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1 **FORMATION OF CO<sub>2</sub>, H<sub>2</sub> AND CONDENSED CARBON FROM SIDERITE**  
2 **DISSOLUTION IN THE 200 – 300°C RANGE AND AT 50 MPa**

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43

#### 44 **Abstract**

45 Laboratory experiments were conducted to investigate the chemical processes governing the  
46 carbon speciation associated to hydrothermal decomposition of siderite. Experiments were  
47 carried out in sealed gold capsules using synthetic siderite and deionised water. The samples  
48 were reacted at 200 and 300°C, under a pressure of 50 MPa. Siderite dissolved to reach the  
49  $3\text{FeCO}_3 + \text{H}_2\text{O} = \text{Fe}_3\text{O}_4 + 3\text{CO}_2 + \text{H}_2$  equilibrium and magnetite,  $\text{Fe}_3\text{O}_4$ , was produced  
50 accordingly. The gas phase was dominated by  $\text{CO}_2$ ,  $\text{H}_2$  and  $\text{CH}_4$ , the latter being in strong  
51 thermodynamic disequilibrium with  $\text{CO}_2$ . Contrary to the other gas products,  $\text{H}_2$  concentration  
52 was found to decrease with run duration. TEM observations showed the occurrence of  
53 condensed carbon phases at the surfaces of magnetite and residual siderite grains.  
54 Thermodynamic calculations predict the formation of condensed carbon in the experiments  
55 according to the reaction:  $\text{CO}_2 + 2\text{H}_2 \Rightarrow \text{C} + 2\text{H}_2\text{O}$ , which accounted for the observed  $\text{H}_2$   
56 concentration decrease up to the point where  $\text{H}_2$  and  $\text{CO}_2$  activities were buffered by the  
57 graphite – siderite – magnetite assemblage. The well-organized structure of the carbon coating  
58 around magnetite emphasizes the high catalytic potential of magnetite surface for carbon  
59 reduction and polymerization. The formation of such C-rich phases may represent a potential  
60 source of  $\text{CH}_4$  by hydrogenation. On the other hand, the catalysis of Fischer-Tropsch type

61 reactions may be poisoned by the presence of carbon coating on mineral surfaces. In any case,  
62 this study also demonstrates that abiotic H<sub>2</sub> generation by water reduction, widely studied in  
63 recent years in ultrabasic contexts, can also occur in sedimentary contexts where siderite is  
64 present. We show that, in the latter case, natural H<sub>2</sub> concentration will be buffered by a  
65 condensed carbon phase associated with magnetite.

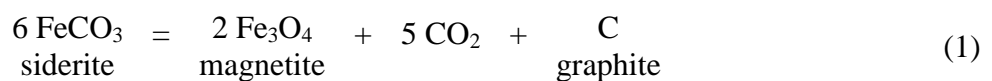
66

## 67 **1. INTRODUCTION**

68 Abiotic conversion of CO<sub>2</sub> into methane and more complex organic compounds is of  
69 interest for a number of geochemical issues such as the global carbon cycle (e.g., Manning et  
70 al., 2013) or the origin of life (e.g., Martin et al., 2008) and it has become a matter of interest  
71 in the context of anthropogenic CO<sub>2</sub> sequestration (e.g., Petersen et al., 2005). In addition to  
72 the thermal decomposition of organic matter, abiotic methane synthesis can be achieved  
73 naturally by the hydrothermal alteration of ultrabasic rocks through serpentinization reactions  
74 which generate highly reducing conditions (e.g., Neal and Stranger, 1983; Frost, 1985;  
75 Abrajano et al., 1988; Kelley, 1996; Charlou et al., 1998; Kelley et al., 2001; Klein et al.,  
76 2009; McCollom and Bach, 2009). Abiogenic methane associated with the serpentinization of  
77 ultramafic rocks has been described in subaerial contexts (e.g., Abrajano et al., 1988; Lyon et  
78 al., 1990; Fritz et al., 1992; Sano et al., 1993; Hosgormez et al., 2008; Etiope et al., 2011;  
79 Suda et al., 2014) as well as in submarine environments from hydrothermal vents associated  
80 with slow-spreading centers (e.g., Holm and Charlou, 2001; Kelley et al., 2001; Charlou et al.,  
81 2002). Experimental studies suggested that under the hydrothermal conditions of  
82 serpentinization reactions, abiotic generation of organic compounds can be attributed to a  
83 Fischer-Tropsch-type (FTT) reaction (e.g., Berndt et al., 1996; Horita and Berndt, 1999;  
84 McCollom and Seewald, 2001; Foustoukos and Seyfried, 2004; Fu et al., 2007), which

85 generally refers in the geological literature (and in the present study) to a surface-promoted  
86 reduction of an inorganic carbon source (frequently dissolved CO<sub>2</sub>) to organic compounds.

87 Highly reducing hydrothermal conditions in a CO<sub>2</sub>-bearing environment can also be  
88 achieved through the decomposition of siderite (FeCO<sub>3</sub>) which is a ubiquitous carbonate  
89 component in sedimentary and metasedimentary rocks. Recently, Milesi et al. (2013)  
90 proposed that unconventional hydrocarbons could arise from siderite – water interactions in  
91 the source rock of the Solimões sedimentary basin in the North-West Brazil, which underwent  
92 high thermal stress due to magmatic intrusions (Mosmann et al., 1987; Rodrigues et al., 1990;  
93 Eiras and Lima, 2008). At higher temperatures, the decomposition of siderite has also often  
94 been invoked to explain the occurrence of reduced carbon in metamorphic rocks (e.g., Perry  
95 and Ahmad, 1977; Ueno et al., 2002). For example, van Zuilen et al. (2003) suggested that, in  
96 the carbonate-rich metasomatic rocks of the 3.8 Ga Isua Supracrustal Belt (Greenland), the  
97 presence of graphite was due to thermal decomposition of siderite at peak temperature  
98 conditions (between 500 and 600°C) according to the reaction:



99

100 Zolotov and Shock (2000) and Steele et al. (2012) also proposed the decomposition of  
101 Fe-bearing carbonate as a source of reduced carbon in Martian meteorites. McCollom (2003)  
102 studied siderite decomposition in the presence of water vapor at 300°C. Magnetite was  
103 formed, along with CO<sub>2</sub> and H<sub>2</sub> as main gas products. Trace amounts of methane and light  
104 hydrocarbons were detected as well as alkylated aromatic compounds including polycyclic  
105 aromatic hydrocarbons (PAH).

106 In order to investigate the potential of siderite – water interactions to promote the  
107 formation of H<sub>2</sub>-rich fluids and reduced carbon species, we carried out siderite dissolution

108 experiments at 200 - 300°C and 50 MPa. Dissolved organic compounds and gaseous species  
109 (H<sub>2</sub>, CO<sub>2</sub>, and CH<sub>4</sub>) were analyzed on quenched samples. In addition, solid carbon products  
110 were looked for using transmission electron microscopy (TEM). Finally, the corresponding  
111 analytical results were discussed on the basis of a thermodynamic analysis.

