

1 Revision 2

2 Experimental determination of siderite stability at high pressure

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9 **Abstract**

10 The stability field of siderite has been determined up to 10 GPa. Decarbonation of siderite  
11 occurs at pressures below 6 GPa with a Clapeyron slope of about 0.0082 GPa/K. At higher  
12 pressure, we observed direct melting of siderite without decarbonation. The melting temperature  
13 is about 1550°C at 10 GPa. Our experimental results, compared with previous studies on the  
14 decomposition curve of magnesite, indicate that Fe has a significant effect on the stability of  
15 magnesite-siderite solid solutions under upper mantle conditions. The reaction products are  
16 strongly dependent on the oxygen fugacity of the system. The disproportionation reaction during

17 decomposition of siderite might be an important mechanism to explain the stability of carbon as  
18 graphite (diamond) in the Earth's mantle.

19 **Keywords:** siderite, magnetite, graphite, oxygen fugacity, disproportionation, carbon cycle

20

## 21 **Introduction**

22 The global deep carbon cycle involves the exchange of various carbon-bearing phases  
23 between the Earth's interior and the surface. Carbon is recycled into Earth's deep interior via  
24 subduction in the form of carbonated oceanic crust, and it is partly released to Earth's surface via  
25 volcanism, for example as CO<sub>2</sub> at mid-ocean ridges and arc islands (Poli and Schmidt, 2002;  
26 Sleep and Zahnle, 2001). Therefore, the carbonation and decarbonation processes as well as the  
27 melting and stability of carbonate minerals at high pressure and temperature are of particular  
28 interest in order to understand the global deep carbon cycle (Boulard et al., 2011). Experiments  
29 have shown that magnesite is the most stable host for carbon during subduction at the expense  
30 of calcite and dolomite (Biellmann et al., 1993; Fiquet et al., 2002; Irving and Wyllie, 1975;  
31 Isshiki et al., 2004; Zhang et al., 1997), whereas the siderite component is always present as solid  
32 solution with magnesite in rocks such as Martian meteorite ALH 84001 (Bell, 2007; McCollom,  
33 2003; Thomas-Keprta et al., 2009), metamorphosed iron formations (Klein, 1978; Klein, 2005),

34 altered igneous rocks (Buckley and Woolley, 1990; Laverne, 1993) and subducted carbonated  
35 oceanic and continental crust (Liu et al., 2006; Messiga et al., 1999; Mukherjee and Sachan,  
36 2003; Omori et al., 1998; Zhang et al., 2002b; Zhang et al., 2003b; Zhang and Liou, 1994; Zhang  
37 and Liou, 1996; Zhu, 2005).

38         Solid solution of siderite and magnesite is a significant carbonate constituent of  
39 subducted carbonated oceanic and continental crust and it plays a fundamental role in the  
40 recycling of carbon into Earth's deep interior. Previous experimental and petrologic studies have  
41 focused on the stability of magnesite at high pressure and high temperature and have determined  
42 the phase relationships of magnesite at high temperature in the deep mantle (Fiquet et al., 2002;  
43 Isshiki et al., 2004; Litasov et al., 2008; Zhang et al., 1997). However, data on the phase  
44 relationships of siderite at high pressure are limited. The decarbonation reaction of siderite has  
45 been investigated at pressures less than 1GPa using a cold-seal pressure vessel apparatus (French,  
46 1965; Goldsmith et al., 1962; Weidner, 1972). The stability of siderite also has been calculated  
47 as a function of oxygen fugacity at low temperature (Melnik, 1964; Yui, 1966). Although siderite  
48 is confirmed to be stable up to 47 GPa at 2000K (Santillan and Williams, 2004) and up to 90  
49 GPa at ambient temperature (Lavina et al., 2009) based on results from diamond-anvil cell  
50 experiments, the stability field and melting relationship of siderite are still poorly understood at  
51 high temperature under mantle conditions. Boulard et al. (2012b) demonstrated the formation of

52 reduced carbon compounds such as diamonds or CO accompanied by a new Fe (III)-bearing  
53 high-pressure carbonate phase. In this study, we focus on the decarbonation and melting of  
54 siderite at high temperature up to 10 GPa by conducting experiments in a piston-cylinder  
55 apparatus and multi-anvil devices.

