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1 **FORMATION OF CO₂, H₂ 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, Fe_3O_4 , was produced
50 accordingly. The gas phase was dominated by CO_2 , H_2 and CH_4 , the latter being in strong
51 thermodynamic disequilibrium with CO_2 . Contrary to the other gas products, 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 H_2
56 concentration decrease up to the point where H_2 and 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 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 H₂ 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 H₂ concentration will be buffered by a
65 condensed carbon phase associated with magnetite.

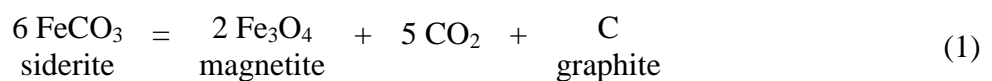
66

67 **1. INTRODUCTION**

68 Abiotic conversion of CO₂ 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 CO₂ 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 CO₂) to organic compounds.

87 Highly reducing hydrothermal conditions in a CO₂-bearing environment can also be
88 achieved through the decomposition of siderite (FeCO₃) 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 CO₂ and H₂ 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 H₂-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 (H₂, CO₂, and CH₄) 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 (FeSO₄·7H₂O) and 2 g of urea (CO(NH₂)₂)
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 10⁶ 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 H₂O. The dissociation of iron sulfate and the total hydrolysis of
123 urea resulted in high Fe²⁺ and dissolved inorganic carbon (DIC) concentrations. At 180°C, the
124 NH₄⁺/NH₃ 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 H₂, CH₄ and CO₂ to be determined with detection limits of ~ 0.01, 0.05
156 and 0.5 mmolal respectively (mmolal equals mmol·kg⁻¹ of solvent) . The GC column that we
157 used did not allow separating CO from air (N₂ and O₂) 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 H₂, CH₄ and CO₂, 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⁻¹ as
164 calculated with the SUPCRT package (Helgeson et al., 1978; Johnson et al., 1992). Therefore
165 H₂, CH₄, and CO₂ will mostly concentrate in the gas phase and remaining dissolved H₂ and
166 CO₂ 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 α radiation. The instruments were operated
186 with a step size of 0.026° 2 θ 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 ΔH_f° value adopted here for siderite was taken from
204 Chai and Navrotsky (1994) of -750.6 (± 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° 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 (± 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°C and 50 MPa, the saturation concentrations of H_2 , CH_4 , and 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°C . Thereby, H_2 , CO_2 and 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 CO₂ 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, H₂ and CH₄ formed at concentrations two to three orders of
228 magnitude lower than CO₂ concentrations. From sample *S300-1* to *S300-4*, the CO₂ and CH₄
229 concentrations increased while the maximal H₂ 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 CO₂, H₂ and the magnetite content remained constant suggesting attainment
232 of a steady state. In contrast, the CH₄ concentration kept increasing but more slowly than in
233 the first 168 hours. The slow accumulation of CH₄ throughout the run indicated a strong
234 kinetic control over CH₄ formation (Table 1, Fig. 2).

235 In the 200°C experiments, CO₂ was the only detected gas; H₂ 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 CO₂ 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 (CH₃COOH), methanol (CH₃OH), ethanol (C₂H₅OH), propanol
245 (C₃H₇OH) and acetone (C₃H₆O) 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 CO₂
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 Fe₃O₄ 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, Fe₃O₄ 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 Fe₃O₄ 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.

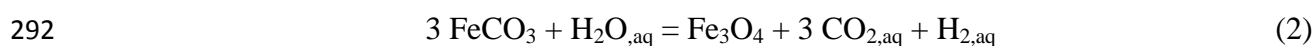
270 In the 200°C experiments, another carbon-rich phase was observed as regular nm-
271 sized coats around magnetite and siderite grains (Fig. 5). The carbon matter which
272 encapsulates magnetite grains is made of a stack of layers, presumably short graphene units,
273 suggesting a relatively well 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 Fe₃O₄) closely
280 associated to a solid carbon-rich phase (Fig. 6).

