

The solubility of FeS

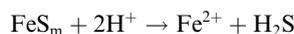
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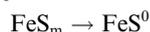
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Abstract

The solubility of FeS_m, synthetic nanoparticulate mackinawite, in aqueous solution was measured at 23 °C from pH 3–10 using an in situ precipitation and dissolution procedure and the solution species was investigated voltammetrically. The solubility is described by a pH-dependent reaction and a pH-independent reaction. The pH-dependent dissolution reaction can be described by



and $\log K_{\text{sp},1}^* = 3.5 \pm 0.25$ ($n = 84$). The pH-independent dissolution reaction involves the formation of the aqueous FeS cluster complex, FeS_{aq}, and can be represented by the intrinsic solubility



where FeS⁰ is a monomeric representation of the aqueous cluster complex, Fe_xS_x, and $\log K_0(\text{FeS}_m) = -5.7$. The overall process is described by the relationship

$$\log \sum [\text{Fe(II)}] = \log K_0(\text{FeS}_m) + \log K_{\text{sp},1}^* - \log \{\text{H}_2\text{S}\} - 2\text{pH},$$

where $\sum [\text{Fe(II)}]$ is the total dissolved Fe(II) concentration. The model closely describes the solubility of FeS_m at 23 °C for pH 3–10 and total dissolved S(-II) concentrations, $\sum [\text{S(-II)}] = 10^{-1}$ to 10^{-6} M. The results show that in neutral to alkaline environments with greater than micromolar $\sum [\text{S(-II)}]$, the total solubility of Fe(II) in equilibrium with FeS_m approaches 1 μM and the dominant species is FeS_{aq}. Relative to oxic ocean water, Fe(II) is transportable in solution at quite significant concentrations in sulfidic sediments in the presence of FeS_m. However, the availability of the hexaqua Fe(II) ion, which may be significant biologically, is correspondingly reduced in these environments although it dominates in all systems with $<10^{-6}$ M $\sum [\text{S(-II)}]$.

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1. Introduction

In 1967, R.A. Berner published a seminal paper on the thermodynamic stability of sedimentary iron sulfides. He measured the solubility of three phases, greigite (Fe₃S₄), mackinawite (tetragonal FeS_m) and precipitated FeS, a form which did not display a crystalline structure on contemporary XRD systems. His measurements showed that precipitated FeS was unstable with respect to mackinawite,

and that both mackinawite and greigite were metastable with respect to pyrite and pyrrhotite.

Berner's precipitated FeS has often been referred to as amorphous FeS, even though Berner (1967) correctly defined the material as poorly crystalline mackinawite rather than a true amorphous phase. Wolthers et al. (2003) showed that it consists of nanoparticulate mackinawite and it is referred to as FeS_m throughout this paper. Berner (1963, 1964) proposed that FeS_m was a key component in determining the concentrations of dissolved Fe(II) and S(-II) in sedimentary systems. FeS_m has been suggested to be a significant constituent of the acid volatile sulfide (AVS) component of sediments (Aller, 1977) and has been

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consequently been implicated in the simultaneously extracted metal-acid volatile sulfide (SEM-AVS) protocol for estimation of metal toxicity in anoxic aqueous environments (e.g., DiToro et al., 1990). FeS_m has been widely implicated in the global biogeochemical sulfur cycle (Goldhaber, 2004), sulfur isotopic systematics of anoxic sulfidic systems (e.g., Jørgensen et al., 2004) and as a precursor to the biogenic greigite of magnetotactic bacteria (Posfai et al., 1998).

Previous studies of the solubility of FeS_m have mainly concerned the reaction in acid solutions. The results have been shown to be consistent with the reaction



where

$$\log K_{\text{sp},1}^* = \log\{\text{Fe}^{2+}\} + \log\{\text{H}_2\text{S}_{\text{aq}}\} + 2\text{pH} \quad (2)$$

and $\{\}$ refers to activity, Fe^{2+} is shorthand for hexaqua Fe(II) and aq distinguishes the aqueous species. Since, S^{2-} has no significant concentration in most aqueous solutions, metal sulfide solubilities are conventionally represented by the bisulfide reaction

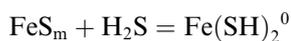


where

$$\log K_{\text{sp},2}^* = \log\{\text{Fe}^{2+}\} + \log\{\text{HS}^-\} + \text{pH} \quad (4)$$

Earlier measurements of $\log K_{\text{sp},2}^*$ are reviewed by Morse et al. (1987) and Davison (1991). Since that time, $\log K_{\text{sp},2}^*$ values of -3.00 ± 0.12 (20 °C, Davison et al., 1999), and -3.88 to -3.98 (25 °C, Benning et al., 2000) have been reported. The differences in $\log K_{\text{sp},2}^*$ are quite significant. In a solution at pH 5 and with $\{\text{H}_2\text{S}\} = 10^{-4}$, these solubility products define an $\{\text{Fe}^{2+}\}$ of $10^{-1.6}$ or 0.025 and $10^{-2.9}$ or 0.00125. The difference in the Fe^{2+} activity in the two measurements is a factor of about 20.