56 The thermal decomposition of siderite can be expressed by different types of reactions  
57 with respect to a variety of oxides in the reaction system (French, 1965; French, 1971). Siderite  
58 can decompose into different products under various experimental and geological conditions and  
59 its stability is controlled in part by the oxygen fugacity and carbon dioxide fugacity. Therefore,  
60 siderite is of interest as an indicator of oxygen fugacity and carbon dioxide fugacity in the  
61 experimental and geological environments. A two-step mechanism has been suggested for the  
62 thermal decomposition of siderite. Initially, siderite ( $\text{FeCO}_3$ ) decomposes to wüstite ( $\text{FeO}$ ) and  
63 carbon dioxide ( $\text{CO}_2$ ), similar to decomposition of magnesite ( $\text{MgCO}_3 = \text{MgO} + \text{CO}_2$ ). Then,  
64 reduction of  $\text{CO}_2$  to CO or C could occur accompanied by partial or total oxidation from wüstite  
65 ( $\text{FeO}$ ) to magnetite ( $\text{Fe}_3\text{O}_4$ ) (Chang and Ahmad, 1982; Powell, 1965).

66 For given oxygen fugacity, the siderite thermal decomposition reactions can be expressed  
67 as:



69 or



71            Depending on the oxygen fugacity, the ferrous iron in the siderite can be oxidized to  
72 produce either  $\text{Fe}_3\text{O}_4$  or coexisting  $\text{Fe}_3\text{O}_4$  and  $\text{FeO}$  within geological temperature and pressure  
73 range, accompanied by release of  $\text{CO}_2$  and  $\text{CO}$ . Nevertheless, under the reaction conditions  
74 presumed for siderite decomposition,  $\text{CO}$  would be thermodynamically unstable with respect to  
75 the disproportionation via the Boudouard reaction  $2\text{CO} = \text{CO}_2 + \text{C}$ , and graphite could be  
76 precipitated from the gas/fluid phase at appropriate oxygen fugacity (French, 1965; Weidner,  
77 1972; Yui, 1966). The reaction  $2\text{CO} = \text{CO}_2 + \text{C}$  has smaller total gas volume on the right side, so  
78 graphite and  $\text{CO}_2$  are the favored run product at high pressure in a closed system. Consequently,  
79 the reactions 1 and 2 at high pressure in a closed system should be expressed as:



81 and



83            The mechanism of siderite decomposition in a more oxidized environment is likely more  
84 complex and depends on the ratio of siderite and oxidant (Chang and Ahmad, 1982). Reaction of

85 siderite with hematite or oxygen results in formation of magnetite via reactions 5 and 6. At  
86 higher oxygen fugacity, hematite can be the reaction product via reaction 7.



90 In order to understand the stability field of siderite at high pressure and the role of Fe in  
91 the stability of Fe-bearing magnesite in the mantle, we have conducted a series of experiments on  
92 siderite up to 10 GPa in the temperature range of 800-2000 °C.

### 93 **Experimental and analytical methods**

94 The starting material for all the experiments is a natural siderite (Ivigtut, Greenland)  
95 provided by the Smithsonian Institution, Washington DC. The composition of the siderite was  
96 accurately determined with JEOL 8900 microprobe at the Geophysical Laboratory. The  
97 operating conditions were 15 kV accelerating voltage, a 20 nA beam current and a counting time  
98 of 20-30 seconds. The beam diameter was set to a point spot for the measurements. Natural  
99 siderite with known composition was used as a standard. The measurements yielded a molecular  
100 formula  $(\text{Fe}_{0.950}\text{Mn}_{0.046}\text{Mg}_{0.004})\text{CO}_3$ , indicating that the siderite is almost a pure end-member. A