112

## 113 **2. MATERIALS AND METHODS**

### 114 **2.1 Starting materials**

115 Siderite was synthesized in 25 mL stainless-steel Parr® autoclaves with a Teflon liner  
116 by dissolving 800 mg of iron sulfate heptahydrate (FeSO<sub>4</sub>·7H<sub>2</sub>O) and 2 g of urea (CO(NH<sub>2</sub>)<sub>2</sub>)  
117 in 15 mL of oxygen-free deionized water. Oxygen-free water was prepared by bubbling argon  
118 into deionized water (Milli-Q) for one hour. In order to avoid iron oxidation, 40 mg of  
119 ascorbic acid were added to lower the pH down to a value of ~ 4, decreasing by 10<sup>6</sup> the  
120 kinetics of iron oxidation (e.g., Stumm and Lee, 1961; Singer and Stumm, 1970; Millero et  
121 al., 1987). The Parr bomb was then closed and heated at 180°C during 48 hours at the  
122 saturation vapor pressure of H<sub>2</sub>O. The dissociation of iron sulfate and the total hydrolysis of  
123 urea resulted in high Fe<sup>2+</sup> and dissolved inorganic carbon (DIC) concentrations. At 180°C, the  
124 NH<sub>4</sub><sup>+</sup>/NH<sub>3</sub> couple released by the hydrolysis of urea imposed a basic pH of ca. 9.1 which  
125 promoted the precipitation of iron carbonate. The recovered material was rinsed three times in  
126 50 mL of ethanol to eliminate water and potential organic contaminants generated from  
127 ascorbic acid. To eliminate traces of ethanol, the powder was dried by gradual heating from  
128 25 to 70°C under primary vacuum during two hours. The synthesized material was then  
129 transferred into an argon box and stored into hermetic vials. The solid product was  
130 characterized as being single-phase siderite by X-ray powder diffraction (XRPD) (Fig. 1).  
131 Scanning electron microscopy (SEM) observations indicated typical grain sizes of tens of

132 micrometers (Fig. 1). This relatively large grain size prevented siderite from significant  
133 oxidation in air as indicated by the absence of iron oxide (XRPD and SEM) even in siderite  
134 products heated at 80°C in air for 12 hours (XRPD).

135

## 136 **2.2 High-pressure and high-temperature experiments**

137 The sample was contained in cylindrical gold capsules with a length of 20 mm and an  
138 outer diameter of 3.6 mm (wall thickness of 0.2 mm). Approximately 50 mg of siderite along  
139 with 100 µL of MilliQ water were loaded in the Au capsules, leaving a small headspace of air  
140 of less than 1/5 of the capsule volume. The capsule was welded shut and loaded in an  
141 externally heated cold-seal vessel (see Brunet and Chopin, 1995 for experimental details).  
142 Experiments were run from 3 hours to 4 months at 200 or 300°C under an argon pressure of  
143 50 MPa. The uncertainty on the measured temperature is of +/- 1.5%. At the end of each  
144 experiment, power supply was switched off and the autoclave was quenched with an air  
145 stream. A single experiment was carried out at 300°C and 50 MPa using siderite in the  
146 absence of water (dry-siderite experiment).

147

## 148 **2.3 Sampling and analysis methods**

### 149 *2.3.1 Gas products*

150 The gaseous products trapped in the gold capsules at the end of the experiments were  
151 recovered and analyzed according to the procedure described in Malvoisin et al. (2013). This  
152 procedure consists in piercing the gold capsule in a plastic syringe containing a known  
153 volume of argon. A 250 µL aliquot of the gas mixture (gaseous products + Ar) was injected  
154 into a gas chromatograph coupled with a thermal conductivity detector (GC-TCD), allowing



155 the concentrations of H<sub>2</sub>, CH<sub>4</sub> and CO<sub>2</sub> to be determined with detection limits of ~ 0.01, 0.05  
156 and 0.5 mmolal respectively (mmolal equals mmol·kg<sup>-1</sup> of solvent) . The GC column that we  
157 used did not allow separating CO from air (N<sub>2</sub> and O<sub>2</sub>) contamination. Therefore, only high  
158 CO concentrations were detectable.

159 The gaseous products were recovered at ambient temperature and pressure. Under  
160 these conditions, the Henry's Law constants ( $k_H$ ) for H<sub>2</sub>, CH<sub>4</sub> and CO<sub>2</sub>, which are defined by

$$k_{Hi} = \frac{p_i}{c_i}$$

161  
162 where  $p_i$  is the partial pressure of species  $i$  in the gas phase and  $c_i$  the concentration of species  
163  $i$  in the aqueous phase, have respective values of 127.4, 70.8 and 2.94 MPa·L·mol<sup>-1</sup> as  
164 calculated with the SUPCRT package (Helgeson et al., 1978; Johnson et al., 1992). Therefore  
165 H<sub>2</sub>, CH<sub>4</sub>, and CO<sub>2</sub> will mostly concentrate in the gas phase and remaining dissolved H<sub>2</sub> and  
166 CO<sub>2</sub> will be ignored in further mass balance calculation.

167

### 168 2.3.2 Dissolved organic compounds

169 In some experiments, a duplicate was carried out and devoted only to the analysis of  
170 dissolved organic compounds. The aqueous solution was injected in a gas-chromatograph  
171 coupled to a mass-spectrometer (GCMS). A GCMS-QP2010 Plus Shimadzu system with a  
172 TRB-FFAP capillary columns (30 m × 0.25 mm ID × 0.5 μm; Teknokroma) was used. The  
173 oven temperature was maintained at 40°C for 5 minutes and the heating program is as  
174 follows: from 40 to 150°C at a rate of 10°C/min and maintain at 150°C for 5 minutes, then at  
175 a rate of 40°C/min up to 275°C. The injection port temperature was 200°C, and helium was  
176 used as the carrier gas at a pressure flow control mode of 110 kPa. A 1 μL sample aliquot was  
177 injected in direct or split mode. The electron ionization energy was 70 eV, the ion source

178 temperature was 200°C, and the scan range was 30 – 150 m/z. The detection limits for  
179 carboxylic acids, alcohols and acetone are of ~ 0.2 mmolal, ~ 0.01 mmolal and ~ 0.01 mmolal  
180 respectively. Due to evolution in time of the samples, only qualitative data of concentrations  
181 could be obtained for these dissolved organic compounds.

182

### 183 2.3.3 Solid products

184 The recovered powders were characterized by X-ray powder diffraction (XRPD) with  
185 a Bruker D5000 or D8 diffractometer using CuK $\alpha$  radiation. The instruments were operated  
186 with a step size of 0.026° 2 $\theta$  and a counting time of 8 s. The divergence slit, anti-scatter slit,  
187 and detector slit were 0.6, 0.6, and 0.2 mm, respectively. The X-ray patterns were analyzed by  
188 Rietveld using the BGMN software (Taut et al., 1998). The recovered powders were observed  
189 by Scanning Electron microscopy (SEM), and Transmission Electron microscopy (TEM).  
190 SEM was performed on a Zeiss Ultra 55 FEG microscope operated at 10 kV and a working  
191 distance of 7.5 mm using mostly a detector of bacscattered electrons for imaging. This SEM  
192 is equipped with an energy dispersive X-ray system from Bruker. TEM was performed on a  
193 Jeol FEG 2100F operated at 200 kV equipped with an energy dispersive X-ray system from  
194 Jeol. Suspension in clean freshly opened absolute ethanol was prepared from the sample  
195 powders for TEM characterization. Vortex mixer and ultrasonic bath were used to disperse  
196 the powder homogenously within the ethanol medium. Five microliters of suspension were  
197 then deposited on a carbon filmed grid and left 10 minutes under confined atmosphere for  
198 ethanol evaporation.

199

## 200 2.4 Thermodynamic calculations

201           Reaction constants were calculated with the SUPCRT package (Johnson et al., 1992).  
202   The thermodynamic properties of siderite from Helgeson et al. (1978) were adjusted in order  
203   to better fit the experimental data. The  $\Delta H_f^\circ$  value adopted here for siderite was taken from  
204   Chai and Navrotsky (1994) of  $-750.6$  ( $\pm 1.1$ )  $\text{kJ}\cdot\text{mol}^{-1}$ , close to that of Helgeson et al. (1978)  
205   of  $-749.6$   $\text{kJ}\cdot\text{mol}^{-1}$ . The  $S^\circ$  value of  $105$   $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$  given by Helgeson et al. (1978) for siderite  
206   was reevaluated to  $111.5$   $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ , which is a good compromise between the best  
207   experimental value of  $109.5$  ( $\pm 2$ )  $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$  determined by Bénézech et al. (2009) and the  
208   best fit to the observed magnetite-siderite equilibrium (Figure 7).