The solubility of FeS_m in the important environmental area above pH 6, is poorly understood. Wolthers et al. (2005) reported that the pH dependence of the dissolved Fe(II) activity is >-2 above pH 6 and therefore reaction (1) does not control the solubility. They reported a solubility constant of $10^{-2.13 \pm 0.27}$ between pH 6.5 and 8, suggesting that the solubility in this pH region was almost a magnitude greater than the value predicted from the Davison et al. (1999) measurements. Davison et al. (1999) found that at low H_2S_g partial pressures, ($p\text{H}_2\text{S}_g \leq 0.001$ MPa), the data fitted a single plot with a slope of -2 ; at $p\text{H}_2\text{S}_g = 0.1$ MPa the slope was found to be greater than -2 and approach 0. They interpreted their data in this pH range to suggest that solubility of FeS_m was dependent on $\{\text{HS}^-\}$. The system could then be modelled assuming that $\text{Fe}(\text{SH})_2^0$ was the dominant dissolved Fe(II) species with $\log \beta_2 = 6.45 \pm 0.12$ for the reaction



The situation is complicated by the discovery of aqueous FeS clusters (Buffle et al., 1988; Theberge and Luther, 1997). These species have modelled stoichiometries of $\text{Fe}_n\text{S}_n \cdot 4\text{H}_2\text{O}$ where $n = 2$ or 4 (Buffle et al., 1988; Theberge and Luther, 1997) and are herein referred to as FeS_{aq} . The important aspect of these species is that they are not protonated and their formation from FeS_m is pH-independent. Rickard and Luther (1997) and Theberge and Luther (1997) suggested that FeS_{aq} was a product of FeS_m dissolution and Wolthers et al. (2005) suggested that FeS_{aq} might control the dissolution in alkaline solutions.

The significance of these results is that neither the value nor the process controlling the solubility of FeS_m , in the important environmental pH range of 6–8.5, is well constrained. As shown by Davison et al. (1999) and Wolthers et al. (2005), the extrapolation of the process described for acid pH values is wrong, since the process changes—possibly due to a more-or-less pH independent mechanism. The purpose of this paper is to report the results of an experimental investigation into the solubility of FeS_m in this environmentally important pH range and to determine its solubility in acid solutions.

2. Experimental

2.1. Apparatus

FeS was precipitated in situ in a 250 ml three neck round bottom flask. Fitted into the ground glass joints of this vessel were a half cell pH probe, a 4 M KCl-agar salt bridge with a calomel reference electrode and a two neck parallel Quickfit™ adapter fitted with a Quickfit™ sintered glass gas distributor, a modified cone/screw thread with rubber septum for sample extraction and a gas outlet. The temperature of the system was controlled with a water bath and a thermocouple; which was taped to the outside of the vessel. All experiments were carried out at 23 ± 0.5 °C. The solution was stirred with a 1.5 cm plastic bar stirrer. pH measurements were calibrated before and after runs and no drift correction was introduced. Errors introduced through electrode drift are within the error of the data set.

2.2. Materials

All the chemicals used were analytical grade. The matrix of the solution consisted of 0.1 M NaCl made up in 18.2 MΩ water and deoxygenated with O_2 -free N_2 . The pH probe and reference electrodes were calibrated using phthalate buffer (pH 3.990 at 25 °C) and phosphate buffer (pH 7.020 at 25 °C). The pH was recorded using an Orion 720A research pH meter. Mohr's salt, $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, was used as the Fe(II) reagent. Ideally salts such as $\text{Fe}(\text{ClO}_4)_2$ would be used for solubility measurements (cf. Davison et al., 1999). However, our experience in the Cardiff laboratory has been that it is difficult to precipitate FeS_m from $\text{Fe}(\text{ClO}_4)_2$ without some oxidation occurring. Likewise, simple Fe(II) salts, such as FeSO_4 or FeCl_2 , are

also prone to oxidation in solution at ambient temperatures. It has been previously shown that $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ avoids the oxidation problem (Rickard, 1995).

2.3. Solubility measurements

There are two alternative approaches to solubility measurements. In the experimental arrangement used by Berner (1967) and Davison et al. (1999), FeS_m is precipitated in alkaline conditions and acid is added to the precipitate. From the point of precipitation, the FeS_m continues to dissolve until acid addition is stopped and equilibrium is reached. In the present experimentation and that of Benning et al. (2000) hydroxide is added to an acid solution of Fe(II) and S(-II) and the FeS_m precipitates. In this case, the FeS_m continues to precipitate until the addition of hydroxide is stopped and equilibrium is reached. The advantage of this approach is that the time to reach equilibrium for measurements in the neutral to alkaline region is experimentally reasonable.

Pre-weighed $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ was added to the solution, the electrodes inserted and the system further purged with O_2 -free N_2 . Deoxygenated 10% HCl was added to bring the pH of the solution to below 3. H_2S gas was passed through the solution for 45 min, to saturation. Aliquots of deoxygenated 4 M NaOH were added dropwise to induce precipitation of FeS_m and bring the solution to the required pH. Equilibrium was assumed to be approached when a rate of change in pH of no more than ± 0.02 pH units per hour was observed. The time taken for this to occur varied systematically with the H_2S gas concentration from 2 h (at 100% H_2S gas and $\text{pH} < 6$) to 6 h (at 0.03% H_2S gas and $\text{pH} > 6$). The solution was sampled by inserting 30 cm of flexible PEEK tubing connected to a 10 ml air tight syringe through the rubber septum of the sample port. 10 ml of FeS_m suspended solution was drawn into the syringe, which was then filtered using 0.45 μm filter paper.