101 diffraction pattern of the starting siderite was also collected using a Rigaku R-Axis Rapid-S  
102 microdiffractometer operating at 40 kV and 30 mA with an imaging plate area detector and Mo  
103 K-alpha radiation. The lattice parameters ( $a=4.6883 \text{ \AA}$ ,  $c=15.3478 \text{ \AA}$ ) were determined by a  
104 least-squares Rietveld refinement of the XRD data (Fig 1) using Software GSAS (Larson and  
105 Dreele, 2004). The lattice parameters and the composition of the siderite-magnesite solid  
106 solution showed a linear correlation based on previous published data (Boulard et al., 2012a;  
107 Effenberger et al., 1981; Litasov et al., 2008; Markgraf and Deeder, 1985; Zhang et al., 1997).  
108 The lattice parameters of our sample are plotted on the almost pure siderite side of the solid  
109 solution (Fig 2). Similar linear correlation between the lattice parameters and the Mg/Fe  
110 substitution was also observed in the solid solutions of ankerite and dolomite (Reeder and  
111 Dollase, 1989).

112 In order to avoid oxidizing siderite, we ground the siderite starting material in a glove  
113 box in an agate mortar and stored the powdered sample in vacuum desiccators. Because siderite  
114 can be easily oxidized in air, we have detected some hematite in the starting material (about 5  
115 mole% according to the refinement of the XRD pattern) (Fig. 1). To confine gas/fluid released  
116 from the siderite decomposition, the siderite starting material was loaded in a sealed platinum  
117 capsule for all the experiments. Before the sample loading, the platinum capsules were annealed  
118 in air at  $1000^{\circ}\text{C}$ , boiled in dilute HCl for 30 minutes, ultrasonically cleaned in ethanol (for 10

119 min), and then stored in an oven in air at 110°C. The end of the capsule was three-way crimped,  
120 and finally sealed by arc welding. Wet tissue surround the capsule was used to ensure the sample  
121 is not overheated. Some of the experiments failed likely due to blow-out caused by the high gas  
122 pressure produced by the decomposition of siderite. For this reason we loaded a small amount of  
123 sample in a double capsule (small inner one and bigger outer one).

124 Experiments at 2.5 GPa were carried out in a piston-cylinder apparatus. Experiments  
125 between 4 and 6 GPa were carried out in a multi-anvil apparatus using an 18/11 assembly  
126 (octahedral edge length/truncated edge length) and between 8 and 10 GPa, using a 10/5 assembly.  
127 Temperatures were measured with a type C ( $W_5Re_{95}$ - $W_{26}Re_{74}$ ) thermocouple at the center of the  
128 furnace without correcting for the pressure effect on e.m.f. Details of the cell assemblies and the  
129 pressure and temperature calibrations have been described in a previous publication (Bertka and  
130 Fei, 1997). The estimated temperature gradient across a 2-mm platinum capsule for the 18/11  
131 assembly is about 25°C, and the temperature gradient for the 10/5 assembly is less than 30°C  
132 because of shorter sample capsules (<1 mm). Both pressure and temperature were automatically  
133 controlled during the runs. Samples were first pressurized to the desired pressure, then heated at  
134 a rate of 50°C/min and held at a constant temperature for enough time (see Table 1) to determine  
135 the reaction direction. Each experiment was quenched by shutting off the power supply to the  
136 furnace, followed by automatic depressurization to atmospheric pressure at a rate of -1.0 GPa/ h.



137           After each experiment, the recovered sample was carefully picked out from the assembly.  
138   Some of the samples (about 1mm size) were mounted on a glass fiber for collecting X-ray  
139   diffraction (XRD) patterns, and the rest of the sample was mounted in epoxy resin, sectioned and  
140   polished with aluminum oxide powder for measurements by scanning electron microscope  
141   (SEM).

142           The X-ray diffraction pattern for each sample was analyzed by Jade 6.0 software and  
143   compared with PDF card data to identify mineral phases. The observed diffraction peaks match  
144   well with those of the expected phases in the run products based on the standard X-ray PDF data,  
145   as shown in Figure 3. Coexisting phases were often observed in the run products. The mole  
146   percentage of each phase was calculated according to the Rietveld refinement of the collected  
147   XRD pattern using the software GSAS (Larson and Dreele, 2004). The results are listed in Table  
148   1. Typical error in the calculated phase proportion is about 2%. Some recovered samples were  
149   also analyzed using scanning electronic microscope (SEM) with EDS to identify the stable  
150   phases and to image the quench textures. The BSE images and EDS spectra were collected on a  
151   field emission SEM JEOL 6500F or a FIB/SEM Zeiss Auriga crossbeam instrument operated at  
152   15 kV. Figure 4 shows representative BSE images of the run products recovered from different  
153   pressures and temperatures.