209           No free gas phase was considered in the thermodynamic model. Indeed, calculations  
210   suggested that at the HP - HT experimental conditions of the experiments, gases from the  
211   headspace initially introduced in the gold capsule were entirely dissolved in the aqueous  
212   phase. Furthermore, at  $300^\circ\text{C}$  and  $50$  MPa, the saturation concentrations of  $\text{H}_2$ ,  $\text{CH}_4$ , and  $\text{CO}_2$   
213   are of  $1.67$ ,  $1.92$ , and  $5.28$   $\text{mol}\cdot\text{L}^{-1}$  respectively. These values are several orders of magnitude  
214   higher than those measured in the quenched samples (Table 1). Calculations showed that the  
215   same conclusion applies at  $200^\circ\text{C}$ . Thereby,  $\text{H}_2$ ,  $\text{CO}_2$  and  $\text{CH}_4$  were consequently considered  
216   as aqueous species in further thermodynamic modeling.

217

### 218   **3. RESULTS**

219           We performed a series of eight HP - HT experiments at  $50$  MPa using siderite as  
220   starting material. Experimental conditions and gas analysis are listed in Table 1. Apart from  
221   the dry-siderite experiment, all samples reacted and yielded magnetite; however, residual  
222   siderite represented by far the most abundant phase in the recovered samples.

223

### 224 3.1 Gas products

225 All experiments performed in the siderite – water system yielded CO<sub>2</sub> as major  
226 component of the gas phase (Table 1). No gaseous product was detected in the dry-siderite  
227 experiment. In the 300°C runs, H<sub>2</sub> and CH<sub>4</sub> formed at concentrations two to three orders of  
228 magnitude lower than CO<sub>2</sub> concentrations. From sample *S300-1* to *S300-4*, the CO<sub>2</sub> and CH<sub>4</sub>  
229 concentrations increased while the maximal H<sub>2</sub> concentration observed was after 3 hours and  
230 then started decreasing (Fig. 2). In the longest experiments, i.e., *S300-3* to *S300-5*, the  
231 concentrations of CO<sub>2</sub>, H<sub>2</sub> and the magnetite content remained constant suggesting attainment  
232 of a steady state. In contrast, the CH<sub>4</sub> concentration kept increasing but more slowly than in  
233 the first 168 hours. The slow accumulation of CH<sub>4</sub> throughout the run indicated a strong  
234 kinetic control over CH<sub>4</sub> formation (Table 1, Fig. 2).

235 In the 200°C experiments, CO<sub>2</sub> was the only detected gas; H<sub>2</sub> concentrations remained  
236 below the detection limit of the GC-TCD, i.e., <0.01 mmolal. The experiments *S200-1* and  
237 *S200-2* yielded similar CO<sub>2</sub> concentrations around 4.5 mmolal, i.e., approximately one order  
238 of magnitude lower than in the 300°C experiments (Table 1). In the two sets of experiments at  
239 200 and 300°C, no significant CO signal was observed.

240

### 241 3.2 Dissolved organic compounds

242 To test potential contamination, the residual powder recovered from the dry-siderite  
243 experiment was rinsed with MilliQ water which was further analyzed. Formic-acid  
244 (HCOOH), acetic-acid (CH<sub>3</sub>COOH), methanol (CH<sub>3</sub>OH), ethanol (C<sub>2</sub>H<sub>5</sub>OH), propanol  
245 (C<sub>3</sub>H<sub>7</sub>OH) and acetone (C<sub>3</sub>H<sub>6</sub>O) were detected. Formic acid, acetic acid and ethanol were the  
246 main species observed in the 0.1 – 1 mmolal range, while methanol, propanol and acetone  
247 were detected at concentrations one order of magnitude below. Similar ranges of

248 concentration were measured in the hydrothermal experiments on siderite at 200 and 300°C.  
249 In the following mass balance calculations, the concentrations of these dissolved organic  
250 compounds, which are more than one to two orders of magnitude lower than CO<sub>2</sub>  
251 concentrations, will be neglected.

252

### 253 **3.3 Solid products**

254 XRPD patterns are dominated by siderite along with minor magnetite (Fig. 3).  
255 Quantitative XRPD analysis allowed estimation of the Fe<sub>3</sub>O<sub>4</sub> content to less than 5 wt.% (+/-  
256 1%) of the powder in all experiments. The XRPD pattern of the residual powder from *S300-1*  
257 showed that at 300°C, Fe<sub>3</sub>O<sub>4</sub> had already formed after three hours. In the experiments  
258 performed at 200°C, the magnetite content was constant with values of ~ 3 wt.% (+/-1%) of  
259 the powder.

260 On SEM images in backscattered electron mode, iron oxide shows typical grain sizes  
261 of ~ 100 nm but grains of magnetite larger than 1 μm were also observed (Fig. 3a). The  
262 presence of etch pits on the siderite surface indicates partial dissolution and confirms thereby  
263 the residual character of siderite. Furthermore, magnetite grains are partly embedded in the  
264 siderite surface emphasizing the genetic link between Fe<sub>3</sub>O<sub>4</sub> and the iron carbonate (Fig. 3b).

265 TEM analyses of the solid products of the two sets of experiments at 200 and 300°C  
266 showed the presence of a condensed phase, rich in carbon (Fig. 4). Such a phase was carefully  
267 looked for in the starting materials but was never observed. This phase appeared to be highly  
268 unstable under the electron beam and could therefore be hydrated or hydrogenated. It showed  
269 no obvious spatial relationship with siderite or magnetite.

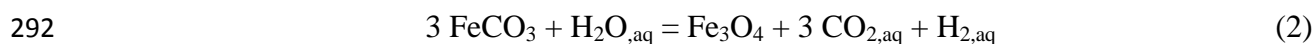
270 In the 200°C experiments, another carbon-rich phase was observed as regular nm-  
271 sized coats around magnetite and siderite grains (Fig. 5). The carbon matter which  
272 encapsulates magnetite grains is made of a stack of layers, presumably short graphene units,  
273 suggesting a relatively well organized state (Fig. 5a). When associated to siderite, the carbon  
274 coats are less continuous and displayed a lower organization level (Fig. 5b). In both *S200-1*  
275 and *S200-2*, the carbon coat is ~ 5 nm thick. In the 300°C experiments, well defined carbon  
276 layers are not observed. At the surface of magnetite grains, they are present on some faces and  
277 are less than 1 nm thick. They would deserve further studies. At the surface of siderite, larger  
278 reaction zones are made of a complex phase assemblage. Electron diffraction patterns and  
279 EDXS analyses suggest that they are constituted of iron oxide (either FeO or Fe<sub>3</sub>O<sub>4</sub>) closely  
280 associated to a solid carbon-rich phase (Fig. 6).

281

## 282 4. THERMODYNAMIC MODEL

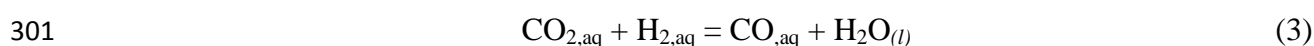
### 283 4.1 Mass balance

284 Thermal decomposition of siderite upon heating occurs between ~ 400 and 600°C  
285 depending on pressure, heating rate, CO<sub>2</sub> and O<sub>2</sub> fugacities (e.g. French and Rosenberg, 1965;  
286 Gallagher and Warne, 1981; Dhupe and Gokarn, 1990; Jagtap et al., 1992; Pillot et al., 2013).  
287 The dry-siderite experiment performed at 300°C and 50 MPa yielded no detectable gaseous  
288 phases nor secondary solid products, indicating that thermal decomposition of siderite was not  
289 substantial and yielded fugacities of CO<sub>2</sub> which were not detected. In experiments with water  
290 at 300°C (50 MPa), the production of magnetite, CO<sub>2</sub> and H<sub>2</sub> is thus consistent with  
291 decomposition of siderite due to a dissolution process:



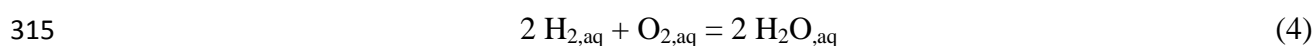
293 At 200°C and 50 MPa whatever the run duration, CO<sub>2</sub> and magnetite formed but no H<sub>2</sub> was  
294 detected. Calculations with SUPCRT under these temperature and pressure conditions  
295 indicated that magnetite is stable for a H<sub>2</sub> concentration above 10<sup>-3</sup> mmolal. Such H<sub>2</sub>  
296 concentration threshold is below detection limit of our GC but yet corresponds to significant  
297 yields of H<sub>2</sub>, suggesting that Reaction (2) also occurred at 200°C.