2.4. Analyses

The problem of simply bubbling H_2S at atmospheric pressure for the estimation of the aqueous sulfide concentration was noted by Davison et al. (1999). This is facile since $p\text{H}_2\text{S}_g$ is related directly to $\{\text{H}_2\text{S}_{\text{aq}}\}$ by the relationship



for which the equilibrium constant is well known (Morse et al., 1987). However, it does introduce an intrinsic error into the solubility measurements since atmospheric pressure can vary by $\pm 10\%$, and this error is propagated through the calculations. In this study the total concentration of dissolved sulfide, $\sum[\text{S}(-\text{II})]$, where $[\]$ refers to concentration, was analysed using two methods: iodometric titration and methylene blue (Rickard, 1997) depending on the $\sum[\text{S}(-\text{II})]$.

After filtration and S(-II) analysis, the filtrate was purged of H_2S with N_2 . Depending upon the Fe(II) concentration, varying volumes of filtered solution were taken and complexed with Ferrozine™ (Stookey, 1970) or potassium thiocyanate (after permanganate oxidation) to determine Fe(II) concentration. The Ferrozine™ method gave precisions of $\pm 2\%$ (1σ) and a linear response down to 10^{-9} M Fe(II). The Ferrozine™ method was standardized against instrument-based analyses of Fe(II) in sulfidic solutions including ICP-AES and AAS.

2.5. Voltammetry

Solution speciation was probed with an EG&G Princeton Applied Research Model 384B polarographic analyzer in conjunction with a Model 303A static mercury drop electrode, with a saturated calomel electrode. Instrumental parameters for the square wave mode were typically 200 mV/s scan rate over the potential range -0.1 to -1.3 V with a 25 or 50 mV pulse height. Solutions from the solubility experiments were filtered and analyzed in an anoxic cell under O_2 -free N_2 . The pH of the solution in the voltammetric cell was measured in situ.

2.6. Modelling

The results were modelled with (1) Geochemist's Workbench (GWB) 5.0 using the standard thermodynamic database (Bethke, 1996) and the B-dot version of the Debye-Huckel approach to activity estimations and (2) MINEQL+ v. 4.5 which uses the updated MINTQA database (Serkiz et al., 1996) and the Davies equation activity calculation. The modelled results were compared with simple thermodynamic calculations using the Davies equation, the empirical Setchenow equation and Millero and Schreiber's (1982) salting out coefficient for aqueous H_2S . The measured $\sum[\text{S}(-\text{II})]$ was compared with calculated $\sum[\text{S}(-\text{II})]$ as a means to checking the approach to equilibrium using $\log K_{0,\text{H}_2\text{S}} = -1.02$ and $\log K_{1,\text{H}_2\text{S}} = -6.98$ (Suleimenov and Seward, 1997).

3. Results

3.1. Solubility of FeS_m

The results are summarised in Table 1. The raw data are listed and no smoothing of values by averaging measurements at similar pH values is made. A plot of the raw data in terms of $\log \sum[\text{Fe}(\text{II})]$ versus pH is shown in Fig. 1. This plot shows some scatter since the data are not corrected for varying dissolved S(-II) concentrations with pH nor for variations in the activities of the various species. Even so, it is clear that the dissolution reaction is divided into two main regions for each $p\text{H}_2\text{S}_g$ value: (1) in more acid solutions, $\log \sum[\text{Fe}(\text{II})]$ is inversely proportional to pH and (2) in more alkaline regions, $\log \sum\{\text{Fe}(\text{II})\}$ appears to be independent of pH and $p\text{H}_2\text{S}_g$. The results demonstrate