154

## Results and Discussion

155 We have conducted 18 experiments on siderite stability at high pressure in sealed  
156 capsules. The experimental conditions and phase proportions of the run products are listed in  
157 Table 1. For run products without melt, the phase proportion is refined from the X-ray diffraction  
158 pattern. We also estimated the phase proportion in the quenched melt by XRD refinements. The  
159 proportion of the solid and melt phase is estimated according to the SEM images (e.g., Fig. 4c).  
160 Siderite was present in all the quenched samples, even in the experiments run for as long as 36  
161 hours, indicating that the decarbonation reaction is rather sluggish due to the gas phase produced  
162 in the run product. The small amount of hematite (5%) in the starting material can be exhausted  
163 via reaction 5 and produce some inherited magnetite (~7%). The small amount of hematite in the  
164 starting material has limited effect on the oxygen fugacity of the experimental run because of the  
165 small quantity. The intrinsic oxygen fugacity of the assembly should be close to the wüstite (FeO  
166 in siderite)-magnetite (run product) buffer. There should be smaller amount of magnetite  
167 produced via reaction 6 due to the trapped air in the capsule. The total amount of magnetite  
168 produced by reactions 5 and 6 is expected to be less than 15%. In order to determinate the phase  
169 boundary of reaction 3, we established criteria to determine the reaction direction. We consider  
170 that siderite present at abundances >85% is in the siderite stable region and magnetite present at  
171 abundances >75% is in the magnetite stable region. At pressures below 6 GPa, siderite undergoes

172 decarbonation as temperature increases, producing magnetite, graphite, and CO<sub>2</sub> fluid. Further  
173 increase of temperature leads to melting. The Clapeyron slope of the siderite decomposition  
174 reaction via reaction 3 is about 0.0082 GPa/K. At pressures above 6 GPa, we observed direct  
175 melting of siderite without decarbonation. The melting temperature is about 1550°C at 10 GPa.  
176 Figure 5 shows the decomposition and melting curves of siderite at high pressure and  
177 temperature.

178         Figure 3 shows the change of the X-ray diffraction patterns of the experimental products  
179 run at 6 GPa. At 1300°C, the dominant phase is siderite (94 %), indicating that siderite is the  
180 stable phase. The presence of a small amount of inherited magnetite is the result from the  
181 oxidized starting materials via reaction 5. At 1350 °C, we observed almost equal amounts of  
182 magnetite and siderite in the recovered sample. The decarbonation reaction was not complete  
183 even at a run time of 20 hours at this temperature, but the run condition (1350 °C and 6 GPa)  
184 must be near or on the decomposition curve of siderite. By increasing temperature to 1400 °C,  
185 the recovered sample contains mainly magnetite (88%), signifying that the reaction almost  
186 reached completion in about 12 hours. At 1450 °C, melting features were observed, as shown in  
187 the SEM images (Fig. 4b). The fine-grained siderite and magnetite show characteristics of  
188 melting quench texture. The melt coexists with large magnetite crystals (>100µm) (Fig 4b),  
189 suggesting that siderite underwent a decarbonation reaction first during heating, and then melting

190 at higher temperature. The proportion of melt and magnetite crystals from decarbonation is likely  
191 controlled by the heating rate. The recovered sample had high porosity and was hard to polish in  
192 the platinum capsule, consistent with partial decarbonation. The experiments of 1300-1450 °C at  
193 6 GPa indicate that the boundaries of decomposition and melting of siderite are very close,  
194 within 100°C (Fig. 5).

