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Influence of arsenic on iron sulfide transformations

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Published in *Chemical Geology*, 2007.

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ABSTRACT

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17

18 The association of arsenate, As(V), and arsenite, As(III), with disordered
19 mackinawite, FeS, was studied in sulfide-limited (Fe:S = 1:1) and excess-
20 sulfide (Fe:S = 1:2) batch experiments. In the absence of arsenic, the sulfide-
21 limited experiments produce disordered mackinawite while the excess-sulfide
22 experiments yield pyrite with trace amounts of mackinawite. With increasing
23 initially added As(V) concentrations the transformation of FeS to mackinawite
24 and pyrite is retarded. At S:As = 1:1 and 2:1, elemental sulfur and green rust
25 are the end products. As(V) oxidizes S(-II) in FeS and (or) in solution to S(0),
26 and Fe(II) in the solid phase to Fe(III). Increasing initially added As(III)
27 concentrations inhibit the transformation of FeS to mackinawite and pyrite and
28 no oxidation products of FeS or sulfide, other than pyrite, were observed. At
29 low arsenic concentrations, sorption onto the FeS surface may be the reaction
30 controlling the uptake of arsenic into the solid phase. Inhibition of iron(II)
31 sulfide transformations due to arsenic sorption suggests that the sorption sites
32 are crucial not only as sorption sites, but also in iron(II) sulfide transformation
33 mechanisms.

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35 Keywords: iron sulfides, pyrite, arsenate, arsenite

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1. INTRODUCTION

39

40 During oxic to anoxic transitions, arsenic is released from dissolving iron
41 hydroxides into the surrounding pore water or groundwater. While many metals
42 form insoluble sulfides in sulfidic environments, arsenic is distinctive in being
43 relatively soluble at $\text{pH} > 5.5$, and is mobile over a wide range of redox
44 conditions (Smedley and Kinniburgh, 2002). Consequently, sorption onto
45 particulate phases is a crucial control on arsenic mobility (Mok and Wai, 1994),
46 especially iron (II) sulfides, which are ubiquitous in anoxic sulfidic settings. At
47 present, there are limited published data concerning the influence of arsenic
48 during iron sulfide mineral transformations at ambient temperatures.

49

50 Pyrite, the most stable iron(II) sulfide phase in the Earth's surface environment,
51 can incorporate large amounts of arsenic (Huerta-Diaz and Morse, 1992;
52 Morse and Luther, 1999), retarding arsenic migration in anoxic environments.
53 Huerta-Diaz and Morse (1992) found arsenic concentrations in marine
54 sedimentary pyrite of up to 0.93 wt.%, as inferred from sequential extractions.
55 Their results indicated that pyrite is an important arsenic sink, even if only
56 minor pyrite formation has taken place.

57

58 Arsenic sorption onto metal oxides has been examined intensively (e.g. Pierce
59 and Moore, 1982; Waychunas et al., 1996; Fendorf et al., 1997; Hiemstra and

60 Van Riemsdijk, 1999; Swedlund and Webster, 1999; Ding et al., 2000). By
61 contrast, relatively few studies of arsenic sorption onto Fe(II) sulfides exist
62 (Farquhar et al., 2002; Bostick and Fendorf, 2003). Farquhar et al. (2002)
63 investigated the mechanisms of aqueous As(III) and As(V) (pH 5.5–6.5)
64 interaction with crystalline mackinawite (tetragonal FeS) and pyrite (FeS₂)
65 surfaces using As *K*-edge XAS. At low As(V) and As(III) concentrations, they
66 observed similar surface complex structures for both As species.. At higher
67 As(V) and As(III) concentrations, Farquhar et al. (2002) observed the
68 formation of different surface complexes along with poorly crystalline arsenic
69 sulfide. Bostick and Fendorf (2003) studied reactions of As(III) with troilite
70 (hexagonal FeS) and pyrite surfaces. At low pH and low As(III) concentrations,
71 Langmuir–type isotherms were obtained, although XAS analyses indicated
72 surface precipitates at all arsenic concentrations. Their data showed As(III)
73 reduction and a structural environment similar to As in arsenopyrite (FeAsS).
74 Although H₃AsO₃⁰ or H₂AsO₃⁻ dominated the aqueous As(III) speciation in
75 their experiments (pH 3-11), they observed a pH-dependence typical of cation
76 sorption (e.g. Stumm, 1991) i.e. sorption increased with pH. They explained
77 this behavior by the formation of ferrihydrite associated with FeAsS
78 precipitation.

79

80 The mineralogy of solid phase arsenic in sediments has been mostly inferred
81 from indirect measurements using selective chemical extraction (cf. Huerta–
82 Diaz and Morse, 1992), and so structural information on arsenic incorporation

83 into pyrite is absent and results may be biased (Wilkin and Ford, 2002). By
84 contrast, hydrothermal arsenian pyrites have been studied in detail. From XAS
85 studies, it was proposed that arsenic substitutes for sulfur in pyrite (Tingle et
86 al., 1996; Savage et al., 2000; Bennet and Benning, 2004). The arsenic
87 concentration in arsenian pyrite studied by Savage et al. (2000) was on average
88 1.2 wt.%, with a range from ~0 to 5 wt.%. These concentrations were
89 insufficient to cause local structural transformation of pyrite to arsenopyrite,
90 although lattice deviations from pyrite towards the orthorhombic structure of
91 arsenopyrite were observed (Savage et al., 2000).