281

282 4. THERMODYNAMIC MODEL

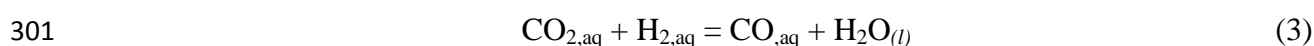
283 4.1 Mass balance

284 Thermal decomposition of siderite upon heating occurs between ~ 400 and 600°C
285 depending on pressure, heating rate, CO₂ and O₂ 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 CO₂ which were not detected. In experiments with water
290 at 300°C (50 MPa), the production of magnetite, CO₂ and H₂ is thus consistent with
291 decomposition of siderite due to a dissolution process:



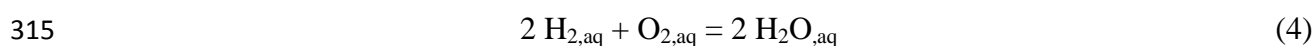
293 At 200°C and 50 MPa whatever the run duration, CO₂ and magnetite formed but no H₂ was
294 detected. Calculations with SUPCRT under these temperature and pressure conditions
295 indicated that magnetite is stable for a H₂ concentration above 10⁻³ mmolal. Such H₂
296 concentration threshold is below detection limit of our GC but yet corresponds to significant
297 yields of H₂, suggesting that Reaction (2) also occurred at 200°C.

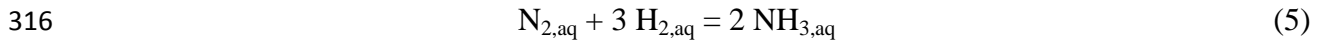
298 In all experiments, no significant CO signal was observed; Seewald et al. (2006)
299 showed that in reducing hydrothermal conditions, CO equilibrates rapidly with CO₂ thanks to
300 kinetically fast water-gas shift reaction



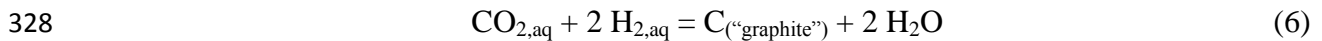
302 According to Reaction (3), CO concentrations at 200 and 300°C must have reached 10⁻⁷ and
303 10⁻² mmolal respectively, which is negligible in comparison to the amount of produced CO₂.

304 In experiments of siderite decomposition in the presence of water vapor at 300°C,
305 McCollom (2003) found a CO₂/H₂ ratio of 2.5 consistent with Reaction (2). In our
306 experiments, considering Reaction (2), it is possible to calculate the H₂ concentration
307 corresponding to the amount of measured CO₂ and to compare it with the measured H₂ (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 CO₂. From experiments *S300-*
310 *1* to *S300-5*, the amount of missing H₂ increases from ~ 20 to 150 mmolal. The amounts of O₂
311 and N₂ introduced initially in the Au capsule through the headspace of air were estimated to
312 10 and 40 mmolal, respectively. Part of the missing H₂ can potentially be accounted for by the
313 reaction of O₂ and N₂ with H₂ to form H₂O and NH₃, respectively according to the following
314 reactions:





317 Considering an H₂ concentration at equilibrium with the siderite – magnetite – graphite
318 mineral assemblage, ~ 20 and 4 mmolal of H₂ would be consumed through reactions (4) and
319 (5), respectively. The amount of missing H₂ in experiment *S300-1* is consistent with a total
320 reduction of O₂ (Table 2); however, after complete O₂ consumption, H₂ concentration should
321 increase with the advancement of Reaction (2). In contrast, the H₂ concentration decreased
322 from 12.1 to 1.5 mmolal between samples *S300-1* and *S300-5*. Neither the reduction of O₂
323 (Reaction 4) nor the production of ammonia (Reaction 5) can account for the ~ 150 mmolal of
324 missing H₂ in experiment *S300-5*. The dissolved organic compounds detected in the mmolal
325 range cannot either explain the lack of H₂. The formation of condensed carbon that is
326 observed at 200 and 300°C (Fig. 4 and 5) is another way to consume H₂ 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 CO₂
332 reduction in our experiments. Considering a typical grain size of the starting siderite material
333 of 20 μm (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 CO₂ – 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 H₂ and higher CO₂
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 CO₂ - H₂ concentrations plot
350 near the magnetite – siderite – graphite equilibrium point. This suggests that the evolution of
351 CO₂ and H₂ activities towards this point results from the production of a carbon-rich phase,
352 arising from the reduction of CO₂ 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 CO₂-H₂ 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 Fe₃O₄) 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 CO₂
372 initially contained in siderite, has been reduced. The CO₂ reduction in the presence of H₂ 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 CO₂
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 CO₂ mass balance that they explained by the likely precipitation of graphite or
381 amorphous carbon. In experiments with CO₂ - H₂ 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 Σ CO₂ (total dissolved carbonate species) and CH₄ 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⁻), carbon monoxide or condensed carbon phases
386 could have acted as a carbon sink. It can be shown that CO₂ and H₂ 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 H₂ 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 CO₂ - H₂ 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 H₂/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 H₂ to
406 form alkanes produced collateral H₂O, which oxidized the carbide-iron catalyst (Fe₅C₂) 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 CO₂ 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 CO₂ - H₂ rich fluids in hydrothermal
420 conditions. In experiments with CO₂ - H₂ 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.

