manning, 2015). Transport of  $\text{CaCO}_3$  to the deep mantle would require  
250 carbonate to reside in layers or regions thin enough to be entrained with the cold slab, but thick  
251 enough that slow diffusion blocks reaction of carbonate with silicates.

252 Observations in this and other experimental studies challenge interpretation of oxide  
253 inclusions identified in diamonds. While traditionally  $(\text{Mg,Fe})\text{O}$  inclusions have been  
254 considered to be a smoking gun for formation in the Earth's lower mantle, as a leftover from the  
255 breakdown of  $\text{Mg}_2\text{SiO}_4$  to lower mantle bridgmanite (Kaminsky, 2012), carbonate  
256 disproportionation is another possible mechanism for oxide formation (Tappert et al., 2005;  
257 Thomson et al., 2016). Direct observation of lower mantle silicates of appropriate compositions  
258 is necessary to confirm ultra-deep diamond origin.

## 259 **5. Conclusions**

260 Magnesite-siderite is not a likely host phase for carbonate in reduced regions of the deep  
261 lower mantle, but post-aragonite-type  $\text{CaCO}_3$  may be stable in carbonate-rich lithologies. While  
262  $\text{CaCO}_3$  undergoes more pressure-induced polymorphic transitions than  $(\text{Mg,Fe})\text{CO}_3$  in the deep  
263 mantle and may be more likely to react with lower mantle silicates, relative to  $(\text{Mg,Fe})\text{CO}_3$  it is  
264 less likely to participate in redox reactions. A low  $f_{\text{O}_2}$  environment in the lower mantle (Frost and

265 McCammon, 2008; Rohrbach and Schmidt, 2011) will promote breakdown of ferromagnesite but  
266 CaCO<sub>3</sub> will remain stable to pressure, temperature and redox conditions near the base of the  
267 lower mantle if isolated from silicates. A carbonate-rich heterogeneity near the base of the  
268 mantle could be a high-pressure marble, with CaCO<sub>3</sub> associated with diamonds formed by  
269 breakdown of MgCO<sub>3</sub>.

270 Diamond-bearing marble in the lower mantle is not likely to be directly observable by  
271 seismic tomography, but could impact observations of heterogeneous redox conditions at depth  
272 due to mantle convection and subduction and/or signatures of Earth's chemical evolution.  
273 Heterogeneous oxygen fugacity at depth is evident in diamond inclusions (Brenker et al., 2007;  
274 Walter et al., 2011; Ryabchikov and Kaminsky, 2013; Smith et al., 2016; Kaminsky, 2012) as  
275 well as chemical variation in both mid-ocean ridge basalts due to relative contributions of  
276 depleted and primitive mantle sources (Cottrell and Kelley, 2013) and ocean island basalts  
277 potentially sourced from the core-mantle boundary (White, 2010). The interpretation of available  
278 redox proxies for the deep mantle over deep time, particularly presence of carbonate (e.g.  
279 Brenker et al., 2007) and speciation of iron (Frost and McCammon, 2008), must be evaluated in  
280 the light of the multivariable dependence of stability of MgCO<sub>3</sub> and CaCO<sub>3</sub> on temperature, bulk  
281 composition of the phase assemblage and  $f_{O_2}$ .

## 282 **Acknowledgments:**

283 The authors acknowledge M. Hirschmann for thoughtful comments that improved this  
284 manuscript. We thank A. Magrez for assistance with X-ray diffraction and X-ray fluorescence  
285 characterization of the starting material. F. Bobard, D. Alexander and E. Oveisi provided training  
286 and advice for focused ion beam and transmission electron microscopy. S. M. Dorfman  
287 acknowledges the Marie Heim-Vögtlin program of the Swiss National Science Foundation for  
288 financial support through project PMPDP2\_151256. J. Badro acknowledges the financial support  
289 of the Sloan Foundation's Deep Carbon Observatory and UnivEarthS Labex program at  
290 Sorbonne Paris Cité (ANR-10-LABX-0023 and ANR-11-IDEX-0005-02). GeoSoilEnviroCARS

291 is supported by the National Science Foundation - Earth Sciences (EAR-0622171), Department  
292 of Energy - Geosciences (DE-FG02-94ER14466) and the State of Illinois.

293 Data reported in this paper are available by request from S. M. Dorfman at  
294 [dorfman3@msu.edu](mailto:dorfman3@msu.edu).