92

93 Wolthers et al. (2005 a) synthesized pyrite in the presence of aqueous arsenite
94 at conditions and concentrations approaching those in ambient environments, in
95 a continuous-flow reaction system at pH 6 and 25°C. They observed no
96 unequivocal effect of As(III) on the amount of pyrite or on the textures formed.
97 Pyrite growth in these experiments resulted in a continued uptake and
98 incorporation of arsenic, implying the formation of a stable arsenic sink, which
99 would only release incorporated arsenic during oxidative dissolution. At
100 ambient temperatures, pyrite may form via several pathways (cf. Rickard,
101 1975; Luther, 1991; Rickard and Luther, 1997), with iron(II) monosulfide, FeS,
102 being the initial precipitate for kinetic reasons (cf. Rickard, 1969; Schoonen
103 and Barnes, 1991). Wolthers et al. (2003) have shown that the first FeS
104 precipitate is nanoparticulate mackinawite with an average primary particle size
105 of ~ 5 nm. Ofhuji and Rickard (2006), confirmed this using high resolution

106 transmission electron microscopy (TEM). In the literature, this material has
107 been variously referred to as FeS, amorphous FeS (FeS_{am}) and disordered
108 mackinawite. The characteristic broad, low-intensity Bragg peaks associated
109 with X-ray powder diffraction of this material are a consequence of its
110 nanoparticulate size and an expanded lattice relative to crystalline mackinawite.
111 Herein we refer to this material as FeS. The hydrated FeS surface was
112 described by strongly acidic mono-coordinated, and weakly acidic tri-
113 coordinated sulfur sites as the reactive sites within a surface chemistry model
114 (Wolthers et al., 2005 b). This model has subsequently been applied to As(V)
115 and As(III) sorption onto FeS (Wolthers et al., 2005c). Analogous to pyrite,
116 FeS has been recognized as a scavenger of trace elements in anoxic
117 environments (Kornicker, 1988; Morse and Arakaki, 1993; Arakaki and Morse,
118 1993; Morse and Luther, 1999; Watson et al., 2000; Wharton et al., 2000).

119

120 In this study, batch experimental techniques were used to study the behavior
121 and influence of As(V) and As(III) at various concentrations during the
122 transformation of FeS to mackinawite and the reaction of FeS to form pyrite.
123 The arsenic concentrations were chosen to cover the range from natural arsenic
124 concentrations in anoxic sulfidic environments to arsenopyrite stoichiometry.
125 The results are interpreted and discussed in terms of arsenic uptake
126 mechanisms, redox reactions and the effect of arsenic uptake on iron(II) sulfide
127 transformation mechanisms.

128

128

129

2. MATERIALS AND METHODS

130

131 2.1. Materials

132

133 All reagents were analytical grade and used without further purification.

134 Solutions were prepared in 18 MΩ distilled deionized water which was sparged

135 for 60 minutes with O₂-free grade N₂ (O₂ < 1ppm). O₂-free N₂ was scrubbed

136 with pyrogallol to remove traces of O₂. A 0.01 M pH 6.00 ± 0.01 tri-sodium

137 citrate pH-buffer solution was used as the reaction matrix solution and was

138 purged for 60 minutes with O₂-free N₂ gas before use. The initial reaction

139 redox potential was poised with Ti(III) citrate solution (Zehnder and Wuhrman,

140 1976). Addition of 2 mL Ti(III) citrate solution poised the initial reaction redox

141 potential below -400 mV (cf. Zehnder and Wuhrman, 1976; Rickard, 1997).

142 However, over the course of the experiment, the redox potential was likely to

143 be controlled by the S(-II)/S(0) (in excess sulfide experiments), the

144 Fe(II)/Fe(III) (in sulfide limited experiments) and, at high arsenic

145 concentrations, possibly by the As(V)/As(III) redox couples.

146

147 Freeze-dried FeS reactant was prepared by mixing 100 mL Fe(II) solution (0.6

148 M Fe(NH₄)₂(SO₄)₂·4H₂O) with 100 mL S(-II) solution (0.6 M Na₂S·9H₂O)

149 under N₂(g), filtering the suspension within minutes after mixing on a

150 WhatmanTM No.1 filter, and freeze drying the product for 3 to 4 days.
151 Effectively, the freeze-dried FeS has aged for less than half an hour (cf.
152 Wolthers et al., 2003). After freeze drying, the FeS was stored under an N₂
153 atmosphere at -18°C before use.