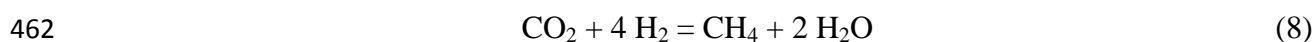
443 In the 300°C experiments especially, graphitic carbon was also observed closely
444 associated to aggregates of magnetite or FeO at the siderite surface (Fig. 6). The reduction of
445 CO₂ released by the carbonate may have been catalyzed by the iron oxide present on the
446 siderite surface, resulting 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 (Fe₅C₂) and
448 water producing closely associated magnetite and elemental carbon.

449

450 **5.3 H₂ and CH₄ generation**

451 A main implication of our study to natural systems is that abiotic H₂ 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, H₂
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 H₂-CO₂ activity to values which allowed the production of

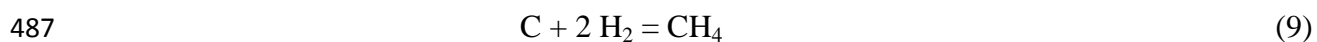
459 condensed carbon from CO₂. However, it remains unclear whether the CH₄ produced in our
460 experiments is also related to siderite dissolution. Abiotic generation of CH₄ is frequently
461 attributed to the reduction of CO₂ according to the reaction



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 CH₄ 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 CH₄.

471 Considering Reaction (8), the thermodynamic calculation predicts a CO₂/CH₄ 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 CH₄ formation through
475 CO₂ reduction by H₂-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 CO₂ to CH₄. As a consequence, in serpentinization experiments,
479 the generation of CH₄ through CO₂ 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 CO₂ reduction. On

483 the other hand, the presence of condensed carbon shows that CO₂ 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 CH₄ through hydrogenation reactions



488 However, considering Reaction (9), the CH₄ concentrations in our experiments remained far
489 from equilibrium with the carbonaceous material, which suggests that this alternative route to
490 produce CH₄ 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

Experiments	Temperature (°C)	Time (hours)	CO₂	H₂	CH₄
S200-1	200	67	6.1	b.d.l.	b.d.l.
S200-2	200	1080	3.7	b.d.l.	b.d.l.
S300-1	300	3	101	12.1	b.d.l.
S300-2	300	48	213	6.9	0.07
S300-3	300	144	478	2.1	0.18
S300-4	300	168	368	0.9	0.13
S300-5	300	2880	453	1.5	0.36
Dry-Siderite	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

Experiments	Time (h)	Measured CO₂	Expected H₂^a	Measured H₂
S300-1	3	101	10	12.1
S300-5	2880	453	127	1.5

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

^aExpected H₂ = H₂ produced by reaction (2) calculated from measured CO₂ minus H₂ consumed by reaction (4) and (5) due to O₂ and N₂ introduced in the Au capsule (see text). Calculations are performed assuming an H₂ 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 ~ 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).