295

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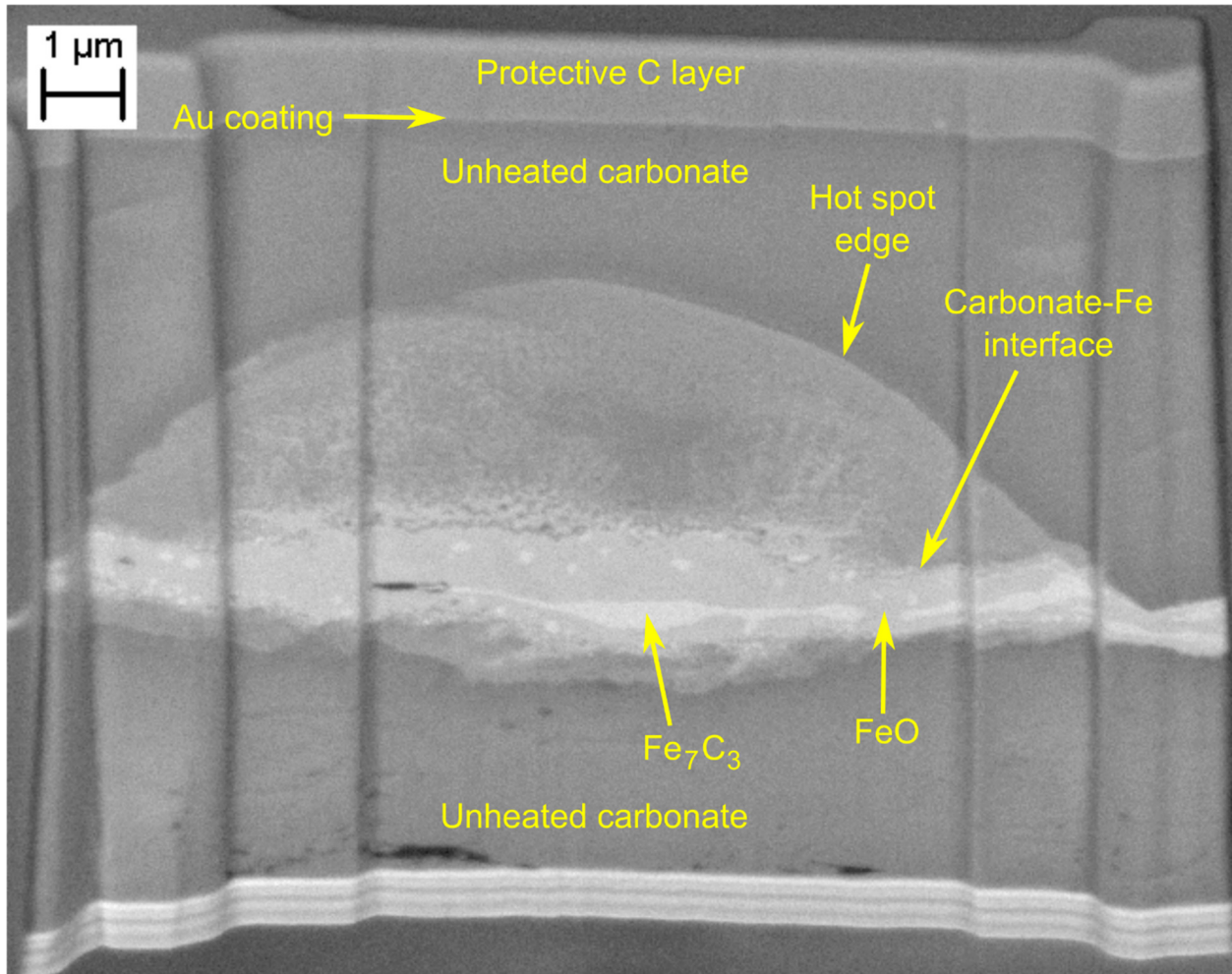
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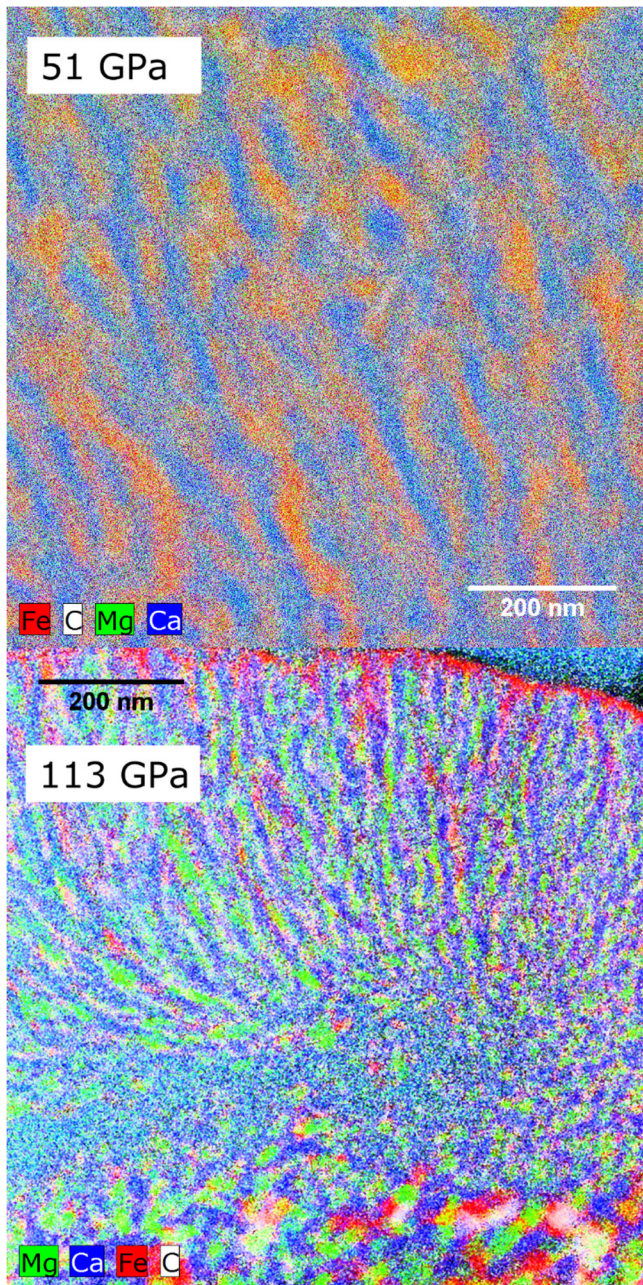
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508 Figure 1: Backscattered scanning electron image recorded at 4 kV of dolomite-iron reaction  
509 interface in sample thin section recovered from 66 GPa and 1900-2200 K. The iron-rich region in  
510 the center appears brightest due to its high density. The extent of iron diffusion into and reaction  
511 with the Fe-poor carbonate is also evident based on density. A few micron offset in alignment of  
512 upstream and downstream lasers may be responsible for asymmetry of heated spot.