195 At 8 and 10 GPa, we observed direct melting of siderite. At 8 GPa and 1500 °C, a melt  
196 fraction (which occupied about one third of the capsule) is segregated at the top, in contact with  
197 siderite (Fig. 4c). The small amount of magnetite dispersed in siderite was inherited from the  
198 oxidized starting material (hematite) via reaction 5. At higher temperature (1650 °C), the sample  
199 was completely molten with homogeneous melting quench texture (Fig. 4d). Siderite does not  
200 quench to glass and it recrystallizes very rapidly during quenching. The quenched crystalline  
201 phases were identified by X-ray diffraction, containing about 70 mole% of recrystallized siderite  
202 and 30% of magnetite according to the XRD data refinements. The XRD data provided  
203 additional support for direct melting of siderite without decarbonation reaction. The onsets of  
204 melting temperatures at 8 and 10 GPa are 1500 and 1550 °C, respectively. The quenched melt  
205 shows a dendritic quench texture of siderite and magnetite (Fig. 4d). The amounts of magnetite  
206 (~30%) in the quenched melt are more than the amounts that could have resulted from the  
207 oxidized starting material, implying that some siderite was oxidized during either melting or

208 quenching. The exact cause for the extra magnetite is not clear. Siderite melts over a very small  
209 temperature interval ( $<50$  °C). The observed coexisting siderite and melt in the experiments SD-4  
210 and SD-17 is likely due to the thermal gradient in the sample chamber rather than incongruent  
211 melting. The fact that the proportions between siderite and magnetite in the quenched melt do not  
212 change with increasing temperature further rules out incongruent melting. The alternative  
213 interpretation is that the apparent 30% of magnetite in the quenched melt is overestimated  
214 because of the smaller grain size of the quenched magnetite crystals. The smaller grain size  
215 would lead to high estimate of the magnetite proportion based on the XRD refinements.

216         The products of siderite decomposition are not only dependent on P-T conditions, but are  
217 also sensitive to oxygen fugacity. At 4 GPa and 1200 °C (SD-1), we observed two iron oxides  
218 (wüstite and magnetite). The phase identities were confirmed by the XRD patterns of the  
219 quenched sample. The intergrowth texture of wüstite and magnetite was observed by the SEM  
220 image (Fig 4a). The observation may imply that the intrinsic oxygen fugacity of the assembly  
221 was very close to the wüstite-magnetite buffer. The result is a representative of reaction 4. It is  
222 not clear why this particular run contains both wüstite and magnetite whereas only magnetite is  
223 observed in all other runs. Further experiments under controlled oxygen fugacity condition are  
224 needed to resolve the issue.

225 Previous phase equilibrium studies on reaction 3 using synthetic siderite as the starting  
226 material by sealed-capsule and quenching technique were performed systematically from 0.5 to  
227 10 kbar, 450-760 °C, and the melting point of pure siderite at 8 kbar was estimated at 1200±  
228 100 °C (Weidner, 1972). The melting curve of magnetite + graphite = melt +vapor also has been  
229 experimentally determined in the range 0.5-2 kbar and 880-950 °C by cold-seal pressure vessel  
230 apparatus (Weidner, 1982). The pressure-temperature equilibrium curve of reaction 5 was  
231 determined in the range of 5-12 kbar and 480-650 °C by piston-cylinder experiments on  
232 synthetic siderite and hematite and natural magnetite (Koziol, 2004), and the decomposition  
233 temperature of reaction 5 is slightly lower than that of reaction 3 determined by Weidner (1972)  
234 at the same pressure. Reaction 5 occurring in a higher oxygen fugacity environment has a lower  
235 decomposition temperature than reaction 3. This is consistent with the formation of the inherited  
236 magnetite via reaction 5 in our study. The stability and thermal decomposition of siderite at  
237 atmospheric pressure are well documented (Chai and Navrotsky, 1994; French, 1965; French,  
238 1971; Gallagher and Warne, 1981; Goldsmith et al., 1962; Gotor et al., 2000). The  
239 decomposition boundary of siderite determined at higher pressure in this study is in general  
240 agreement with the low-pressure data (Weidner, 1972) (Fig. 5), but the exact location of the  
241 boundary could be influenced by the products of the decomposition reaction. The melting curve  
242 of siderite above 6 GPa was also experimentally determined in this study. The extension of the

243 melting curve of siderite in this study to the magnetite and graphite field is also consistent with  
244 the melting curve of magnetite + graphite = melt at lower pressure documented by Weidner (1982)  
245 (Fig. 5).