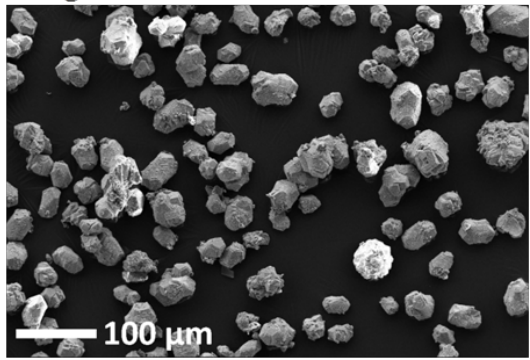
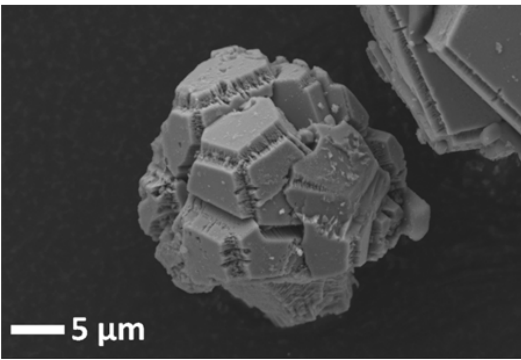
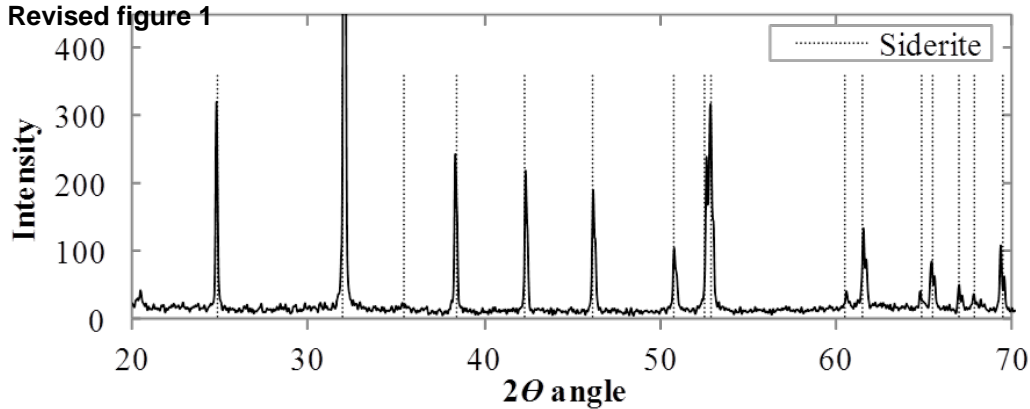
Figure 4. TEM image of sample *S300-3* showing, attached to the carbon film, a porous C-rich phase unstable under the electron beam, interpreted as an hydrated or hydrogenated carbonaceous phase. Such phase was never observed in the starting materials.

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.

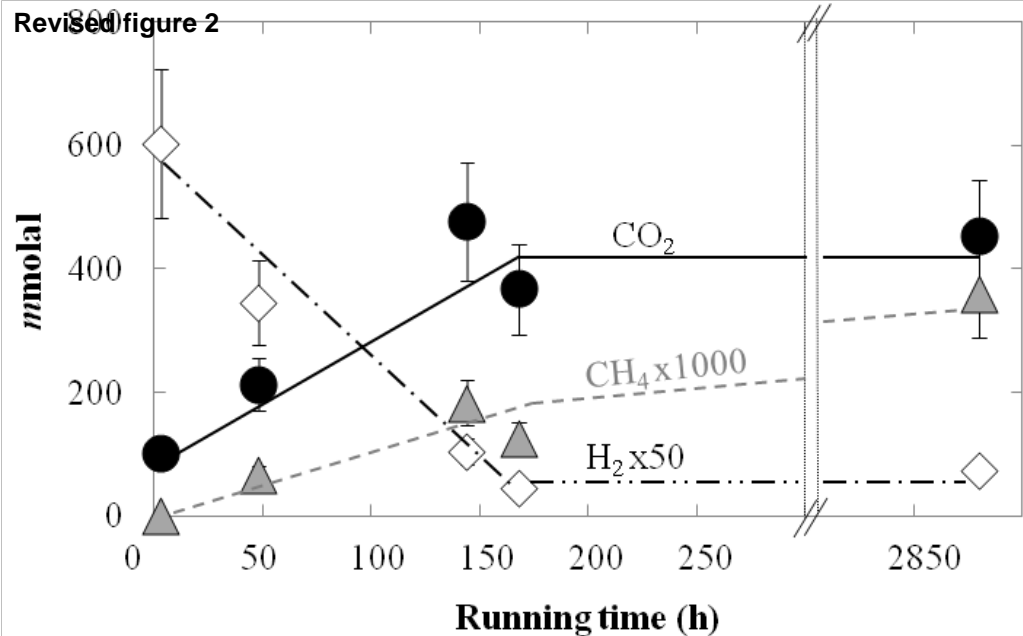
Figure 6. High-resolution TEM images of sample *S300-3* showing iron oxide (either FeO or Fe_3O_4) closely associated to the solid carbon-rich phase at the surface of the siderite.