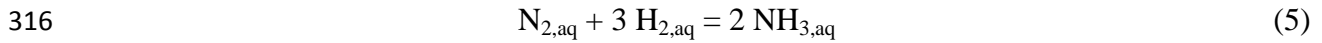
298 In all experiments, no significant CO signal was observed; Seewald et al. (2006)  
299 showed that in reducing hydrothermal conditions, CO equilibrates rapidly with CO<sub>2</sub> thanks to  
300 kinetically fast water-gas shift reaction



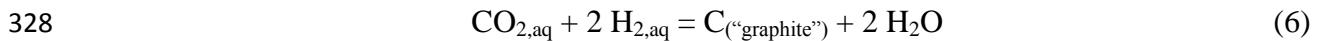
302 According to Reaction (3), CO concentrations at 200 and 300°C must have reached 10<sup>-7</sup> and  
303 10<sup>-2</sup> mmolal respectively, which is negligible in comparison to the amount of produced CO<sub>2</sub>.

304 In experiments of siderite decomposition in the presence of water vapor at 300°C,  
305 McCollom (2003) found a CO<sub>2</sub>/H<sub>2</sub> ratio of 2.5 consistent with Reaction (2). In our  
306 experiments, considering Reaction (2), it is possible to calculate the H<sub>2</sub> concentration  
307 corresponding to the amount of measured CO<sub>2</sub> and to compare it with the measured H<sub>2</sub> (Table  
308 2). Organic molecules detected by GCMS were neglected in the carbon and hydrogen mass  
309 balance due to their low concentration in comparison to that of CO<sub>2</sub>. From experiments *S300-*  
310 *1* to *S300-5*, the amount of missing H<sub>2</sub> increases from ~ 20 to 150 mmolal. The amounts of O<sub>2</sub>  
311 and N<sub>2</sub> introduced initially in the Au capsule through the headspace of air were estimated to  
312 10 and 40 mmolal, respectively. Part of the missing H<sub>2</sub> can potentially be accounted for by the  
313 reaction of O<sub>2</sub> and N<sub>2</sub> with H<sub>2</sub> to form H<sub>2</sub>O and NH<sub>3</sub>, respectively according to the following  
314 reactions:





317 Considering an  $\text{H}_2$  concentration at equilibrium with the siderite – magnetite – graphite  
318 mineral assemblage, ~ 20 and 4 mmolal of  $\text{H}_2$  would be consumed through reactions (4) and  
319 (5), respectively. The amount of missing  $\text{H}_2$  in experiment *S300-1* is consistent with a total  
320 reduction of  $\text{O}_2$  (Table 2); however, after complete  $\text{O}_2$  consumption,  $\text{H}_2$  concentration should  
321 increase with the advancement of Reaction (2). In contrast, the  $\text{H}_2$  concentration decreased  
322 from 12.1 to 1.5 mmolal between samples *S300-1* and *S300-5*. Neither the reduction of  $\text{O}_2$   
323 (Reaction 4) nor the production of ammonia (Reaction 5) can account for the ~ 150 mmolal of  
324 missing  $\text{H}_2$  in experiment *S300-5*. The dissolved organic compounds detected in the mmolal  
325 range cannot either explain the lack of  $\text{H}_2$ . The formation of condensed carbon that is  
326 observed at 200 and 300°C (Fig. 4 and 5) is another way to consume  $\text{H}_2$  according to the  
327 reaction:



329 Considering Reaction (6), ~ 60 mmol of condensed carbon per kg of solution could have  
330 formed. That is, 1.6% of the carbon initially introduced as siderite would have been converted  
331 into a carbonaceous phase, which would then be the dominant species produced by  $\text{CO}_2$   
332 reduction in our experiments. Considering a typical grain size of the starting siderite material  
333 of 20  $\mu\text{m}$  (Fig. 1), calculations show that such an amount would be equivalent to a carbon  
334 layer of 20 nm in thickness at the surface of siderite grains, which is qualitatively consistent  
335 with the TEM observations (Fig. 6). We note that the organic contamination in the starting  
336 material would not contribute significantly to solid-state organic carbon even though it would  
337 be totally converted into this phase.

338

#### 339 **4.2 Thermodynamic calculations**



340 Data obtained at 300°C were plotted along with the calculated stability domains of  
341 hematite, magnetite, wüstite and siderite as well as the CO<sub>2</sub> – graphite equilibrium in a  
342  $\log m_{\text{H}_2(\text{aq})} - \log m_{\text{CO}_2(\text{aq})}$  diagram (Fig. 7). Mineral stability domains were calculated at  
343 300°C (+/- 1.5%). The best consistency between calculation and measured data is achieved at  
344 a temperature of 295 °C which is within the experimental error bar. All the data points plot  
345 close to the siderite-magnetite equilibrium (Fig. 7), including *S300-1* (3 hours). At the  
346 timescale of the experiments, the relatively fast kinetics of Reaction (2) should impose a  
347 constant  $a_{\text{H}_2}/a_{\text{CO}_2}$  ratio. However, the constant evolution towards lower H<sub>2</sub> and higher CO<sub>2</sub>  
348 concentrations indicates that a slower reaction operated concurrently. In experiments *S300-3*  
349 to *S300-5* which lasted 144 and 2880 hours, respectively, the CO<sub>2</sub> - H<sub>2</sub> concentrations plot  
350 near the magnetite – siderite – graphite equilibrium point. This suggests that the evolution of  
351 CO<sub>2</sub> and H<sub>2</sub> activities towards this point results from the production of a carbon-rich phase,  
352 arising from the reduction of CO<sub>2</sub> according to Reaction (6). This is consistent with the TEM  
353 observations of condensed carbon products (Fig. 4, 5 and 6). After ~ 150 hours (i.e.,  
354 experiments *S300-3* to *S300-5*), the magnetite – siderite – “graphite” mineral assemblage  
355 buffers the CO<sub>2</sub>-H<sub>2</sub> concentrations (Fig. 2 and 7). Neglecting further hydrocarbons  
356 production, an equilibrium for siderite dissolution might thus have been reached.  
357 Alternatively, the dissolution of siderite could have stopped for kinetic reasons due to  
358 secondary phases deposited at its surface. The detailed composition of the aqueous phase  
359 would be required to investigate this issue.

360

## 361 **5. DISCUSSION**

### 362 **5.1 Occurrence of condensed carbonaceous matter**

363 Different forms of condensed carbonaceous material were observed under the TEM in  
364 samples reacted at 200 and 300°C. At 200°C, condensed carbon is located at magnetite and  
365 siderite grain surfaces and occurs in the form of a few stacks of graphene layers (ca. 5 nm),  
366 especially when encapsulating magnetite (Fig. 5a). At 300°C, condensed carbon was found  
367 intimately associated with aggregates of iron oxide of yet undetermined form (either FeO or  
368 Fe<sub>3</sub>O<sub>4</sub>) covering siderite crystals (Fig. 6). In addition, in the two sets of experiments (200 and  
369 300°C), an electron-beam sensitive carbonaceous compound was observed which is  
370 interpreted as hydrated or hydrogenated carbon, possibly a PAH (Fig. 4). The occurrence of  
371 condensed carbonaceous material in relatively large amount, indicates that part of the CO<sub>2</sub>  
372 initially contained in siderite, has been reduced. The CO<sub>2</sub> reduction in the presence of H<sub>2</sub> to  
373 form condensed carbon, assumed to be graphite for the sake of the calculation, is consistent  
374 with thermodynamic predictions. In turn, the proximity of experimental data points to the CO<sub>2</sub>  
375 - graphite equilibrium suggests that the thermodynamic properties of the observed  
376 carbonaceous phases are in first approximation well described by those of graphite.