154

155 As(III) and As(V) solutions were prepared fresh for each batch of experiments
156 by dissolving Na₂AsO₂ and Na₂HAsO₄·7H₂O in purged 18 MΩ water while
157 constantly purging with O₂-free N₂.

158

159 **2.2. Batch experimental method**

160

161 The batch reactions were performed following the method of Rickard (1997)
162 and Butler and Rickard (2000). Under an N₂ atmosphere in a glove box, 0.40 g
163 of freeze-dried FeS was weighed into in 100-mL long-necked pyrex ampoules.
164 Subsequently, the ampoules were filled with 2 mL Ti(III) citrate, 10 mL arsenic
165 solution, and 40 mL of pH-buffer solution. The reaction ampoule was then
166 attached to a gas transfer manifold.

167

168 The manifold and it's operation are described by Rickard (1997). It permits
169 gases to be added and extracted from the reaction ampoules under strictly O₂-
170 free conditions. After attachment to the manifold, the reaction ampoules were
171 evacuated and flushed with O₂-free N₂ three times. The third time, the vessel

172 was either filled with N₂ to slightly less than atmospheric pressure (sulfide-
173 limited experiments 1a to 1e and 3a to 3e, Tables 1 and 2) or filled with N₂,
174 evacuated and filled with an H₂S/N₂ gas mixture to atmospheric pressure
175 (excess-sulfide experiments 3a to 3e and 4a to 4e, Tables 1 and 2). H₂S was
176 generated by acid decomposition of Na₂S•9H₂O in serum bottles as described
177 by Rickard (1997). Finally, the reaction ampoule was hermetically sealed with
178 a glass-blowers torch and the ampoule was detached from the manifold. The
179 ampoules were fitted to an orbital shaker in an oven at 25°C. The orbital shaker
180 was set to ~300 rpm, which was sufficient to keep the solids in suspension, and
181 the experiments were run for four weeks.

182

183 At the end of the experiments, the ampoule neck was broken and the solid
184 products collected on a 0.02 µm Millipore™ filter under flowing N₂. The solid
185 product was freeze-dried for ~24 hrs and stored under an N₂ atmosphere at
186 -18°C before analysis. The supernatant pH was measured using an Orion™
187 Ross combination glass pH electrode. A 5 mL sample of the supernatant was
188 stored in a sealed glass vial at 4°C until acidification and analysis.

189

189

190 **2.3. Analysis**

191

192 *2.3.1. Solution analysis*

193

194 Supernatant samples were analyzed for total dissolved arsenic using a Perkin
195 Elmer™ Elan 5000 inductively coupled plasma (ICP) mass spectrometer. The
196 detection limit was 6.5×10^{-9} M, taken as the average blank plus five times its
197 standard deviation. The matrix used for As analyses was 2% HNO₃. Total
198 dissolved iron was measured using a Varian Spectra 300 acetylene–air–flame
199 atomic absorption spectrometer. Since citric acid has been reported to suppress
200 the absorbance by iron up to 50% (Roos and Price, 1971), calibration solutions
201 were made using the tri-sodium citrate pH-buffer solution and were acidified
202 similar to the supernatant samples. The detection limit was 7.4×10^{-9} M, taken
203 as the average blank plus five times its standard deviation.

204

205 *2.3.2. Solid phase characterization*

206

207 XRPD was carried out using a Philips™ PW170 diffractometer (CuK α
208 radiation, 35 kV, 40 mA). Approximately 50 mg of freeze-dried FeS was
209 dispersed in acetone and loaded onto a glass slide under an N₂ atmosphere
210 within a glove-box. XRPD patterns, in the range of 3–80° 2 θ , were collected

211 under air using the following settings: 0.1 mm receiving slit, 0.4 s/0.02° 2θ
212 counting time. A conservative estimate of the detection limit for crystalline
213 phases is ~10%. Characterization of the patterns was performed using the
214 JCPDS library.

215

216 TEM images, selected-area electron diffraction patterns (SAED) and energy-
217 dispersive X-ray (EDX) analyses of freeze-dried FeS were collected on a
218 Philips™ CM200 FEG-TEM (200 kV). Approximately 0.5 mg of solid sample
219 dispersed in acetone was quickly loaded in air onto a carbon-coated copper grid
220 and loaded into a low-background specimen microscope holder. Since the
221 particles may be smaller than the interaction volume of the 200 kV electron
222 beam and since no calibration could be done, the EDX data were used
223 qualitatively; the estimated detection limit is 1 wt.% for As. SAED patterns and
224 TEM images were recorded photographically. In the SAED patterns, reciprocal
225 lattice distances were measured manually and converted to lattice *d*-spacings
226 according to $d = L\lambda R^{-1}$; where *L* is the camera or diffraction length of 0.92 m, λ
227 is 2.508×10^{-12} m and *R* is the measured lattice distance (Grundy and Jones,
228 1976).