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 CO_2 – graphite equilibrium at 50 MPa, 295°C (grey dashed lines) and 300°C (full black lines). The measured CO_2 and 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 O_2 had reacted with H_2 and assuming stoichiometric dissolution of siderite at first.

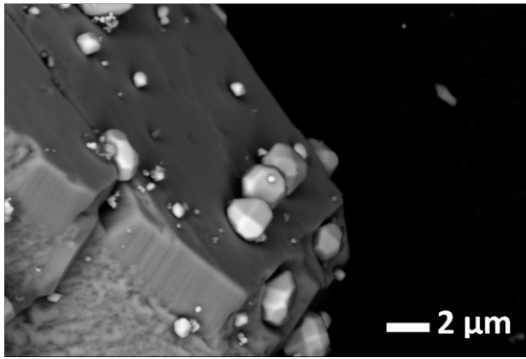
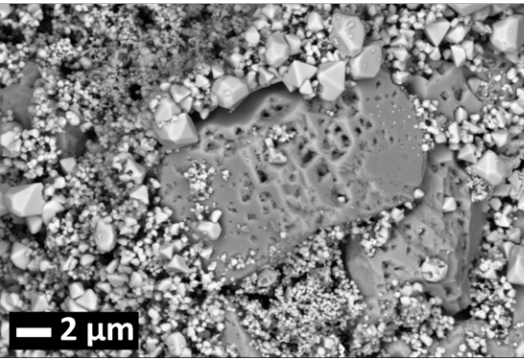
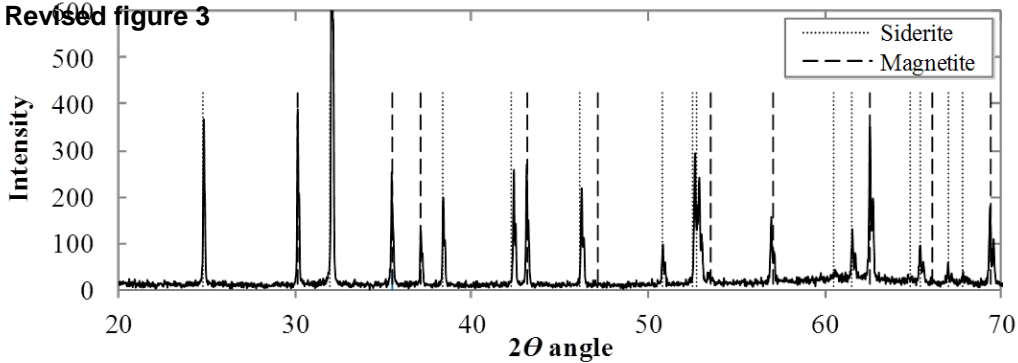
Revised figure 1