Table 1
Results of FeS_m solubility measurements

pH	Mohr's (M)	$\sum[S(II)]$ (M)	$\sum[Fe(II)]$ (M)	<i>I</i>	$[Fe^{2+}]_{calc}$ (M)	$\gamma_{Fe^{2+}}$	$[FeS^0]_{calc}$ (M)	$[H_2S]_{calc}$ (M)	$[HS^-]_{calc}$ (M)	γ_{HS^-}
3.160	0.100	9.30E-02	3.19E-02	0.613	3.19E-02	0.250	9.64E-07	9.30E-02	1.76E-05	0.562
3.200	0.100	9.70E-02	4.68E-02	0.634	4.68E-02	0.248	1.76E-06	9.70E-02	2.02E-05	0.649
3.210	0.100	9.70E-02	4.18E-02	0.627	4.18E-02	0.249	1.65E-06	9.70E-02	2.07E-05	0.649
3.227	0.100	1.00E-01	5.70E-02	0.649	5.70E-02	0.247	2.52E-06	1.00E-01	2.24E-05	0.647
3.254	0.100	9.20E-02	5.49E-02	0.646	5.49E-02	0.247	2.67E-06	9.20E-02	2.15E-05	0.648
3.296	0.100	1.00E-01	4.82E-02	0.637	4.82E-02	0.260	2.96E-06	1.00E-01	2.62E-05	0.648
3.303	0.100	1.00E-01	3.65E-02	0.620	3.65E-02	0.249	2.29E-07	1.00E-01	2.62E-05	0.650
3.400	0.086	9.30E-02	9.18E-03	0.523	9.18E-03	0.260	8.70E-07	9.30E-02	3.02E-05	0.659
3.412	0.100	9.30E-02	2.61E-02	0.606	2.61E-02	0.251	2.50E-06	9.30E-02	3.13E-05	0.651
3.460	0.100	1.00E-01	2.56E-02	0.606	2.56E-02	0.251	3.32E-06	1.00E-01	3.78E-05	0.651
3.465	0.100	1.01E-01	1.22E-02	0.587	1.22E-02	0.253	1.69E-06	1.01E-01	3.89E-05	0.652
3.653	0.100	9.70E-02	8.05E-03	0.582	8.05E-03	0.253	2.45E-06	9.69E-02	5.65E-05	0.653
3.844	0.100	9.70E-02	1.75E-03	0.574	1.75E-03	0.254	1.28E-06	9.69E-02	8.74E-05	0.654
3.888	0.059	1.00E-01	1.73E-03	0.393	1.73E-03	0.279	1.81E-06	9.99E-02	9.79E-05	0.675
4.280	0.010	2.21E-03	6.62E-03	0.160	6.62E-03	0.357	1.18E-06	2.20E-03	4.86E-06	0.736
4.327	0.050	9.70E-02	3.30E-04	0.348	3.30E-04	0.288	2.60E-06	9.67E-02	2.58E-04	0.683
4.358	0.010	2.20E-03	1.02E-02	0.164	1.02E-02	0.355	2.56E-06	2.20E-03	5.81E-06	0.735
4.392	0.010	2.21E-03	4.32E-03	0.157	4.32E-03	0.359	1.29E-06	2.20E-03	6.27E-06	0.737
4.535	0.050	9.70E-02	1.22E-04	0.353	1.20E-04	0.287	2.48E-06	9.66E-02	4.19E-04	0.682
4.711	0.010	2.24E-03	2.26E-03	0.155	2.26E-03	0.360	2.98E-06	2.23E-03	1.32E-05	0.738
4.747	0.010	9.40E-02	2.36E-05	0.153	2.21E-05	0.361	1.47E-06	9.34E-02	6.06E-04	0.739
4.860	0.011	2.42E-03	7.94E-04	0.154	7.92E-04	0.361	2.24E-06	2.40E-03	2.00E-05	0.739
4.870	0.010	2.02E-04	1.48E-02	0.169	1.48E-02	0.352	3.50E-06	2.00E-04	1.73E-06	0.738
4.923	0.010	2.17E-04	8.03E-03	0.161	8.03E-03	0.356	2.65E-06	2.15E-04	2.09E-06	0.736
4.942	0.010	2.15E-04	5.96E-03	0.159	5.96E-03	0.358	2.14E-06	2.13E-04	2.16E-06	0.739
4.978	0.010	1.91E-04	6.81E-03	0.160	6.81E-03	0.357	2.55E-06	1.89E-04	2.08E-06	0.736
4.998	0.010	9.00E-02	1.36E-05	0.154	1.13E-05	0.361	2.27E-06	8.90E-02	1.03E-03	0.739
5.005	0.010	1.39E-04	1.15E-02	0.165	1.15E-02	0.354	3.47E-06	1.37E-04	1.61E-06	0.734
5.052	0.010	2.35E-03	3.19E-04	0.153	3.17E-04	0.362	2.26E-06	2.50E-03	3.25E-05	0.739
5.055	0.010	1.39E-04	4.19E-03	0.157	4.19E-03	0.359	1.63E-06	1.37E-04	1.80E-06	0.739
5.085	0.010	1.41E-04	1.05E-02	0.164	1.05E-02	0.355	4.83E-07	1.39E-04	1.96E-06	0.734