229

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230

231

3. RESULTS AND DISCUSSION

232

233 Two sets of batch experiments were performed: (i) freeze-dried FeS was
234 reacted with 10^{-7} to 10^{-1} M solutions of As(V) and As(III), and (ii) freeze-dried
235 FeS was reacted with 10^{-7} to 10^{-1} M solutions of As(V) and As(III) and with
236 $\text{H}_2\text{S}_{(\text{aq})}$. The first set of experiments, with an Fe(II) to S(-II) ratio of 1:1, are
237 referred to as the *sulfide-limited experiments* and have experiment numbers 1a
238 to 1e, and 3a to 3e (Tables 1 and 2). The second set of experiments, with an
239 Fe(II) to S(-II) ratio of approximately 1:2, are referred to as the *excess-sulfide*
240 *experiments* and have experiment numbers 2a to 2e, and 4a to 4e (Tables 1 and
241 2).

242

243 3.1. As(V)

244

245 The supernatant analysis results are listed in Table 1. The amount of arsenic
246 associated with the solid phase, $[\text{As}]_s$, was calculated by difference between the
247 amount of As(V) initially added, $[\text{As(V)}]_0$, and the concentration measured in
248 the supernatant at the end of the experiments, $[\text{As}]_{\text{aq}}$. As can be seen in Table 1,
249 $[\text{As}]_s$ in the sulfide-limited and excess-sulfide experiments is similar and
250 decreased with decreasing $[\text{As(V)}]_0$.

251

252 Typical XRPD patterns for the experiments with different $[\text{As(V)}]_0$ are shown
253 in Figure 1. A summary of the XRPD results is listed in Table 3. The color of
254 the solid end products changed with increasing $[\text{As(V)}]_0$ from black to grayish-
255 green in the sulfide-limited experiments (1d to 1a; Table 1), and from grayish-
256 black to yellowish-green in the excess-sulfide experiments (2d to 2a; Table 1).
257 This is generally consistent with the results from the XRPD observations. In
258 experiment 1a, the black FeS was replaced by elemental sulfur (white, orange)
259 and green rust (Fig.1a). The yellow color observed may have been caused by
260 arsenic sulfide precipitation (O'Day et al., 2004), however, this was not
261 observed in the XRPD data. Similarly, in experiment 2a, the grayish-black
262 pyrite and black FeS was replaced by elemental sulfur and green rust (Fig. 1b).
263 It can be concluded from these observations that, at $[\text{As(V)}]_0 > 10^{-3}$ M, iron(II)
264 sulfides are oxidized to elemental sulfur and Fe(III). At these high arsenate
265 concentrations, an increase in iron concentration of two orders of magnitude
266 was found (Table 1). This may be explained by a higher solubility of green rust
267 (e.g. Bourrie et al., 1999) compared to FeS (e.g. Wolthers et al., 2005 b).
268 Alternatively, increasing arsenic-sulfide complexation may have resulted in
269 less sulfide being available to react with iron.

270

271 Detailed examination of the iron(II) sulfides from experiments 1d and 2d
272 (Table 1) was conducted using TEM (Fig. 2). Multiple particles, representative
273 of the solid end products formed, were imaged. Figure 2a shows an example of
274 a rectangular particle from experiment 1d (Table 1). EDX measurement of this

275 particle yielded an Fe:S intensity ratio of ~ 0.99 , calculated from the peak
276 surface areas in the spectra. The SAED pattern (Fig. 2b) is consistent with
277 crystalline mackinawite. Figure 2c shows a crystalline particle formed in
278 experiment 2d (Table 1). EDX measurement yielded an Fe:S ratio of ~ 0.67 .
279 The SAED pattern (Fig. 2d) is consistent with pyrite. The imaging, SAED and
280 EDX analyses are consistent with the XRPD observations. For all particles
281 from experiments 1d and 2d, As was below the detection limit of the EDX
282 analyses.

283

284 Savage et al. (2000) performed a TEM study on hydrothermal pyrite with 1.36–
285 1.67 wt.% arsenic and observed arsenic-rich lamellae which, in the SAED
286 pattern, showed lattice deviations from the cubic symmetry of pyrite towards
287 the orthorhombic marcasite-type structure of arsenopyrite. An estimate of the
288 As concentration in the pyrite, assuming all of the solid-phase As is present in
289 pyrite and that $\sim 60\%$ wt% of the total solid phase is pyrite, yielded an As
290 concentration in the ppb (that is, less than 10^{-4} wt.%) range. This explains the
291 absence of both the lattice deviations in the SAED pattern (Fig. 2d) and the As
292 peaks in the EDX spectra.

293

294

294

295 **3.2. As(III)**

296

297 The amount of As(III) associated with the solid phase from the sulfide-limited
298 and the excess-sulfide experiments was similar (Table 2). It decreased with
299 decreasing amounts of As(III) initially added. These results show the same
300 trends as the As(V) results (Table 1). In contrast, the total dissolved iron results
301 for the As(III) experiments (Table 2) differed from the As(V) experiments
302 (Table 1). With increasing $[\text{As(III)}]_0$, the iron concentration increased by one to
303 two orders of magnitude before decreasing at the highest $[\text{As(III)}]_0$. An
304 explanation for this trend might be that at high As(III) concentrations the
305 dissolution of FeS is inhibited. Alternatively, increasing arsenic-sulfide
306 complexation may again have resulted in less sulfide being available to react
307 with iron.