377 The possibility of carbonaceous matter formation in the C-O-H system at high  
378 pressure and high temperature has already been mentioned in several experimental studies. In  
379 serpentinization experiments at 300°C and 50 MPa, Berndt et al. (1996) reported a large  
380 deficit in the CO<sub>2</sub> mass balance that they explained by the likely precipitation of graphite or  
381 amorphous carbon. In experiments with CO<sub>2</sub> - H<sub>2</sub> rich fluids and Fe - Ni catalysts at 50 MPa  
382 in the 200 – 400°C temperature range, Horita and Berndt (1999) showed that combined  
383 concentrations of  $\Sigma$ CO<sub>2</sub> (total dissolved carbonate species) and CH<sub>4</sub> in the fluid decreased in  
384 the early stages of the experiments until it finally rebounded. It was suggested that the  
385 transient formation of formate ion (HCOO<sup>-</sup>), carbon monoxide or condensed carbon phases  
386 could have acted as a carbon sink. It can be shown that CO<sub>2</sub> and H<sub>2</sub> concentrations reported in

387 the studies by Berndt et al. (1996) and Horita and Berndt (1999) clearly plot inside the  
388 graphite stability field, which supports the assumption of carbonaceous matter precipitation.

389 Dufaud et al. (2009) carried out experiments of Mg-rich silicate carbonation at 400 -  
390 500°C and 100 MPa. The authors mentioned the formation of an ill-ordered graphitic phase,  
391 accounting for up to 22% of the total carbon budget. In experiments with C-H-O fluids under  
392 graphite undersaturation, at 600°C and 1 GPa, Foustoukos (2012) reported the formation of  
393 poorly ordered graphitic carbon that may account for up to 60% of the total carbon of the  
394 system. In low-temperature (55 – 100°C) water-rock experiments with ultramafic and mafic  
395 rocks and minerals, Mayhew et al. (2013) showed H<sub>2</sub> production within the first few hours,  
396 followed by a slow decrease with time, as we observed in the present study. Interestingly, in a  
397  $\log m_{\text{H}_2(\text{aq})} - \log m_{\text{CO}_2(\text{aq})}$  diagram, their final CO<sub>2</sub> - H<sub>2</sub> concentrations plot right on the  
398 equilibrium point between magnetite, siderite and graphite; however neither iron carbonate  
399 nor condensed carbon was detected.

400 Precipitation of carbonaceous phases has been frequently described in experimental  
401 studies of Fischer-Tropsch synthesis for industrial purposes. For example, in experiments at  
402 300°C, 1.5 MPa and a H<sub>2</sub>/CO ratio of 1, Galuszka et al. (1992) identified with FTIR  
403 spectroscopy and thermogravimetry five forms of carbonaceous material (aliphatic, aromatic,  
404 oxygenated, carbidic and amorphous) deposited on the iron catalysts. In experiments of  
405 Fischer-Tropsch synthesis at 270°C by Sarkar et al. (2007), reactions between CO and H<sub>2</sub> to  
406 form alkanes produced collateral H<sub>2</sub>O, which oxidized the carbide-iron catalyst (Fe<sub>5</sub>C<sub>2</sub>) into  
407 magnetite. The authors detected ordered and amorphous carbon coatings (ca. 5 nm thick)  
408 encapsulating newly formed magnetite. They attributed the formation of these carbon layers  
409 to Boudouard reactions such as:



411 Although no CO intermediates could be detected in the present experiments, it cannot be  
412 excluded that a similar reaction process led to the formation of the carbon coatings observed  
413 around both magnetite and siderite grains in the present study (Fig. 5).

414

## 415 **5.2 Implication for mineral surface catalysis of CO<sub>2</sub> reduction**

416 The production of complex carbon compounds, such as PAH, in experiments of  
417 hydrothermal decomposition of siderite with water vapor, was interpreted by McCollom  
418 (2003) as related to surface catalyzed processes. Magnetite was proposed by Voglesonger  
419 (2001) to enhance the production of methanol from CO<sub>2</sub> - H<sub>2</sub> rich fluids in hydrothermal  
420 conditions. In experiments with CO<sub>2</sub> - H<sub>2</sub> rich fluids and magnetite at 400°C and 50 MPa, Fu  
421 et al. (2007) measured, using combustion, significant amounts of carbon-bearing compounds  
422 located at the magnetite surface. Magnetite is often invoked as a potential mineral catalyst in  
423 experiments involving FTT reactions (Horita and Berndt, 1999; McCollom and Seewald,  
424 2001; Foustoukos and Seyfried, 2004); however, McCollom (2013) pointed out that none of  
425 the latter studies provides definitive evidence that magnetite can catalyze carbon reduction in  
426 hydrothermal environments. Recently, Mayhew et al. (2013) showed from water-rock  
427 interaction experiments performed at low-temperature (55 – 100°C), that the spinel structure  
428 of Fe-bearing minerals such as magnetite is highly beneficial for electron transfer processes.  
429 In our experiments, observations of condensed carbon encapsulating magnetite and siderite  
430 highlight the catalytic role of mineral surfaces in the processes of carbon reduction and  
431 polymerization (Fig. 5). The relatively high organization degree of the carbon surrounding  
432 magnetite points to a higher catalytic ability for this latter mineral.

433 In addition to the condensed carbonaceous material, the experiments yielded an  
434 electron-beam sensitive carbonaceous compound, interpreted as hydrated or hydrogenated

435 carbon, possibly a PAH (Fig. 4). McCollom et al. (1999) and McCollom and Seewald (2003)  
436 carried out experiments with aqueous solution of formic acid at temperature higher than  
437 175°C. McCollom and Seewald (2003) observed that only the experiments containing a  
438 gaseous phase, i.e., that of McCollom et al. (1999), yielded complex hydrocarbons. They  
439 suggested that the presence of liquid water may interfere with the formation of C-C bonds on  
440 the catalyst surface. As our experiments operated without a gaseous phase, a measurable yield  
441 of hydrated or hydrogenated chains of carbon suggests that presence of liquid water does not  
442 entirely preclude the polymerization of carbon.

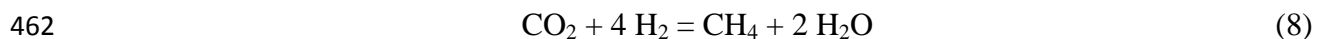
443 In the 300°C experiments especially, graphitic carbon was also observed closely  
444 associated to aggregates of magnetite or FeO at the siderite surface (Fig. 6). The reduction of  
445 CO<sub>2</sub> released by the carbonate may have been catalyzed by the iron oxide present on the  
446 siderite surface, resulting in a local and rapid precipitation of graphitic carbon. A similar  
447 process was proposed by Sarkar et al. (2007) with reaction between carbide iron (Fe<sub>5</sub>C<sub>2</sub>) and  
448 water producing closely associated magnetite and elemental carbon.

449

### 450 **5.3 H<sub>2</sub> and CH<sub>4</sub> generation**

451 A main implication of our study to natural systems is that abiotic H<sub>2</sub> generation,  
452 widely studied in recent years in ultrabasic contexts, could also occur in sedimentary basin in  
453 conjunction with hydrothermal dissolution of siderite. According to our experiments, H<sub>2</sub>  
454 concentrations of ~ 1 mmolal at 300°C are to be expected in the presence of graphitic carbon,  
455 a potential by-product of siderite dissolution. Such concentrations are comparable to those  
456 reported by Charlou et al. (2001) at the Rainbow hydrothermal field (i.e., 1 – 10 mmolal).  
457 Moreover, TEM observations coupled to thermodynamic modeling showed that siderite –  
458 water interactions drove the H<sub>2</sub>-CO<sub>2</sub> activity to values which allowed the production of

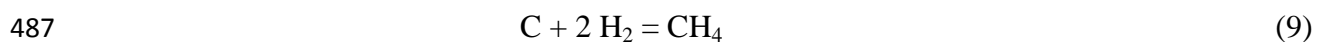
459 condensed carbon from CO<sub>2</sub>. However, it remains unclear whether the CH<sub>4</sub> produced in our  
460 experiments is also related to siderite dissolution. Abiotic generation of CH<sub>4</sub> is frequently  
461 attributed to the reduction of CO<sub>2</sub> according to the reaction



463 (e.g., Berndt et al., 1996; Horita and Berndt, 1999; McCollom and Seewald, 2001; Foustoukos  
464 and Seyfried, 2004; Fu et al., 2007). However, experiments carried out with C-O-H fluids  
465 under hydrothermal conditions with isotope labeling of the carbon source showed that most of  
466 the measured CH<sub>4</sub> often results from a background source (McCollom and Seewald, 2001;  
467 2003a; Seewald, 2006). Detection of carboxylic acids and ethanol in the dry-siderite  
468 experiment indicates that traces of organic compounds were already present in the starting  
469 material. A contribution of this organic contamination to methane production cannot be  
470 excluded and therefore it is not possible to conclude on the origin of the measured CH<sub>4</sub>.