5.110	0.010	1.00E-01	1.14E-05	0.154	8.34E-06	0.361	3.06E-06	9.85E-02	1.46E-03	0.739
5.238	0.010	1.62E-04	1.66E-03	0.154	1.67E-03	0.361	1.75E-06	1.59E-04	3.17E-06	0.739
5.260	0.010	1.62E-04	1.71E-03	0.154	1.72E-03	0.361	1.99E-06	1.59E-04	3.33E-06	0.739
5.344	0.005	1.00E-01	3.87E-06	0.129	1.84E-06	0.379	2.03E-06	9.76E-02	2.42E-03	0.751
5.452	0.010	1.10E-01	2.65E-06	0.156	9.16E-07	0.360	1.73E-06	1.07E-01	3.47E-03	0.738
5.518	0.003	4.45E-05	2.00E-03	0.118	2.01E-03	0.388	2.14E-06	4.29E-05	1.59E-06	0.758
5.547	0.005	1.00E-01	3.32E-06	0.130	8.63E-07	0.378	2.46E-06	9.61E-02	3.87E-03	0.751
5.556	0.005	3.27E-05	3.16E-03	0.130	3.16E-03	0.378	2.76E-06	3.14E-05	1.28E-06	0.751
5.596	0.003	4.88E-05	1.89E-03	0.118	1.89E-03	0.388	3.10E-06	4.67E-02	2.07E-06	0.758
5.614	0.005	1.04E-01	1.52E-06	0.132	3.12E-07	0.377	1.21E-06	9.94E-02	4.60E-03	0.750
5.622	0.001	4.07E-05	5.13E-03	0.111	5.13E-03	0.396	7.10E-06	3.88E-05	1.82E-06	0.762
5.648	0.001	5.88E-05	1.85E-03	0.107	1.85E-03	0.399	4.67E-06	5.60E-05	2.78E-06	0.765
5.660	0.003	4.70E-05	2.67E-03	0.119	2.67E-03	0.388	5.45E-06	4.47E-05	2.30E-06	0.757
5.740	0.001	6.93E-05	1.02E-03	0.106	1.02E-03	0.400	4.65E-06	6.53E-05	4.00E-06	0.765
5.759	0.005	1.16E-01	3.19E-06	0.134	3.39E-07	0.375	2.85E-06	1.09E-01	7.13E-03	0.749
5.773	0.005	1.16E-01	5.01E-06	0.134	5.12E-07	0.375	4.50E-06	1.09E-01	7.29E-03	0.749
5.784	0.010	2.53E-03	3.03E-05	0.153	2.53E-05	0.362	4.97E-07	2.36E-03	1.65E-04	0.739
5.791	0.010	3.30E-04	1.78E-04	0.153	1.74E-04	0.362	4.53E-06	3.08E-04	2.16E-05	0.739
5.831	0.003	4.05E-05	2.06E-03	0.118	2.05E-03	0.388	6.58E-06	3.16E-05	2.30E-06	0.758
5.943	0.003	5.85E-05	1.05E-03	0.117	1.04E-03	0.389	8.78E-06	4.53E-05	4.46E-06	0.758
6.024	0.010	3.35E-04	6.67E-05	0.153	6.21E-05	0.362	4.60E-06	2.95E-04	3.59E-05	0.740
6.028	0.003	4.70E-05	3.95E-04	0.117	3.91E-04	0.390	4.13E-06	3.83E-05	4.59E-06	0.759
6.086	0.010	3.06E-03	5.56E-06	0.153	2.93E-06	0.362	2.63E-06	2.68E-03	3.77E-04	0.739
6.129	0.005	1.16E-01	5.58E-06	0.143	1.30E-07	0.368	5.45E-06	1.01E-01	1.55E-02	0.744
6.136	0.010	1.20E-01	1.88E-06	0.170	4.27E-08	0.351	1.84E-06	1.03E-01	1.66E-02	0.732
6.165	0.005	1.26E-01	6.80E-06	0.145	1.24E-07	0.367	6.68E-06	1.08E-01	1.83E-02	0.743
6.200	0.003	5.17E-05	3.43E-04	0.116	3.35E-04	0.390	7.64E-06	3.74E-05	6.66E-06	0.759
6.202	0.010	3.70E-04	3.14E-05	0.153	2.67E-05	0.362	4.70E-06	2.93E-04	5.66E-05	0.736
6.278	0.010	1.20E-01	2.85E-06	0.174	3.64E-08	0.349	2.81E-06	9.82E-02	2.18E-02	0.730
6.309	0.003	4.00E-05	5.50E-05	0.116	5.33E-05	0.390	1.68E-06	3.12E-05	7.14E-06	0.759
6.339	0.011	3.08E-03	5.88E-06	0.153	1.62E-06	0.362	4.26E+00	2.46E-03	6.19E-04	0.739
6.452	0.005	1.42E-01	2.27E-06	0.162	1.20E-08	0.356	2.26E-06	1.07E-01	3.50E-02	0.736
6.560	0.010	3.56E-03	3.17E-06	0.154	3.76E-07	0.361	2.79E-06	2.51E-03	1.05E-03	0.739