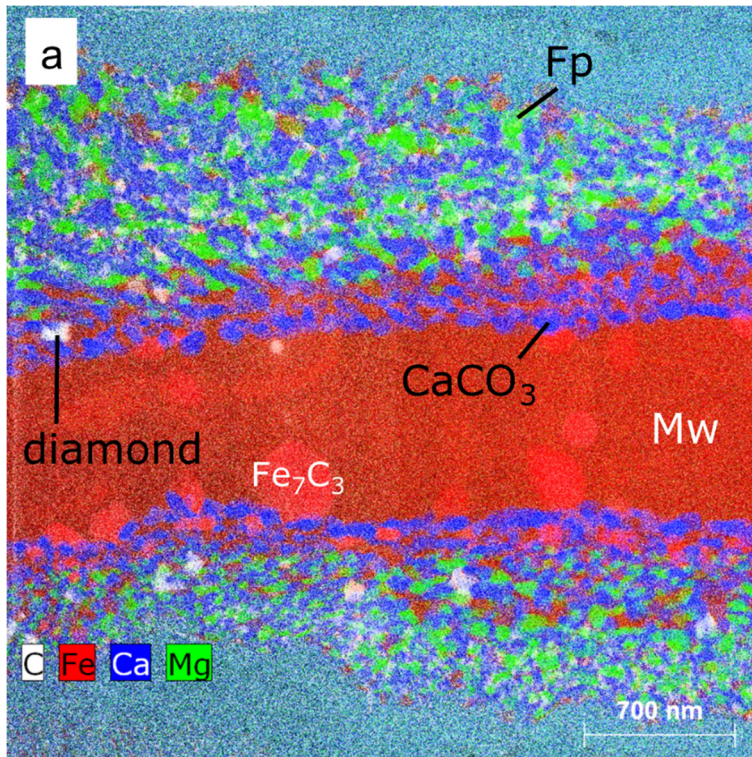
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514 Figure 2: Energy-dispersive X-ray image of a) exsolution of two carbonates from dolomite at 51