471         Considering Reaction (8), the thermodynamic calculation predicts a CO<sub>2</sub>/CH<sub>4</sub> ratio in  
472 our experiments of ~ 1; however, we observed in *S300-5* a ratio of ~ 1000, close to the one  
473 reported by McCollom (2003) in experiments of hydrothermal decomposition of siderite with  
474 water vapor. This result emphasizes the strong kinetics limitation on CH<sub>4</sub> formation through  
475 CO<sub>2</sub> reduction by H<sub>2</sub>-rich aqueous fluids in the 200 – 300°C range. For example, based on  
476 experiments performed with C-O-H fluids and no mineral phases, Seewald et al. (2006)  
477 proposed that kinetic limitations may preclude the reduction of methanol into methane in the  
478 cascade of reduction from CO<sub>2</sub> to CH<sub>4</sub>. As a consequence, in serpentinization experiments,  
479 the generation of CH<sub>4</sub> through CO<sub>2</sub> reduction is frequently assumed to be a surface catalyzed  
480 process (Berndt et al., 1996; Horita and Berndt, 1999; McCollom and Seewald, 2001;  
481 Foustoukos and Seyfried, 2004; Fu et al., 2007). In that respect, coating of mineral surfaces  
482 by carbon as observed here, is expected to poison the surface catalysis of CO<sub>2</sub> reduction. On

483 the other hand, the presence of condensed carbon shows that CO<sub>2</sub> reduction can operate at low  
484 temperature (200 - 300°C) at least in the presence of mineral surfaces (magnetite and to a  
485 smaller extend siderite). Then, the presence of carbonaceous material offers new pathways to  
486 the formation of CH<sub>4</sub> through hydrogenation reactions



488 However, considering Reaction (9), the CH<sub>4</sub> concentrations in our experiments remained far  
489 from equilibrium with the carbonaceous material, which suggests that this alternative route to  
490 produce CH<sub>4</sub> is also kinetically unfavourable. Parameters affecting the thermodynamics or the  
491 kinetics of Reaction (9), such as total pressure, catalysts or the exact structure of the  
492 carbonaceous phase need to be further investigated.

493

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501

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Table 1. Experimental conditions (50 MPa) and gas concentrations

<b>Experiments</b>	<b>Temperature (°C)</b>	<b>Time (hours)</b>	<b>CO<sub>2</sub></b>	<b>H<sub>2</sub></b>	<b>CH<sub>4</sub></b>
<b>S200-1</b>	200	67	6.1	b.d.l.	b.d.l.
<b>S200-2</b>	200	1080	3.7	b.d.l.	b.d.l.
<b>S300-1</b>	300	3	101	12.1	b.d.l.
<b>S300-2</b>	300	48	213	6.9	0.07
<b>S300-3</b>	300	144	478	2.1	0.18
<b>S300-4</b>	300	168	368	0.9	0.13
<b>S300-5</b>	300	2880	453	1.5	0.36
<b>Dry-Siderite</b>	300	144	b.d.l.	b.d.l.	b.d.l.

Concentrations are in *mmolal* – Error bars are of +/-20%

b.d.l – below detection limit. n.a. – not analyzed.



Table 2. Hydrogen mass balance calculation

<b>Experiments</b>	<b>Time (h)</b>	<b>Measured CO<sub>2</sub></b>	<b>Expected H<sub>2</sub><sup>a</sup></b>	<b>Measured H<sub>2</sub></b>
<b>S300-1</b>	3	101	10	12.1
<b>S300-5</b>	2880	453	127	1.5

Concentrations are in *mmolal* – Error bars are of +/-20%

<sup>a</sup>Expected H<sub>2</sub> = H<sub>2</sub> produced by reaction (2) calculated from measured CO<sub>2</sub> minus H<sub>2</sub> consumed by reaction (4) and (5) due to O<sub>2</sub> and N<sub>2</sub> introduced in the Au capsule (see text). Calculations are performed assuming an H<sub>2</sub> concentration at equilibrium with the siderite – magnetite – “graphite” mineral assemblage.

## Figure captions

Figure 1. XRPD pattern and secondary electron images of the synthetic siderite used as starting material. Siderite grains exhibit well-developed faces and a homogeneous grain size distribution centered around ten to twenty of micrometers. Note the absence of iron oxide Bragg's reflections on the XRPD pattern.

Figure 2.  $H_2$ ,  $CO_2$  and  $CH_4$  concentrations as a function of time at  $300^\circ C$  and 50 MPa.  $H_2$  and  $CH_4$  concentrations are multiplied by a factor 50 and 1000, respectively. Note that the horizontal axis (run time) has been truncated.

Figure 3. XRPD pattern and SEM images in backscattered electron mode of sample *S300-3* showing altered siderite (darker minerals) covered up with magnetite grains (lighter grains). Image (a) shows dissolution pits on the siderite surface, surrounded by smaller grains of iron oxide with typical grain sizes of  $\sim 100$  nm. Grains of magnetite larger than  $1 \mu m$  are observed, partly embedded in the siderite surface (Image b). Magnetite (dashed) is the only solid product noticeable in the XRPD pattern, along with the residual siderite (dotted).

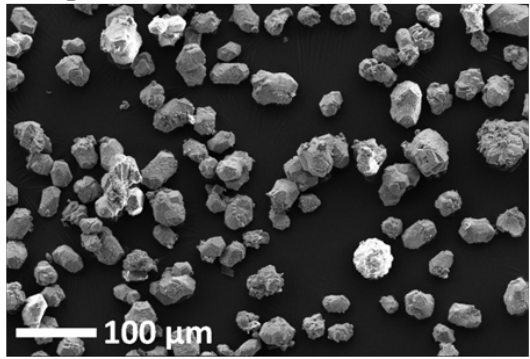
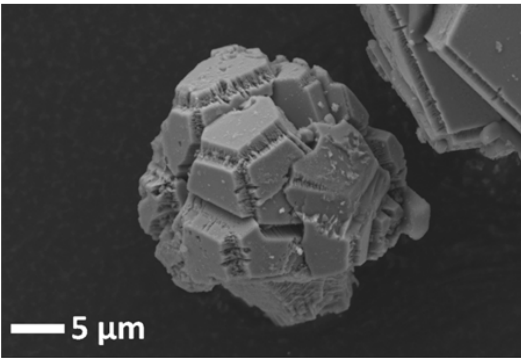
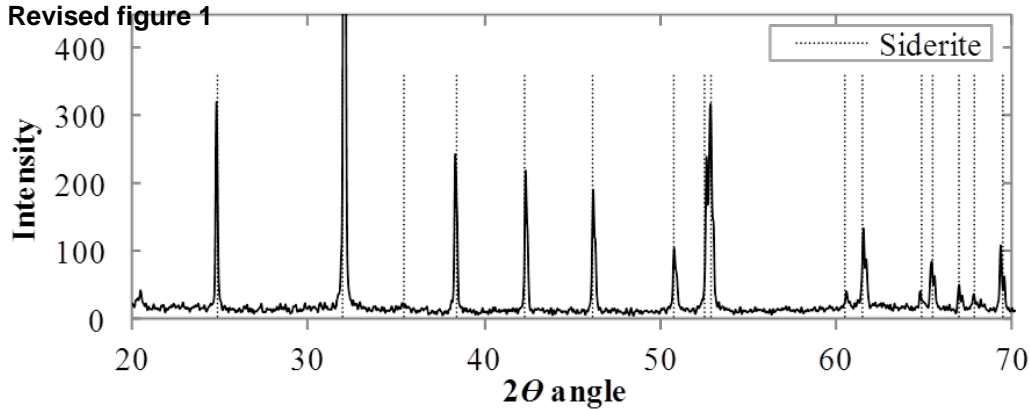
Figure 4. TEM image of sample *S300-3* showing, attached to the carbon film, a porous C-rich phase unstable under the electron beam, interpreted as an hydrated or hydrogenated carbonaceous phase. Such phase was never observed in the starting materials.