Revised figure 2



Revised figure 3

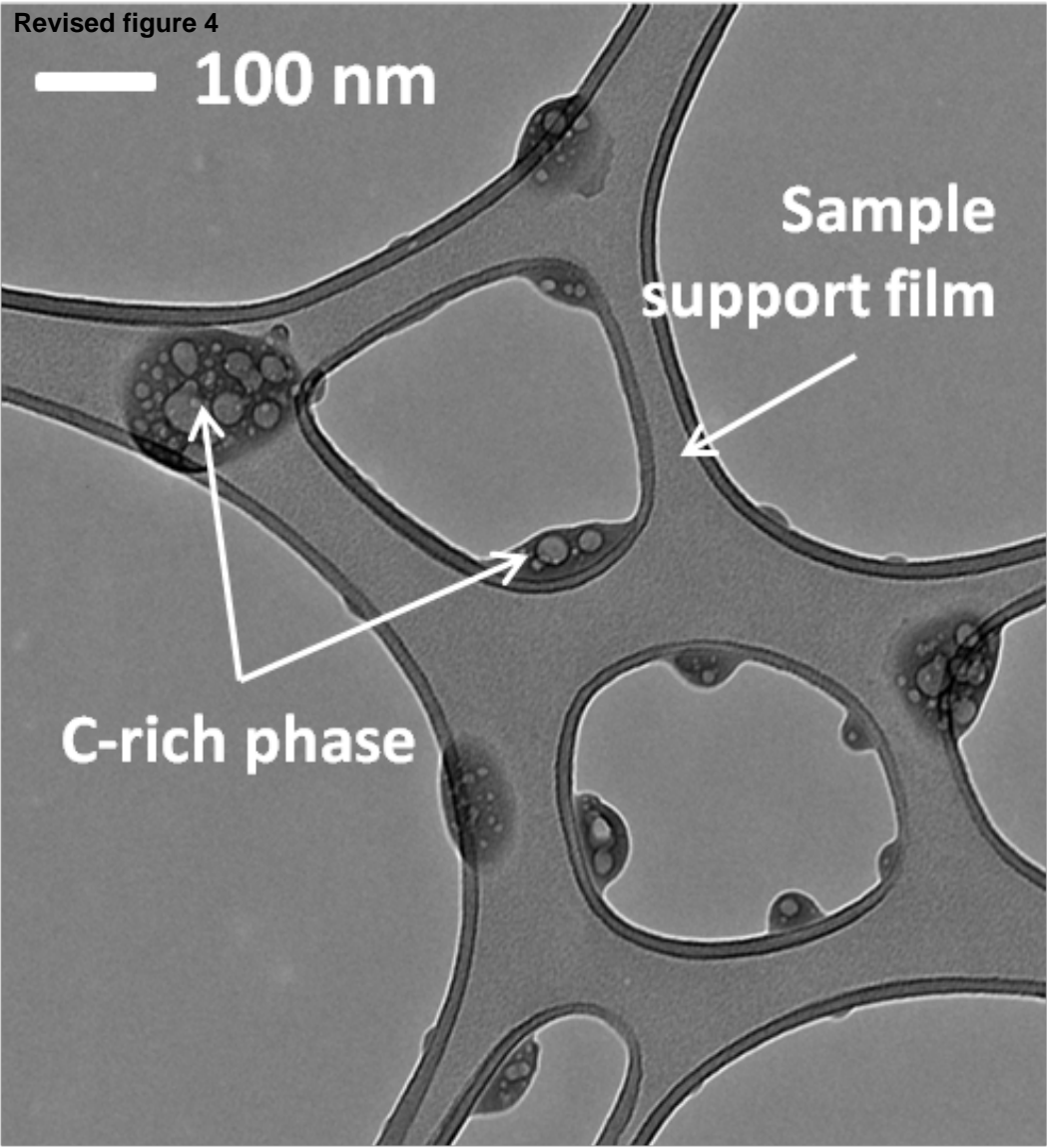


Revised figure 4

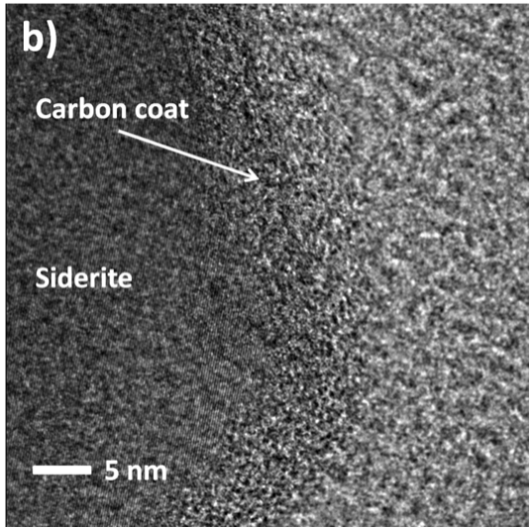
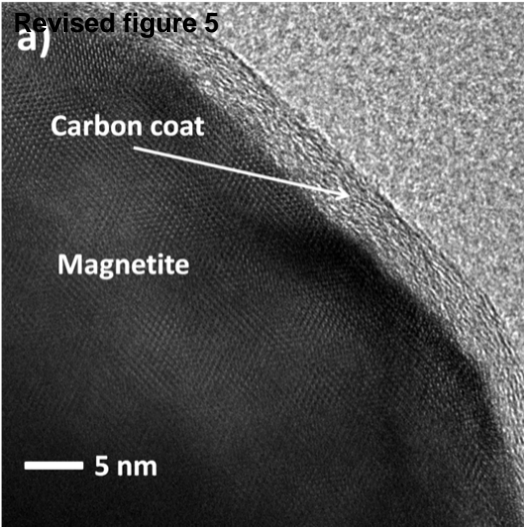
— 100 nm