308

309 Figure 3 shows XRPD patterns for the reaction of As(III) in sulfide-limited
310 (Fig. 3a) and excess-sulfide (Fig. 3b) experiments. A summary of the XRPD
311 results is listed in Table 3. With increasing $[\text{As(III)}]_0$, the color of the solid end
312 products did not significantly change from black or grayish black, consistent
313 with the XRPD observations. Figure 3a shows the broad Bragg peaks of
314 disordered mackinawite at the lowest $[\text{As(III)}]_0$ (spectrum 3d) and no change in
315 the diffraction pattern with increasing $[\text{As(III)}]_0$. At the highest $[\text{As(III)}]_0$, a
316 slight increase in diffraction intensity may have been caused by a more optimal

317 sample loading on the glass slide. All patterns are consistent with FeS
318 (Wolthers et al., 2003). In Figure 3b, the diffraction intensity of the iron(II)
319 sulfides weakens relative to the blank pattern with increasing $[\text{As(III)}]_0$. At the
320 highest $[\text{As(III)}]_0$ (9.1×10^{-2} M; spectrum 4a), only weakened and broadened
321 FeS Bragg peaks remain. Apparently, pyrite formation was inhibited in the
322 excess sulfide experiments. Implications of these results for pyrite formation
323 pathways are discussed in section 4.1.2.

324

325 TEM was used to examine iron(II) sulfides from experiments 3c (9.0×10^{-7} M;
326 Fig. 4a) and 4c (9.0×10^{-7} M; Fig. 4c). Multiple particles, representative of the
327 solid end products formed, were imaged. EDX measurement of the solid
328 formed in experiment 3c yielded an Fe:S ratio of 0.85, and the SAED pattern
329 (Fig. 4b) showed diffraction rings, indicating an amorphous or nanoparticulate
330 material (e.g. Ohfuji and Rickard, 2006), in agreement with the XRPD
331 observations. For all particles analyzed from experiments 3c and 4c, the As
332 concentration was below the EDX detection limit. In future studies on As
333 interactions with Fe(II) sulfides, more sensitive analyses, also analyzing for As
334 speciation, and higher resolution imaging techniques could further clarify the
335 influence of As on iron sulfide mineral transformations, in particular for
336 As(III).

337

337

338 **3.3. Arsenic uptake**

339

340 The solid phase As concentration in the end product of the As(V) experiments
341 was independent of excess H₂S (Table 1), suggesting that pyrite formation was
342 not responsible for extra uptake of As(V). Thus, the uptake of As(V) may be
343 controlled by the FeS reactant. Wolthers et al. (2005c) studied the sorption of
344 As(V) onto FeS. They showed that As(V) sorption onto FeS at pH 7.5 can be
345 described with the following Freundlich equation (solid line in Fig. 5a):

$$(1) \quad [\text{As(V)}]_{\text{ads}} = 0.021[\text{As(V)}]_{\text{aq}}^{0.90}$$

346 where $[\text{As(V)}]_{\text{ads}}$ is adsorbed As(V) in mol g⁻¹ FeS, and $[\text{As(V)}]_{\text{aq}}$ is the
347 aqueous As(V) concentration in M. Their data and the Freundlich equation are
348 plotted in Figure 5a.

349 To test if As(V) uptake by the solid phase in the present experiments is
350 controlled by sorption onto FeS, the data for $[\text{As(V)}]_{\text{s}}$ and $[\text{As(V)}]_{\text{aq}}$ (Table 1)
351 were plotted in the isotherm graph (Fig. 5a). The data for $[\text{As(V)}]_0 < 1 \times 10^{-3}$
352 M plot close to the Freundlich isotherm for the sorption data. It might be
353 concluded from this agreement that As(V) sorption onto FeS controlled As
354 uptake into the solid phase in the experiments. Alternatively, co-precipitation
355 may be occurring, governed by adsorption to a growing surface. The data for
356 $[\text{As(V)}]_0 \approx 9 \times 10^{-2}$ M plot below the Freundlich isotherm; at the same amount
357 of arsenic in the solid, more arsenic was in the aqueous phase than described by
358 equation (1). So, for these experiments, it can not be concluded if sorption onto

359 FeS was the uptake mechanism for arsenic into the solid. This is in agreement
360 with the XRPD data which showed that all Fe(II) sulfides had been oxidized to
361 elemental sulfur and green rust in these experiments.