Table 1 (continued)

pH	Mohr's (M)	$\sum[S(-II)]$ (M)	$\sum[Fe(II)]$ (M)	I	$[Fe^{2+}]_{calc}$ (M)	$\gamma_{Fe^{2+}}$	$[FeS^0]_{calc}$ (M)	$[H_2S]_{calc}$ (M)	$[HS^-]_{calc}$ (M)	γ_{HS^-}
6.642	0.005	1.62E-01	1.98E-06	0.181	4.51E-09	0.345	1.98E-06	1.07E-01	5.48E-02	0.727
6.712	0.005	1.76E-01	6.95E-06	0.192	1.14E-08	0.339	6.94E-06	1.10E-01	6.63E-02	0.723
7.040	0.010	5.66E-04	5.69E-06	0.153	7.39E-07	0.362	4.95E-06	2.48E-04	3.13E-04	0.739
7.100	0.003	6.73E-05	5.36E-06	0.116	2.64E-06	0.390	2.72E-06	2.68E-05	3.78E-05	0.759
7.140	0.010	5.62E-03	2.61E-06	0.156	2.80E-08	0.360	2.58E-06	2.16E-03	3.45E-03	0.738
7.345	0.010	4.94E-03	2.78E-06	0.156	1.82E-08	0.360	2.76E-06	1.39E-03	3.55E-03	0.738
7.417	0.010	5.78E-03	2.99E-06	0.157	1.36E-08	0.359	2.98E-06	1.44E-03	4.34E-03	0.738
7.528	0.010	1.03E-03	2.02E-06	0.153	3.69E-08	0.361	1.98E-06	2.10E-04	8.18E-04	0.739
7.992	0.010	2.46E-03	1.14E-06	0.155	2.64E-09	0.360	1.14E-06	1.99E-04	2.26E-03	0.739
8.017	0.003	7.45E-04	8.51E-07	0.117	5.50E-09	0.389	8.46E-07	5.87E-05	6.86E-04	0.758
8.061	0.001	5.16E-04	8.93E-07	0.106	7.20E-09	0.400	8.86E-07	3.73E-05	4.78E-04	0.765
8.184	0.010	3.67E-03	1.25E-06	0.156	1.22E-09	0.360	1.25E-06	1.97E-04	3.47E-03	0.738
8.189	0.010	1.12E-02	2.25E-06	0.163	7.18E-10	0.355	2.25E-06	5.94E-04	1.06E-02	0.735
8.445	0.010	6.45E-03	1.28E-06	0.159	3.82E-10	0.358	1.28E-06	1.94E-04	6.26E-03	0.737
8.456	0.010	6.61E-03	1.11E-06	0.159	3.15E-10	0.358	1.11E-06	1.94E-04	6.42E-03	0.737
8.510	0.001	6.48E-04	8.53E-07	0.106	1.87E-09	0.400	8.51E-07	1.75E-05	6.30E-04	0.765
9.247	0.010	3.93E-02	1.19E-06	0.191	9.60E-12	0.340	1.19E-06	1.88E-04	3.91E-02	0.724
9.432	0.010	6.01E-02	3.06E-06	0.159	9.82E-11	0.358	3.06E-06	1.91E-05	5.99E-03	0.737
9.455	0.010	6.33E-02	2.09E-06	0.159	6.04E-11	0.358	2.09E-06	1.19E-05	6.31E-03	0.737
9.664	0.001	1.09E-03	8.59E-07	0.107	7.64E-11	0.400	8.59E-07	2.13E-06	1.09E-03	0.765

pH is the value at which the point the analyses were made. [] refer to molar concentrations, M. Mohr's refers to Mohr's salt $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$. $\sum[S(-II)]$ is the analyzed total dissolved S(-II) concentration and $\sum[Fe(II)]$ the analysed total dissolved Fe (II) concentration. The ionic strength, I , the activity coefficients for Fe^{2+} and HS^- , $\gamma_{Fe^{2+}}$ and γ_{HS^-} , calculated concentrations and activities, indicated by the subscript calc, are calculated with Geochemist's Workbench.

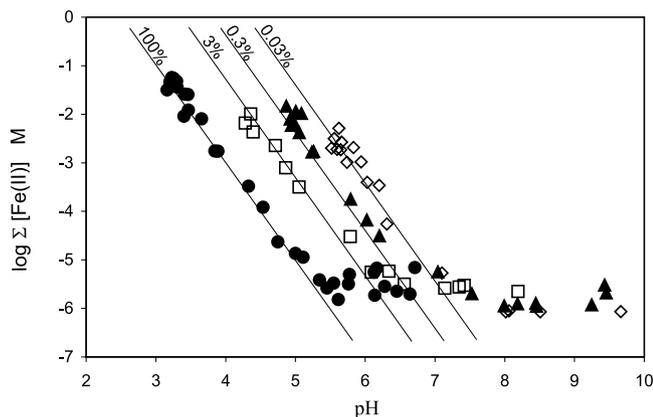


Fig. 1. Plot of the logarithm of the total dissolved Fe(II) concentration against pH for all data. Indicative slopes of -2 for the various H_2S gas concentrations are given. These are raw data, uncorrected for variations in dissolved sulfide concentrations and activities. However, they clearly show the change in dissolution mechanism at more alkaline pH values.

that there is a change in the dominant dissolution reaction as the pH increases.

The limitations of the experimental system mean that each set of experiments with a given pH_2S_g covers a different region of pH space. This is because as $\sum[S(-II)]$ decreases, FeS_m becomes more soluble at higher pH values. Likewise, at high pH_2S_g values the amount of S(-II) dissolved increases substantially with increasing pH and steady state conditions are achieved with increasing difficulty. Since the rate of FeS_m precipitation is a function of both pH and S(-II) (Rickard, 1995), the time for steady state conditions to be reached at very low pH_2S_g values becomes

increasingly long. The cut-off in these experiments was 6 h to reach a point where the pH varied by less than 0.02 pH units per hour.