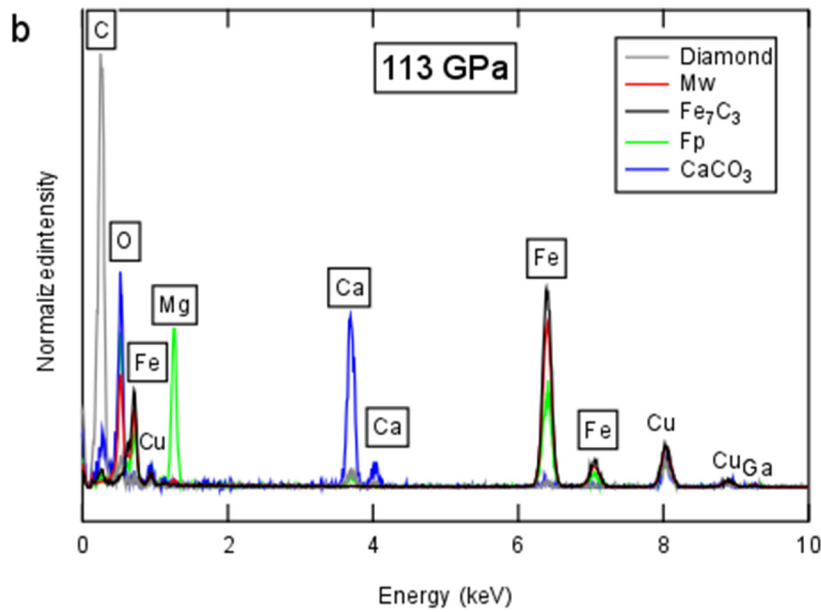
515 GPa and b) formation of  $\text{Fe} + \text{C} + \text{CaCO}_3$  at 113 GPa. Elements color-coded as follows:

516 red=iron, blue=calcium, green=magnesium, white=carbon.

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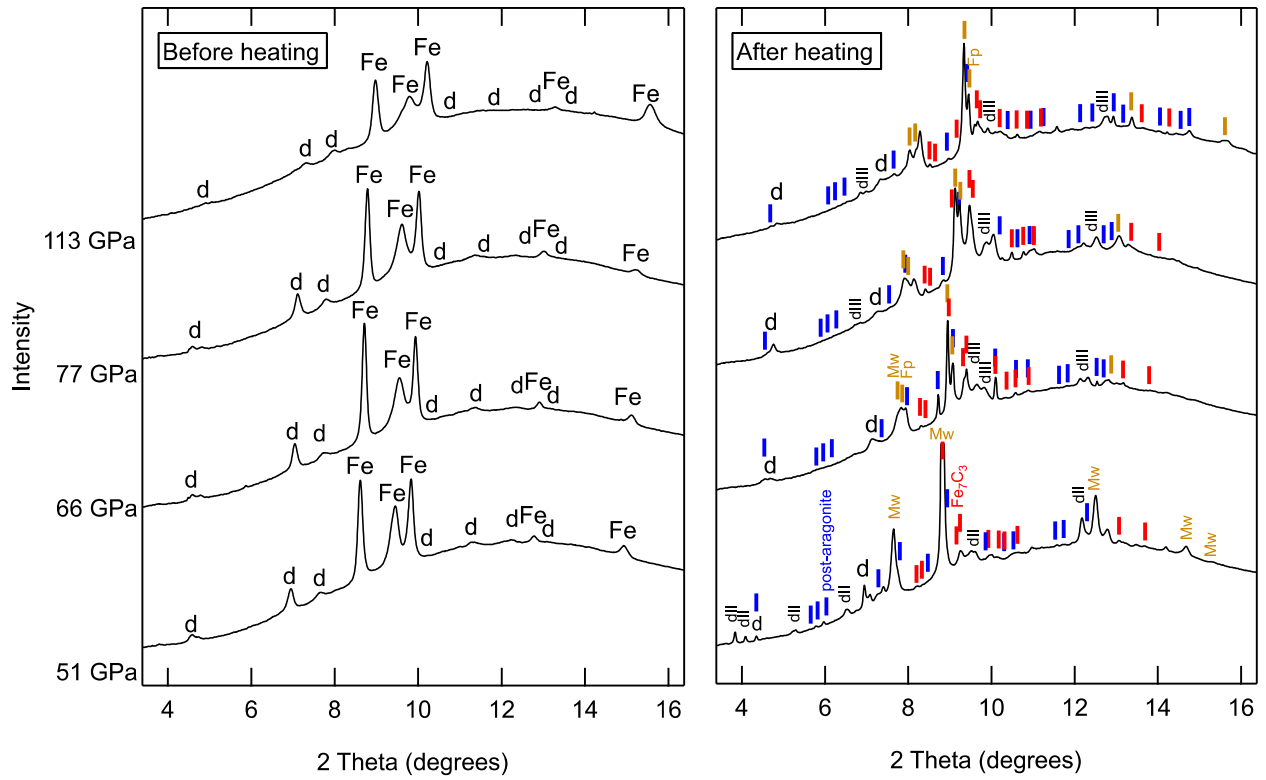
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520 Figure 3: Composition measurements for dolomite-iron sample recovered from 113 GPa and