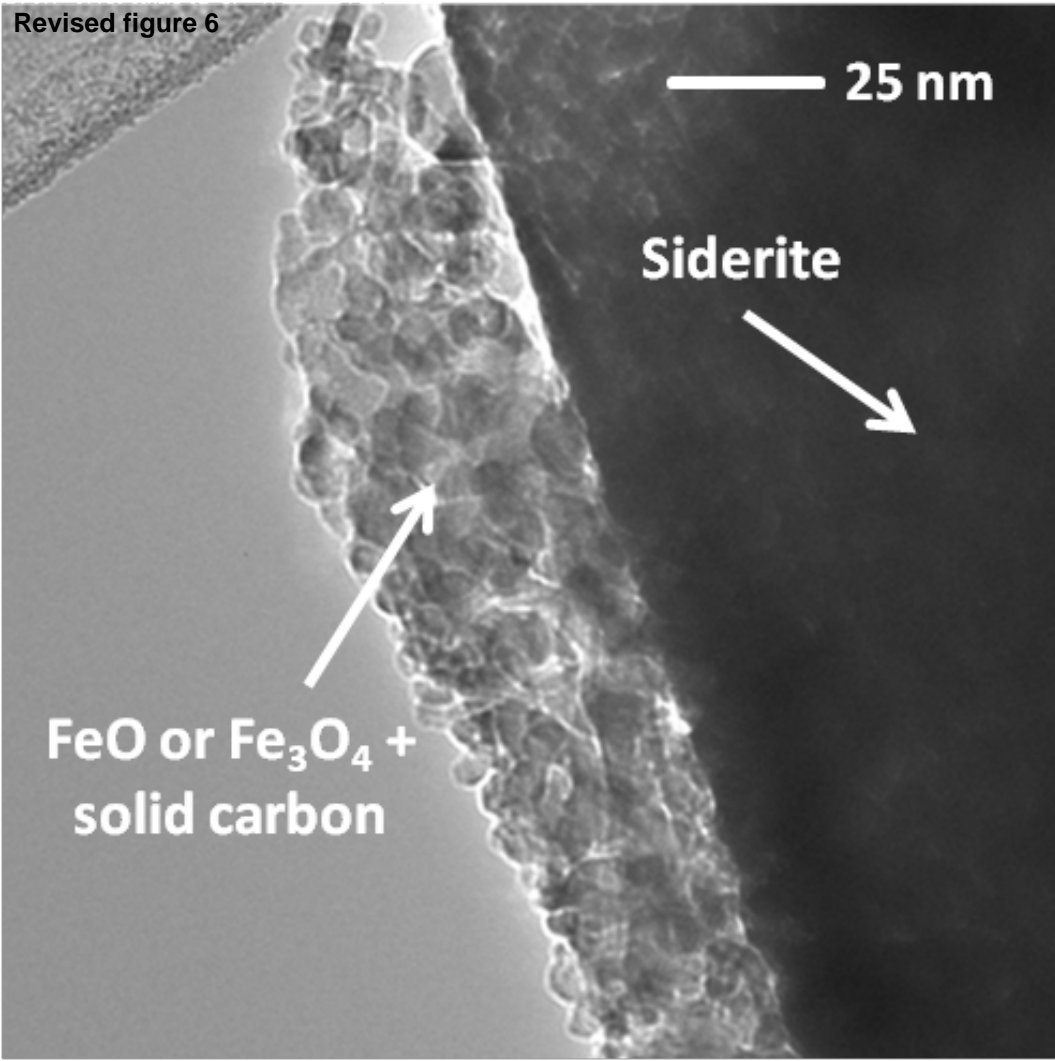
Sample
support film

C-rich phase



Revised figure 5





Revised figure 7