246 In order to understand the mechanism of the decomposition of siderite and the formation  
247 of the reduced graphite, a ternary diagram in the system FeO-C-O is described in Figure 6. All  
248 the possible reactions in this system can be determined by Schreinemakers rules. Figure 6  
249 illustrates all possible reactions (1, 2, 3, 4, 5, 6, 7) that may occur in this system. Theoretically,  
250 siderite can decompose into two phases if siderite plots on the line between the two phases, such  
251 as between FeO and CO<sub>2</sub>. On the other hand, siderite can decompose into three phases which  
252 form a triangle with the siderite in it, such as the triangle formed by Fe<sub>3</sub>O<sub>4</sub>, C and CO<sub>2</sub> (reaction  
253 3). Siderite can also react with oxidizing phases like hematite and O<sub>2</sub> to produce CO<sub>2</sub> and the  
254 corresponding iron oxides according to reactions 5 and 6.

255 We computed the decomposition curves of siderite using the newest THERMOCALC  
256 software (TC3.36i) with thermodynamic data (Holland and Powell, 2011) for several reactions in  
257 the system (Fig. 7). The calculated decomposition boundaries of siderite to Fe<sub>3</sub>O<sub>4</sub> + CO + CO<sub>2</sub>  
258 and to FeO + CO<sub>2</sub> showed higher decomposition temperatures than that of siderite to Fe<sub>3</sub>O<sub>4</sub> + C  
259 + CO<sub>2</sub>. The decomposition boundary determined in this study is more consistent with the

260 calculated boundary of siderite to  $\text{Fe}_3\text{O}_4 + \text{C} + \text{CO}_2$ . Graphite was identified in gas voids at the  
261 top of the capsule in run SD-7 (6 GPa-1450°C) by XRD analysis. It likely precipitated through  
262 the reaction  $2\text{CO}=\text{CO}_2+\text{C}$  at high pressure, suggested in previous studies (French, 1965;  
263 Thomas-Keprta et al., 2009; Weidner, 1972).

264 In natural carbonated oceanic and continental crust, the siderite always occurs as solid  
265 solution with magnesite (Liu et al., 2006; Messiga et al., 1999; Mukherjee and Sachan, 2003;  
266 Shatsky et al., 2005; Smit et al., 2008; Zhang et al., 2002b; Zhang et al., 2003b; Zhang and Liou,  
267 1996; Zhu, 2005). The stability of magnesite at high pressure has been documented previously  
268 (Fiquet et al., 2002; Irving and Wyllie, 1975; Isshiki et al., 2004; Zhang et al., 1997). The  
269 decomposition curve of siderite determined in the present study, compared with previous  
270 experimental and thermodynamically calculated results on the decomposition curve of magnesite  
271 (Fig 8), indicate that Fe has a significant effect on the stability of magnesite-siderite solid  
272 solutions under upper mantle conditions. Siderite decomposes at relatively lower temperature  
273 than magnesite at the same pressure. For example, the temperature differences at 1 GPa and 2  
274 GPa are about 400°C and 500°C, respectively (Fig 8). The temperature difference increases with  
275 increasing pressure until reaching the melting point. Previous thermal decomposition study on  
276 the siderite-magnesite solid solution using differential scanning calorimetry method has also  
277 indicated that the decomposition temperature of the siderite-magnesite solid solution decreased



278 markedly with increasing Fe substitution (Dubrawski, 1991). Recently, univariant equilibrium  
279 decomposition curves (solid lines) calculated for siderite-magnesite solid solution at low  
280 pressure and temperature reached the same conclusion (Thomas-Keprta et al., 2009). We have  
281 extended the decomposition boundary of siderite to higher pressure and documented melting of  
282 siderite at high pressure for the first time. Our experimental results on the stability of siderite  
283 combined with information on the stability of magnetite provide critical constraints on the  
284 stability field of the siderite-magnesite solid solution in the Earth's mantle.