362

363 Similar to the As(V) experiments, the amount of arsenic associated with the
364 solid phase product of the As(III) experiments appeared independent of excess
365 sulfide (Table 2). To test if the uptake of As(III) was controlled by the freeze-
366 dried FeS reactant, the data from the experiments 3a, 3b, 4a, and 4b (Table 2)
367 were plotted on a sorption isotherm graph (Fig. 5b) with the data for As(III)
368 sorption onto FeS (Wolthers et al., 2005c). The sorption data were previously
369 described by the following Freundlich equation (solid line in Fig. 5b):

$$(2) \quad [\text{As(III)}]_{\text{ads}} = 0.026[\text{As(III)}]_{\text{aq}}^{0.98}$$

370 where $[\text{As}]_{\text{ads}}$ is the amount of sorbed As(III) in mol g⁻¹ FeS and $[\text{As}]_{\text{aq}}$ is the
371 dissolved As(III) concentration in M (Wolthers et al., 2005c). The data from
372 experiment 4b (excess-sulfide, $[\text{As(III)}]_0 = 4.5 \times 10^{-4}$ M) plot close to the
373 sorption isotherm (equation 2), which may mean that arsenite sorption onto FeS
374 is the pathway for uptake into the solid phase. However, the other data plot
375 below the isotherm. This indicates that, for these experiments, sorption onto
376 FeS surface was probably not the controlling uptake mechanism for arsenic.
377 However, the XRPD spectra show the presence of FeS, and no other solid. So,
378 from these result, no conclusions can be drawn regarding possible pathways of
379 As(III) uptake.

380

381 **3.4. Redox reactions**

382

383 In the As(V) experiments, the XRPD results showed the oxidation of S(-II) and
384 Fe(II). Bostick and Fendorf (2003) suggested a redox reaction for arsenite with
385 FeS, in which ferrihydrite and pyrite are formed. Hence, this reaction is only
386 favorable at sufficiently basic conditions, where ferrihydrite would be stable.
387 While a mechanism for iron(II) sulfide oxidation by As(V) or As(III) at more
388 acidic conditions has not been previously reported, it might be discussed based
389 on the existing literature for the mechanism of S(-II) oxidation by As(V) in the
390 aqueous phase (Rochette et al., 2000) and XAS data for As(V) and As(III)
391 sorption and coprecipitation onto mackinawite (Farquhar et al., 2002). Rochette
392 et al. (2000) have studied the rate and mechanism of As(V) reduction by S(-II)
393 at pH 4 and a sulfide to arsenate ratio similar to experiment 1a (Table 1). They
394 described the reduction to occur the formation of thioarsenite and subsequent
395 reduction to thioarsenite by release of S(0). Dithioarsenate and thioarsenite
396 complexes at the surface of mackinawite may have been observed by Farquhar
397 et al. (2002). Their coprecipitation experiments with a sulfide to arsenate ratio
398 similar to experiment 2a (Table 1), resulted in arsenic coordinated to 2.5
399 oxygen atoms in the first shell at 0.170 nm, to 1.5 sulfur atoms in the second
400 shell at 0.233 nm and four arsenic atoms in the third shell at 0.335 nm. This can
401 be explained by a mixture of thioarsenate and dithioarsenate species at the
402 mackinawite surface. In their experiments with a sulfide to arsenite ratio

403 comparable with experiment 4a (Table 2), the observed arsenic coordination at
404 the surface of mackinawite can be explained as a dithioarsenite species.

405

406 A similar mechanism for As(V) reduction in the present, slightly acidic (pH 6),
407 FeS-system can be envisaged, either in solution or at the surface of FeS or
408 pyrite. Elemental-sulfur formation, and the absence of ferrihydrite formation, in
409 the present experiments, as observed in the XRPD analyses (Figure 1), would
410 be in support of a mechanism like the one proposed by Rochette et al. (2000).

411

411

412 **3.5. Limitations**

413

414 At initiation of the experiments, reactants, buffers and poises were mixed, the
415 ampoule was sealed and, after four weeks, the solid end products and the
416 supernatant were analyzed. No information about intermediate reaction
417 conditions or products could be collected. After poisoning the initial Eh, the
418 oxidation–reduction potential in the system likely changed during the
419 experiments, as was discussed in section 2.1. Furthermore, the concentration
420 and thus distribution of all species varied strongly over the course of an
421 experiment and, consequently, the ionic strength and mineral saturation states
422 co-varied. Estimating the ionic strength, I , at the start and end of the As(V)
423 experiments, by assuming that aqueous species are not complexed, showed
424 variations of $0.06 < I < 0.08$ M in the highest $[\text{As(V)}]_0$ experiments and $I \approx$
425 0.015 M in the other As(V) experiments. In the As(III) experiments, higher I 's
426 were caused by the increase in dissolved iron: $0.106 < I < 0.107$ M at highest
427 $[\text{As(III)}]_0$, and I decreases with decreasing $[\text{As(III)}]_0$ concentration to $I \approx 0.015$
428 M.