Figure 5. High-resolution TEM images of sample *S200-1* showing details of the carbon coat which covers a magnetite crystal (a) and a siderite grain (b). The carbonaceous material shows a higher structural order when associated with magnetite.

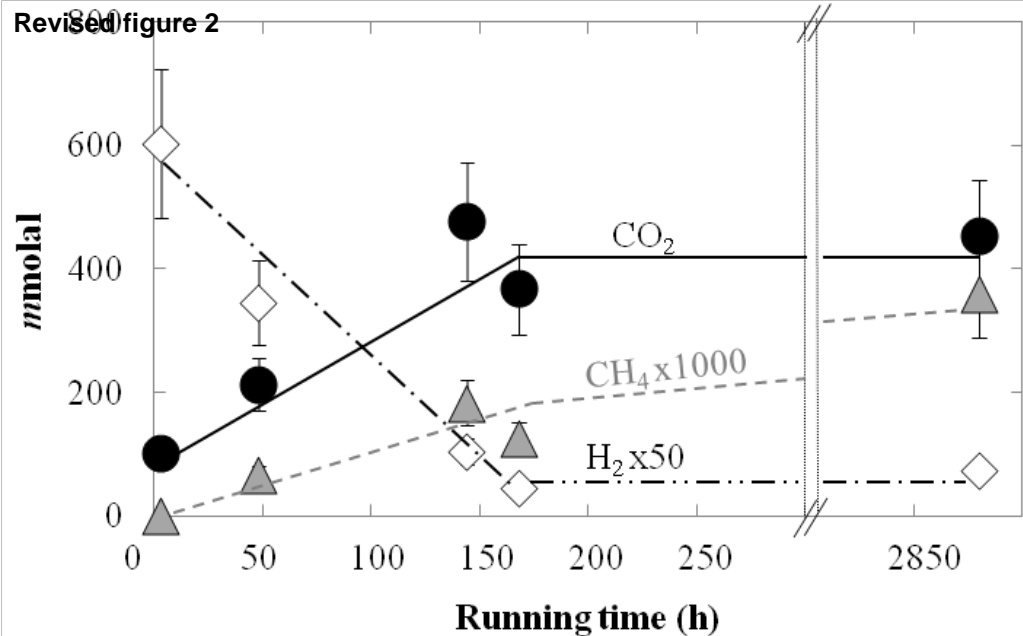
Figure 6. High-resolution TEM images of sample *S300-3* showing iron oxide (either FeO or  $Fe_3O_4$ ) closely associated to the solid carbon-rich phase at the surface of the siderite.

Figure 7.  $\log m_{\text{H}_2(\text{aq})} - \log m_{\text{CO}_2(\text{aq})}$  diagram showing the stability domains of hematite, magnetite, wüstite and siderite as well as the  $\text{CO}_2$  – graphite equilibrium at 50 MPa, 295°C (grey dashed lines) and 300°C (full black lines). The measured  $\text{CO}_2$  and  $\text{H}_2$  molalities of the 300°C experiments are also plotted. Darker symbols correspond to longer run durations. The dotted line represents the potential compositional path followed by the solution after all of the initial  $\text{O}_2$  had reacted with  $\text{H}_2$  and assuming stoichiometric dissolution of siderite at first.

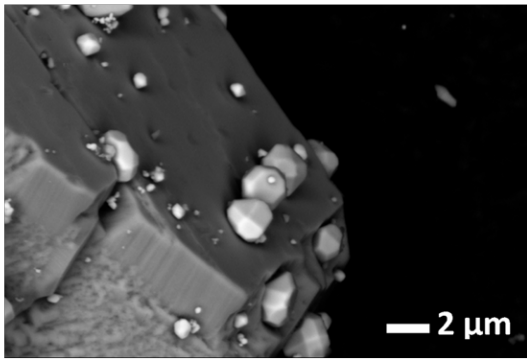
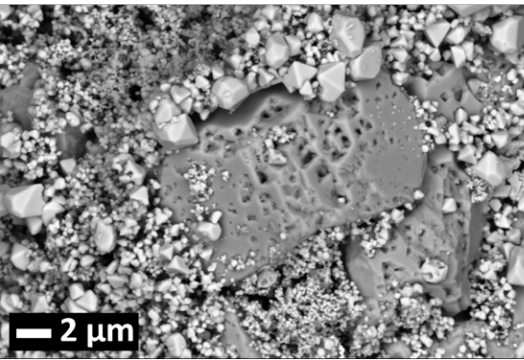
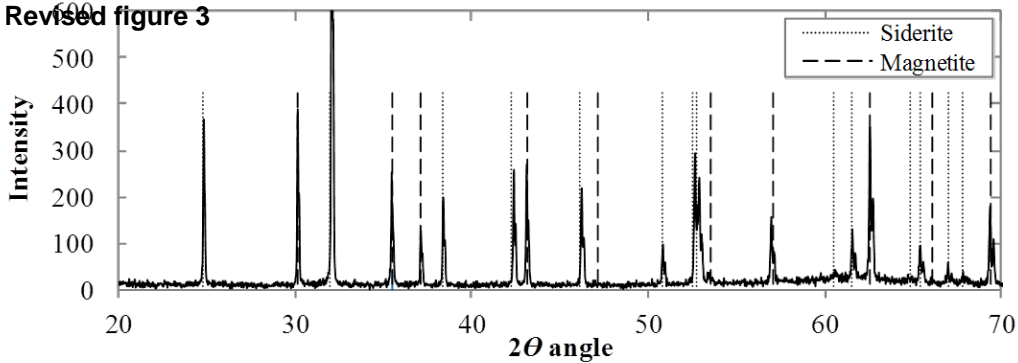
Revised figure 1