285         The typical cold and hot subduction paths are well within the stability fields of both  
286 siderite and magnesite (Fig. 8). The solid solution of siderite and magnesite could be stable and  
287 subducted into the Earth's mantle via the subduction process. However, the decarbonation  
288 boundary of siderite is very close to the average mantle geotherm. Graphite could be produced  
289 via the disproportionation reaction of siderite from the Fe-bearing carbonate in the Earth's upper  
290 mantle. The disproportionation reaction of the Fe-bearing carbonate might be an important  
291 mechanism for the formation of the reduced carbon phase (graphite or diamond) in the Earth's  
292 mantle. The thermal decomposition reaction of siderite to magnetite and graphite at 1 GPa has  
293 been used to explain the presence of graphite in a nepheline syenite complex (Gellatly, 1966),  
294 carbonatite (Doroshkevich et al., 2007), carbonates in the 3.8 Ga old Isua Supracrustal Belt and  
295 southern West Greenland (Van Zuilen et al., 2003), and magnetite nanocrystals in the Martian

296 meteorite ALH84001 (Thomas-Keprta et al., 2009). In situ high-pressure experimental studies in  
297 the siderite and water system in the diamond anvil cell also show that reduced carbon  
298 compounds can be precipitated from the redox reaction of siderite and water (Marocchi et al.,  
299 2011).

300 Melting of carbonates at high pressure and temperature is an important issue for  
301 understanding the carbon cycle in the mantle. Our experimental results showed that the Fe-end  
302 member of carbonates (siderite) had a relatively low melting temperature and its melting curve  
303 might cross the mantle geotherm at transition zone pressures (Fig. 8). The data provide  
304 constraints on the onset of melting of carbonates in the deep mantle. Carbonatitic melts and  
305 carbonate are considered to be unstable when infiltrating the surrounding mantle and they could  
306 be reduced to immobile diamond in the deep mantle where mantle redox conditions are at or  
307 below the iron-wüstite buffer (Frost et al., 2004; Frost and McCammon, 2008; Rohrbach et al.,  
308 2007; Rohrbach et al., 2011; Rohrbach and Schmidt, 2011; Stagno and Frost, 2010; Stagno et al.,  
309 2011).

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493

#### 494 **Figure captions**

495 **Fig 1:** Refined X-ray diffraction pattern of the siderite starting material. The X-ray wave-length  
496 is 0.7093 Å. The black vertical bars below the X-ray pattern indicate the typical X-ray diffraction  
497 peaks of siderite; the red vertical bars indicate the typical X-ray diffraction peaks of hematite.  
498 The mole percentage of hematite is about 5% calculated by the refined X-ray pattern using  
499 Software GSAS (Larson and Dreele, 2004).

500 **Fig 2:** Unit-cell parameters of the magnesite-siderite solid solution as functions of the Fe<sup>#</sup>  
501 content. The black squares and circles represent natural magnesite-siderite solid solutions from  
502 previous publications (Boulard et al., 2012a; Effenberger et al., 1981; Litasov et al., 2008;  
503 Markgraf and Deeder, 1985; Zhang et al., 1997). Red square and circle represent data from this  
504 study.

505  
506 **Fig 3:** Selected X-ray diffraction (XRD) patterns of the run products at 6 GPa and temperatures  
507 from 1300°C to 1400°C. Typical diffraction peaks for the major phases are marked at each peak.  
508 The mole percentages of the two coexisting phases were calculated by Software GSAS.

509 **Fig 4:** Back-scattered electron images of some representative experimental runs, with run  
510 conditions indicated on the figures. (a) and (b) show the polished grains in epoxy resin (dark area)  
511 (a) Run SD-1: Intergrowth texture of wüstite and magnetite. A small amount of unreacted  
512 siderite (7%) occurs as inclusions in grains of magnetite and wüstite. (b) Run SD-7: Large  
513 magnetite crystals in equilibrium with melt. The quench texture of the melt is shown in the inset.  
514 Some of the grains show coexisting magnetite and melt. (c) Run SD-17: Coexisting crystal  
515 siderite and melt. The inset shows the boundary of siderite and melt. (d) Run SD-16:  
516 Homogeneous melt texture. The inset shows the quenched siderite (grey) and magnetite (light).  
517 Abbreviations: Mag, magnetite; Wus: wüstite; Sd: siderite; Melt: quenched melt; Pt: platinum  
518 capsule. The mineral abbreviation followed Whitney and Evans (2009) in all the figures.