429

429

430

4. IMPLICATIONS

431

432 **4.1. Iron(II) sulfide transformations**

433

434 *4.1.1. Ageing of FeS to mackinawite*

435

436 FeS ages to mackinawite (Berner, 1964; Rickard, 1989; Lennie and Vaughan,
437 1996; Benning et al., 2000) and this ageing is observed in the blank
438 experiments with excess sulfide (2e and 4e, Tables 1 and 2). However, in all
439 other experiments, this ageing was not observed. For hydrous ferric oxides,
440 As(V) sorption has been found to stabilize the solid with respect to
441 transformations to more stable crystalline phases due to the modification of the
442 local environment of the iron in the solid (Waychunas et al., 1996; Rancourt et
443 al., 2001). For iron(II) disulfide surfaces, sorption of protons has been reported
444 to distort the S geometry around Fe, causing the pH dependent formation of
445 marcasite in preference to stable pyrite (Tossell et al., 1981). Analogously,
446 Lennie and Vaughan (1996) proposed the pH dependent occurrence of cubic
447 FeS and troilite by interaction of surface bound protons with the electronic
448 structure in the solid. Possibly, sorption of As(V) and As(III) influences the
449 electronic structure of FeS, preventing the ageing of FeS to mackinawite.
450 Alternatively, the sorption of As(V) and As(III) may influence the ageing of
451 FeS to mackinawite by blocking reactive surface sites or through co-

452 precipitation on the FeS surface that are important in the ageing of FeS to
453 mackinawite, resulting in an inhibition of the recrystallisation or of the stacking
454 of nanoparticulate FeS to form mackinawite.

455

456 *4.1.2. The mechanism of pyrite formation*

457

458 In experiments without As, mackinawite and pyrite were readily formed,
459 similarly to Rickard (1997), Benning et al. (2000), and Butler and Rickard
460 (2000). The rate of pyrite formation in this type of experiment is dependent
461 upon the sulfide activity and the FeS concentration (Butler and Rickard, 2000).
462 Progressive increases in As concentration caused the reaction product to
463 deviate from the blank result (Table 3). Therefore, As retards and inhibits
464 pyrite formation.

465

466 Wolthers et al. (2005 a) observed no unequivocal effect of As(III) at a
467 concentration of $\sim 10^{-7}$ M (comparable to experiment 4c, Table 2) on the
468 amount of pyrite or on the textures formed in chemostated experiments. At a
469 similar arsenite concentration (experiment 4c, Table 2), pyrite was formed,
470 albeit less than in the blank experiment (4e, Figure 3). In their chemostated
471 experiments, the controlled conditions were less supersaturated with respect to
472 pyrite than the present experimental conditions and a seed crystal was present
473 to facilitate nucleation. So, while pyrite formation in the present experiments
474 was nucleation dominated (Butler and Rickard, 2000), pyrite formation in the

475 chemostated experiments was dominated by crystal growth. Apparently, low
476 concentrations of As(III) do not affect continued pyrite growth but can affect
477 pyrite formation when no seed crystals are present.

478

479 Previously postulated pyrite formation mechanisms in aqueous solutions at
480 ambient temperatures involve a dissolved stage (Rickard, 1975; Luther 1991;
481 Rickard and Luther, 1997). Any process that affects the dissolved intermediates
482 or the solubility of the disordered mackinawite reactant, will also affect the
483 pyrite formation kinetics. This has been reported by Rickard et al. (2001), who
484 showed that RCH=O in trace amounts inhibits pyrite formation by attacking, or
485 preventing the formation of, $\text{FeS}_{(\text{aq})}$. Similarly, As(V) and As(III) may affect
486 the pyrite forming mechanism. For example, the reactivity of the FeS surface
487 will be changed by As(V) or As(III) sorption. Moreover, possibly the labile
488 $\text{FeS}_{(\text{aq})}$ cluster complex reacts rapidly (Rickard, 1997) with As(V) or As(III)
489 near the FeS surface to form arsenic-sulfide complexes (see section 3.4) or
490 iron(II)-sulfide-arsenic complexes. This would lower the sulfide activity and
491 could inhibit pyrite formation. Likewise, As(V) and As(III) sorption onto the
492 reactant FeS surface may affect pyrite formation by decreasing the solubility of
493 the reactant FeS, and, in the case of As(V), by oxidation of FeS. If the surface
494 of the precursor is modified, and the $\text{FeS}_{(\text{aq})}$ cluster complex is attacked or its
495 formation is inhibited, then the rate of pyrite formation is expected to be
496 reduced.

497

498 **4.2. Arsenic mobility in the anoxic environment**

499

500 At natural levels of aqueous arsenic, 0.02–4.01 μM (Widerlund and Ingri,
501 1995; Sullivan and Aller, 1996; Yan et al., 2000; comparable to our experiment
502 numbers 1d, 2d, 3 and 4), arsenic uptake by a mixture of the environmentally
503 most-abundant iron(II) sulfides seems to be controlled by the most reactive
504 solid phase, FeS (Fig. 5). This uptake can be described using sorption isotherm
505 notations, as was discussed by Wolthers et al. (2005c). Such isotherm data can
506 be used in arsenic transport modeling, to predict the mobility and
507 immobilization of arsenic in the anoxic sulfidic environment. Furthermore,
508 results from this study suggest that the transformation of the precursor FeS to
509 the most stable and ubiquitous iron(II) sulfide pyrite is retarded by As(V) and
510 As(III) sorption, even at natural levels of aqueous arsenic. In this way, possibly
511 depending on the degree of pyrite supersaturation, arsenic sorption may retard
512 the rate of formation of a relatively more stable natural As sink, with
513 implications for the medium term mobility of As in natural environments.