3.2. Fe speciation in solution

Voltammetric analyses on the solutions equilibrated with FeS_m showed only Fe^{2+} in acid solutions and FeS_{aq} , the aqueous FeS cluster complex (Theberge and Luther, 1997) and minor Fe^{2+} in alkaline solutions (Fig. 2). The doublet results from the transfer of 2 electrons from Fe (II) in FeS_{aq} to Fe(0) on deposition on the Hg electrode. Cyclic voltammetry of FeS_{aq} classically shows that the re-oxidation of the Fe(Hg) amalgam produced by the reaction of FeS_{aq} produces Fe^{2+} , and the reaction is not reversible (Theberge and Luther, 1997). Titration of the solutions against HCl reduced the FeS_{aq} signal showing that the cluster dissociated into Fe^{2+} and S(-II). Fe bisulfide species are identified conventionally by the shift in the potential of the HS-peaks (Luther et al., 1996). This experimentation was not designed to measure these complexes, but they did not appear to constitute a major proportion of the dissolved Fe(II). Complexes such as $FeSO_4^0$ and $FeCl^+$ were not observed electrochemically in these experiments. The results suggest that the aqueous FeS cluster is the dominant species in alkaline solutions in equilibrium with FeS_m . The filtered solution was crystal clear and no precipitate was seen. Repeated freezing and thawing of the solution did not appear to modify the result and the cluster is relatively stable. It appears that FeS_{aq} is quite stable in the absence of FeS_m .

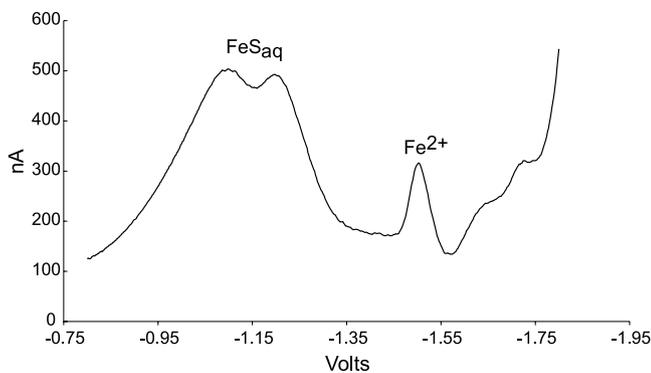


Fig. 2. Square wave voltammetric trace of the solution in equilibrium with FeS_m . (Scan increment 2 mV, pulse height 20 mV, frequency 100 Hz, pH 8.9). The doublet at -1.1 V is characteristic of FeS_{aq} and demonstrates that this is the dominant Fe(II) species in this solution. A small Fe^{2+} signal is also seen.

The presence of significant and variable SO_4 (-II) and Cl (-I) concentrations in the experimental solutions would suggest that Fe(II) sulfate and Fe(II) chloride complexes contribute to the measured total dissolved Fe(II) concentration. The strongest complexes involved would be FeSO_4^0 and FeCl^+ . However, as shown from the results in Fig. 3, experimentally varying $[\text{SO}_4^{2-}]$ and $[\text{Fe(II)}]:[\text{Cl}(-\text{I})]$ produces no systematic variations from Eq. (1).

4. Discussion

4.1. pH dependent FeS_m solubility

The results in more acid regions, where the analyzed $\sum[\text{Fe(II)}]$ closely approximates $[\text{Fe}^{2+}]$, are therefore used to compute primary values for $K_{\text{sp},1}^*$ and $K_{\text{sp},2}^*$. The dominant reaction changes in more alkaline systems. In these pH regions, and in intermediate zones, the analyzed $\sum[\text{Fe(II)}]$ does not describe $[\text{Fe}^{2+}]$ and the analyses cannot be used to determine $K_{\text{sp},1}^*$ and $K_{\text{sp},2}^*$. However, it is obvious that the pH dependent dissolution of FeS_m still contributes to the total dissolved Fe(II) in systems where Fe^{2+} is not the dominant dissolved Fe species. The primary K_{sp} values are used to compute the contribution of Fe^{2+} to the total dissolved Fe(II) in environments where the process is not directly pH dependent. According to Eq. (2), a plot of $\log\{\text{Fe}^{2+}\}$ versus pH will display a slope of -2 across the whole experimental dynamic range (Fig. 3). The plots show good correlations for all pH values and $[\text{S}(-\text{II})]$ with slopes of -2 and R^2 values consistently >0.98 . The assumption that the dominant Fe(II) species in more acid solutions in this experimentation is hexaqua Fe(II), Fe^{2+} , therefore closely describes the experimental data. The slope of the $\log\{\text{Fe}^{2+}\}$ versus pH plots and the consistency of the K_{sp} values over a wide dynamic range of pH, $p\text{H}_2\text{S}_g$, $[\text{Fe(II)}]$, $[\text{S}(-\text{II})]$ and $[\text{SO}_4(-\text{II})]$ constrain alternative interpretations of the data. In particular, they demonstrate that the simple approximation to speciation used in the model predicts the solubility with reasonable accuracy.