519  
520 **Fig 5:** The phase diagram of siderite = magnetite + CO<sub>2</sub> + graphite. The open circle symbols  
521 represent the stability field of magnetite + CO<sub>2</sub> + graphite. The filled black circle symbols  
522 represent the stability field of siderite. The gray filled circle symbols represent melt. The thin

523 solid curve represents the decarbonation boundary and the heavy solid curve represents the  
524 melting curve of siderite. Previous studies on reaction (3) and reaction (5) and melting curve of  
525 magnetite + graphite = melt + vapor at lower pressure (dashed lines) are shown for comparison.  
526 Previous melting point of siderite is shown by a gray filled dash circle with error bar.

527 **Fig 6:** Isothermal-isobaric ternary diagram in the system of the Fe-C-O at an arbitrary  
528 temperature and pressure [modified after Weidner (1972)]. All the possible reactions in this  
529 study can be illustrated on this ternary diagram by the Schreinemakers rules.

530 **Fig 7:** Comparison of decomposition curves of siderite with previous studies and calculations  
531 using Software THERMOCALC (version tc3.66i) with thermodynamic data (Holland and  
532 Powell, 2011). The solid curves show the decarbonation boundary and melting curve of siderite  
533 from this study. The dashed lines show the calculated boundaries for various possible reactions  
534 as indicated. The results of Weidner (1972) for the siderite = magnetite + graphite + CO<sub>2</sub>  
535 reaction are also shown for comparison.

536  
537 Fig 8: Comparison of the decomposition curves of siderite with the stability of magnesite at high  
538 pressure from previous studies and calculations using Software THERMOCALC (version tc3.66i)  
539 with thermodynamic data (Holland and Powell, 2011). The dashed line with one dot shows the  
540 decomposition curve of magnesite documented by Irving and Wyllie (1975) and the dashed line  
541 with two-dots shows the calculated boundary for magnesite. Typical subduction paths (green and  
542 blue lines) are after Peacock and Wang (1999). Average mantle geotherm (red line) is after  
543 Akaogi et al. (1989).

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Table 1 Experimental run conditions and products of siderite decomposition

Run #	P(GPa)	T(°C)	Time (hours)	Run products
Starting material	1atm	25	0	Sd (95%) + Hem (5%)
SD-11	2.5	900	36	Sd (88.3%) + Mag (11.7%)
SD-3	2.5	950	24	Mag (87.6%) + Sd (12.4%)
SD-15	2.5	1000	36	Mag (91.7%) + Sd (8.3%)
SD-6	4	1000	10	Sd (88.4%) + Mag (11.6%)
SD-12	4	1100	24	Sd (50.9%) + Mag (49.1%)
SD-10	4	1150	24	Mag (76.2%) + Sd (23.8%)
SD-1	4	1200	10	Wus (68%) + Mag (25%) + Sd (7%)
SD-5	5	1200	24	Sd (79.4%) + Mag (20.5%)
SD-13	6	1300	12	Sd (94.2%) + Mag (5.8%)
SD-9	6	1350	20	Sd (53.5%) + Mag (46.5%)
SD-2	6	1400	12	Mag (88%) + Sd (12%)
SD-7	6	1450	10	Mag + Melt ( $\approx$ 45%)
SD-17	8	1500	5	Sd + Mag (minor)+ Melt ( $\approx$ 30%)
SD-16	8	1650	5	Melt (100%)
SD-4	10	1550	8	Sd + Mag (minor)+ Melt ( $\approx$ 25%)
SD-18	10	1600	5	Melt (100% )
SD-8	10	1750	5	Melt (100%)
SD-14	10	1850	2	Melt (100%)

Mag: magnetite; Wus: wüstite; Sd: Siderite; Hem: hematite; Mineral amounts in parentheses are the refined phase proportions; Melting amounts in parentheses are visual determinations from the SEM images for the melting sample. Typical error in the calculated phase proportion is about 2%

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Intensity

