514

515 *Acknowledgements:* We gratefully acknowledge Anthony Oldroyd for his
516 assistance with the experiments and XRPD measurements, Sarah Goldsmith for
517 performing the ICP–MS analyses, Colin Lewis for conducting the AAS
518 measurements and Herman van Roermund for his assistance with the TEM.
519 Cornelis H. van der Weijden (Utrecht University) and Peter van der Linde
520 (University of Professional Education Leiden) provided insightful discussions

521 over the course of this study. R. Wilkin (U.S. E.P.A) made valuable critical
522 comments on an earlier version of this manuscript. This research was supported
523 by the Netherlands Organization of Scientific Research (NWO/ALW grant
524 750.197.06 to M.W) and by NERC grant NRE/L/S/2000/00611 to D.R. This
525 research was conducted under the program of the Netherlands Research School
526 of Sedimentary Geology.

527

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661

662

663 FIGURE CAPTIONS

664

665 **Figure 1.** XRPD patterns at the same arbitrary scale for the end products of the reactions of
666 various $[\text{As(V)}]_0$ in (a) the sulfide-limited and (b) the excess-sulfide experiments. Spectrum
667 labels refer to experiment numbers as listed in Tables 1 and 3. Py labels indicate 2θ -values for
668 diffraction by pyrite (JCPDS file 06–0710), Mk for mackinawite (JCPDS file 15–0037), FeS
669 for disordered mackinawite (Wolthers et al., 2003), S for elemental sulfur (JCPDS file 08–
670 0247) and G for green rust (JCPDS file 13–0092).

671

672 **Figure 2.** (a) TEM image of a mackinawite crystal from experiment 1d (Table 1). The Fe:S
673 ratio of this material determined by EDX analysis was 0.99. (b) SAED pattern obtained from
674 the crystal in (a) parallel to (001); $a^* \text{ Mk}$ and $b^* \text{ Mk}$ are the translation vectors in reciprocal
675 lattice which correspond to tetragonal-lattice parameters a and b for mackinawite and 020,
676 220 and 200 points in the reciprocal lattice refer to the (hkl) planes in mackinawite. (c) TEM
677 image of a pyrite crystal from experiment 2d (Table 1). The Fe:S ratio of this material
678 determined by EDX analysis was 0.67. (d) SAED pattern from the crystal in (c) parallel to
679 (001); $a_1^* \text{ Py}$ and $a_2^* \text{ Py}$ are the translation vectors in the reciprocal lattice which correspond
680 to cubic-lattice parameters a_1 and a_2 for pyrite and the 400, 440 and 040 points in the
681 reciprocal lattice refer to the (hkl) planes in pyrite.

682

683

684 **Figure 3.** XRPD patterns at the same arbitrary scale for batch-experiment end product from
685 the reactions at various $[\text{As(III)}]_0$ in (a) the sulfide-limited and (b) the excess-sulfide
686 experiments. Spectrum labels refer to experiment numbers as listed in Tables 2 and 3. Py
687 labels indicate 2θ -values for diffraction by pyrite (JCPDS file 06–0710), Mk for mackinawite
688 (JCPDS file 15–0037), and FeS for disordered mackinawite (Wolthers et al., 2003).

689

690

691 **Figure 4.** (a) TEM image and (b) SAED rings pattern for the FeS end product from
692 experiment 3c (Table 2). The Fe:S ratio of this material determined by EDX analysis was
693 0.85. (c) TEM image for the solid end product from experiment 4c (Table 2). The Fe:S ratio
694 of this aggregate was not determined, on average, the Fe:S ratio in end product, determined by
695 EDX analysis, was 1.2 ± 0.3 .

696

697 **Figure 5.** Sorption-isotherm graphs. **(a)** The As(V) data from experiments 1a to 1c (black
698 triangles; Table 1) and experiments 2a and 2b (grey triangles; Table 1) compared to the
699 sorption data for As(V) onto FeS at pH 7.5 (open triangles; data from Wolthers et al, 2005c).
700 The solid line is the Freundlich isotherm describing the sorption data (equation 1). **(b)** The
701 As(III) data from experiments 3a and 3b (black diamonds; Table 2) and experiments 4a and
702 4b (grey diamonds; Table 2) compared to the sorption data for As(III) onto FeS at pH 7.4
703 (open diamonds; data from Wolthers et al, 2005c). The solid line is the Freundlich isotherm
704 describing the sorption data (equation 2). N.B.: For the sorption data and Freundlich isotherm,
705 the $[\text{As(V)}]_{\text{ads}}$ and $[\text{As(III)}]_{\text{ads}}$ data are plotted on the same scale as $[\text{As}]_{\text{s}}$.