Revised figure 2



Revised figure 3

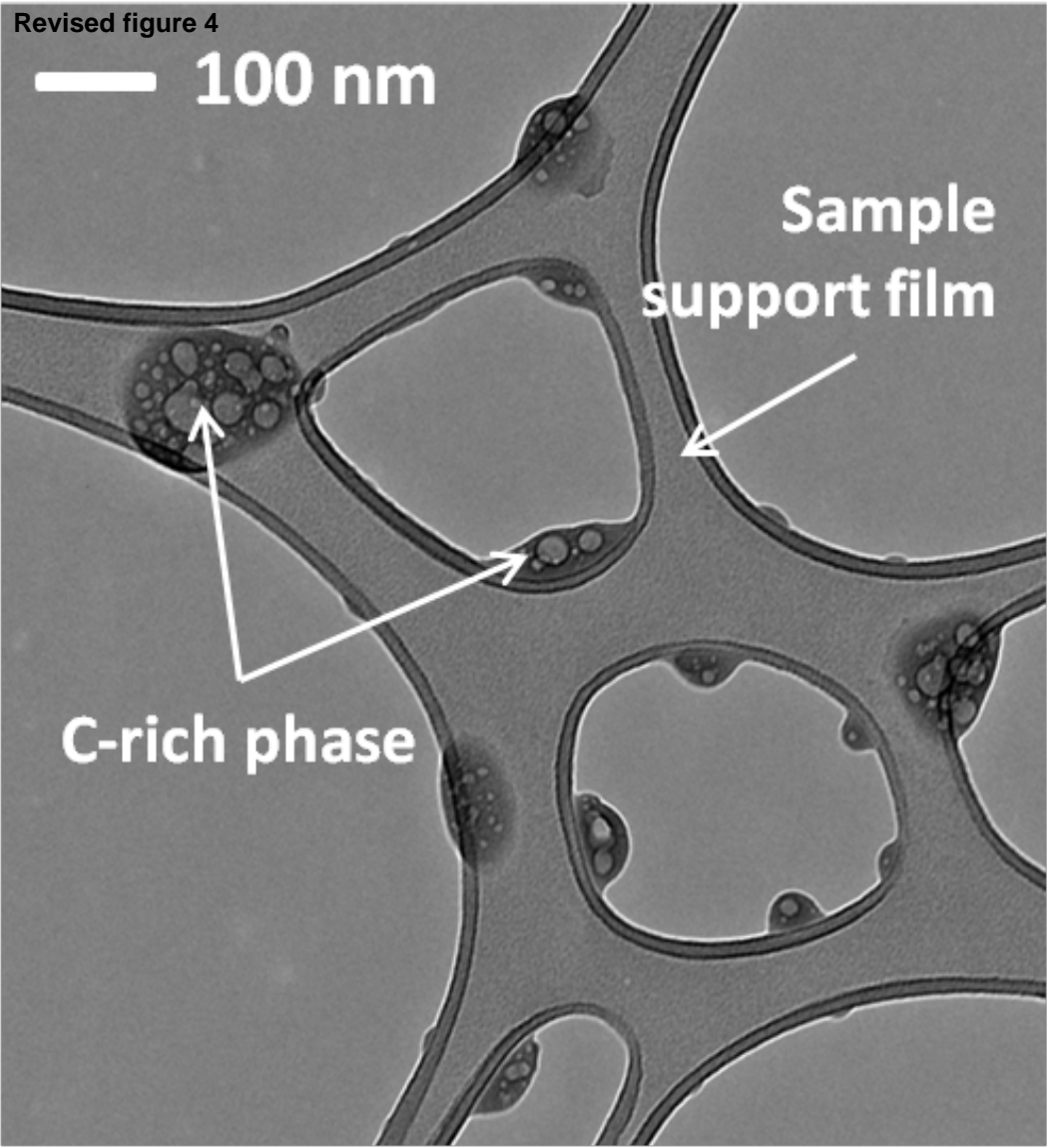


Revised figure 4

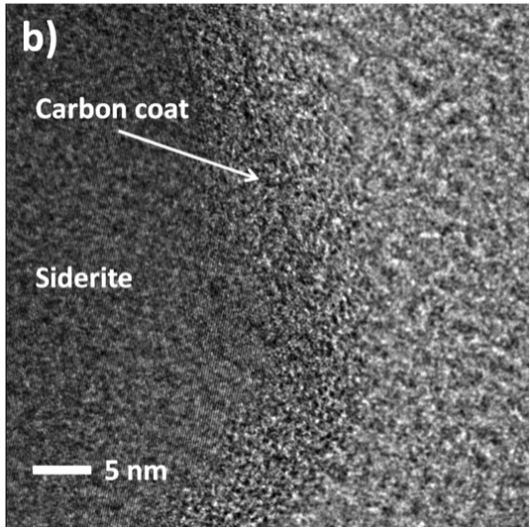
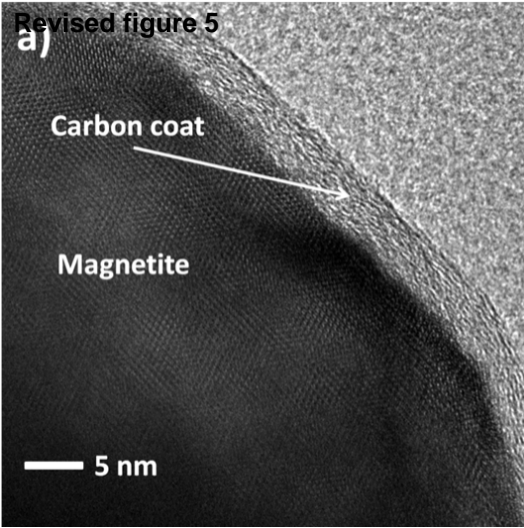
— 100 nm

Sample  
support film

C-rich phase

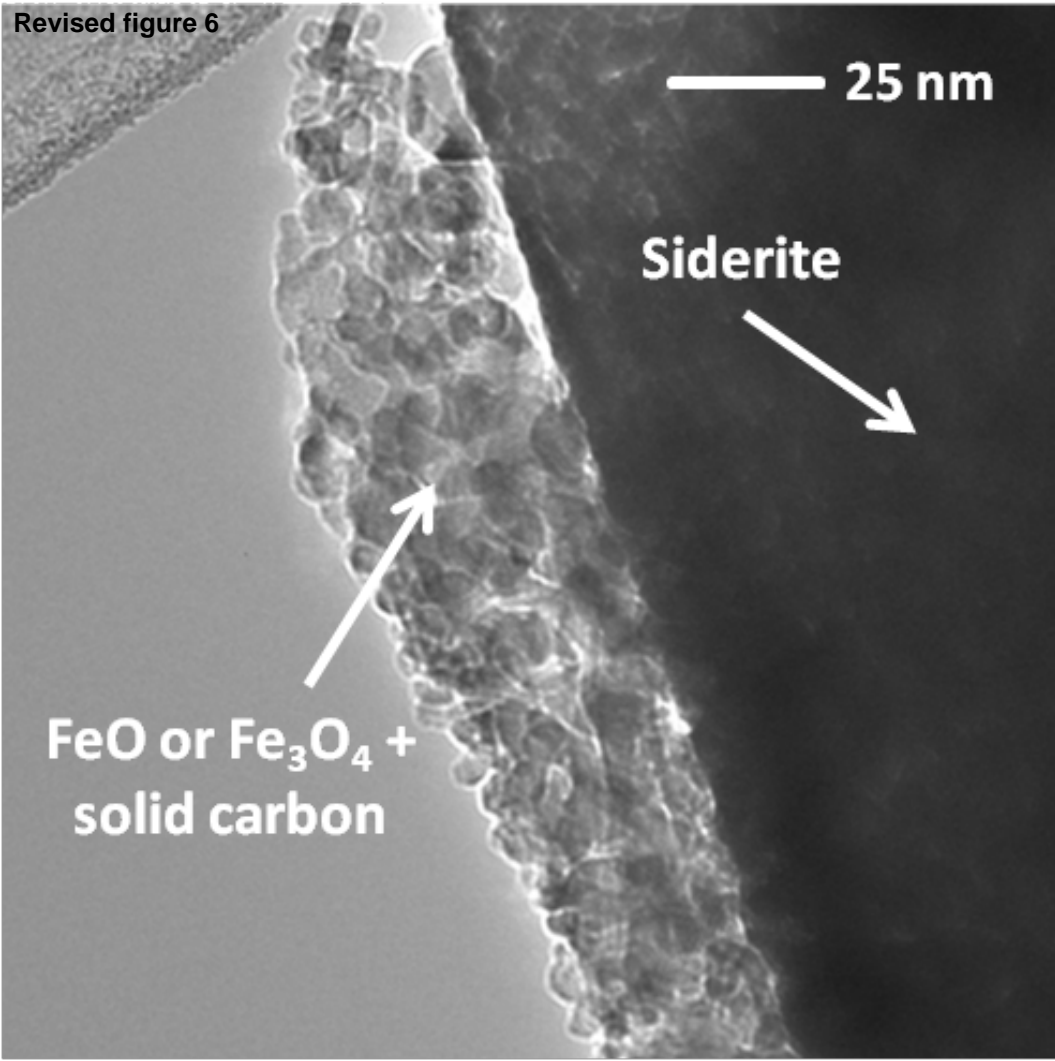


Revised figure 5





Revised figure 6



Revised figure 7