521 2400-2500 K. a) Energy-dispersive X-ray map with elements color-coded as follows: red=iron,

522 blue=calcium, green=magnesium, white=carbon. b) Examples of EDX spectra obtained for each  
523 phase.



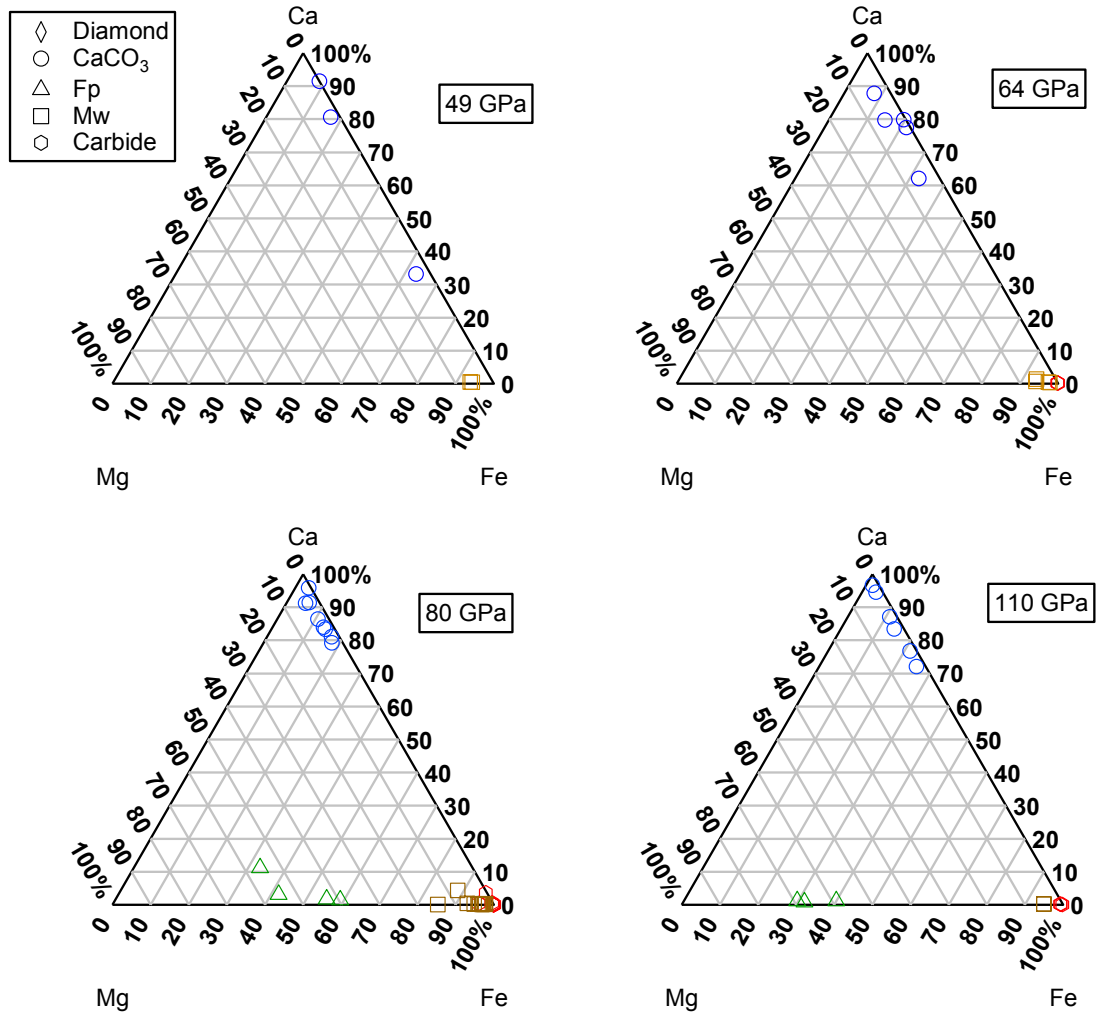


524

525 Figure 4: X-ray diffraction patterns observed before and after transforming samples of dolomite  
 526 (d) and iron foil (Fe) to magnesiowüstite and ferropericlase (gold Mw and Fp), Fe<sub>7</sub>C<sub>3</sub> (red), and  
 527 post-aragonite-type CaCO<sub>3</sub> (blue) at pressures 51-113 GPa and temperatures 1800-2500 K in the

528 laser-heated diamond anvil cell. Additional diffraction peaks from high-pressure polymorphs of  
529 dolomite are labelled dII and dIII. For these experiments  $\lambda=0.3100 \text{ \AA}$ .

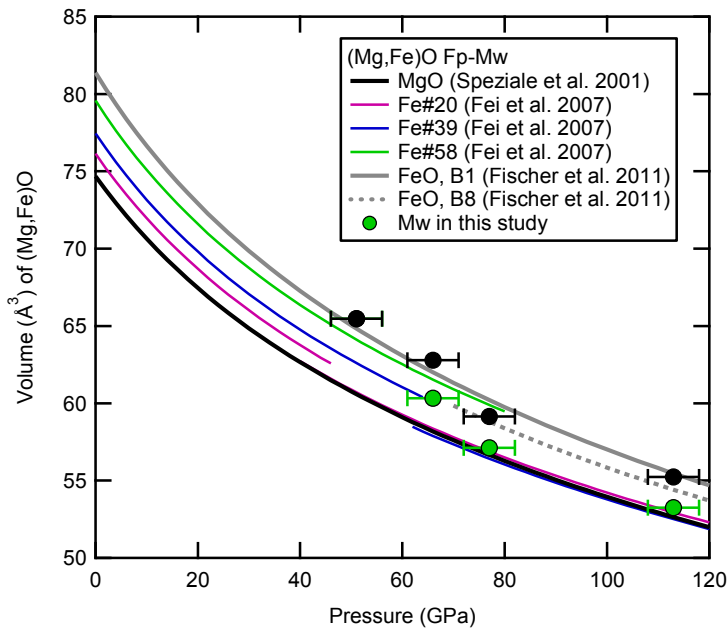
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532 Figure 5: Compositions for observed phases obtained from EDX spectra plotted on Mg-Fe-Ca  
533 ternary diagrams.

534



535

536 Figure 6: Observed unit cell volumes for Mw (black) and Fp (green) in this study plotted relative  
537 to previously-measured equations of state for Fp-Mw compositions with different  
538  $Fe\# = Fe/(Mg+Fe)$  (Fei et al., 2007; Fischer et al., 2011; Speziale et al., 2001). Pressures for data  
539 in this study are assumed to be the same as pressures obtained from the Fe foil before heating.  
540 (Mg,Fe)O diffraction peaks are split, indicating unit cell volumes consistent with coexistence of  
541 FeO at the sample center and  $\sim(Mg_{0.6}Fe_{0.4})O$  produced by breakdown of the dolomite. A  
542 decrease in unit cell volume observed in both oxides between 66 and 77 GPa is consistent with  
543 the spin transition in iron-rich Mw and structural change in FeO under these conditions.

544

545 Table 1.

546 Pressure, temperature, and heating duration for all experiments. Pressures given were obtained  
547 before heating from the equation of state of the iron foil (Mao et al., 1990). Temperature  
548 differences between downstream and upstream sides were typically observed to be ~100 K and  
549 varied by ~100 K over the heating duration.

Pressure before heating (GPa)	Temperature (K)	Duration (min)
51	1800-2050	15
66	1900-2200	10
77	1900-2200	20
113	2400-2500	10