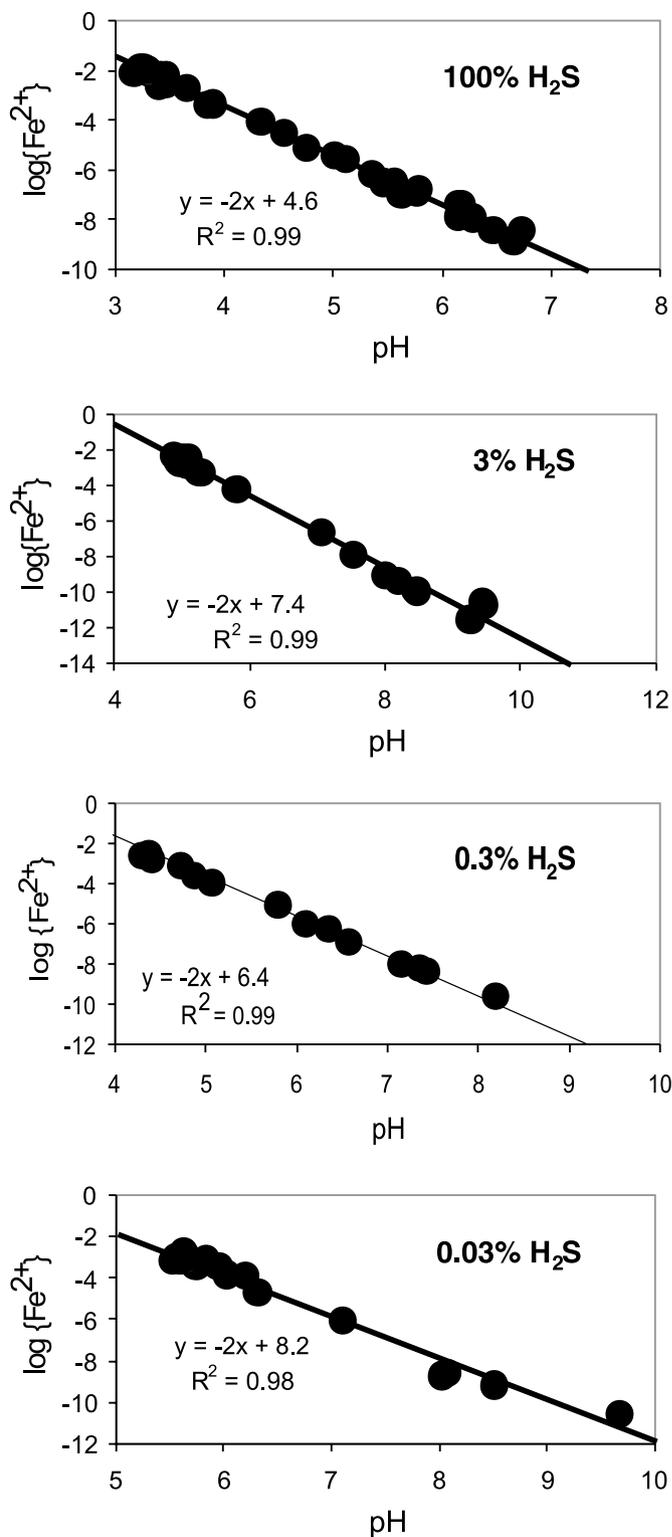


Fig. 3. Plot of logarithm of the calculated Fe^{2+} activity, $\log\{\text{Fe}^{2+}\}$, versus pH for all experimental data using the measured $K_{\text{sp},1}^*(\text{FeS}_m)$ value of 3.5 and $K_0(\text{FeS}_m) = -5.7$. The slope is -2 for all data.

The results show that $K_{\text{sp},2}^*(\text{FeS}_m)$ is -3.5 ± 0.25 ($\pm 1\sigma$, $n = 84$) between pH 3 and 10 and at $\sum[\text{S}(-\text{II})]$ concentrations between 3.27×10^{-5} and 1.76×10^{-1} M. This compares with values of -3.00 ± 0.12 (20 °C, Davison et al., 1999), -2.95 (25 °C, Berner, 1967), -2.94 (25 °C, Theberge

and Luther, 1997) and -3.9 (25 °C, Benning et al., 2000). It is similar to the value for the recalculated value for “mackinawite” of -3.55 ± 0.09 (Davison et al., 1999) originally provided by Berner (1967) which is related to a more crystalline variety of synthetic FeS_m . The Gibbs free energy of formation for FeS_m is then $-98.2 \text{ kJ mol}^{-1}$ using $\Delta G_f^0(\text{Fe}^{2+}) = -90.53 \text{ kJ mol}^{-1}$ (Parker and Khodakovskii, 1995) and $\Delta G_f^0(\text{HS}^-) = 12.2 \text{ kJ mol}^{-1}$ (Cox et al., 1989). Benning et al. (2000) used an earlier value for $\Delta G_f^0(\text{Fe}^{2+})$ chosen by the National Bureau of Standards (Wagman et al., 1968) of $-78.9 \text{ kJ mol}^{-1}$ which has been discarded because of intrinsic oxidation in the primary experiments. Correcting their values gives $\Delta G_f^0(\text{FeS}) = -101.09 \text{ kJ mol}^{-1}$ which compares with Berner’s (1967) values for “precipitated FeS” of -96.4 and “mackinawite” of -100.4 (recalculated for $\Delta G_f^0(\text{Fe}^{2+}) = -90.53 \text{ kJ mol}^{-1}$).

4.2. pH-independent FeS_m solubility

In more neutral to alkaline pH environments, depending on $p\text{H}_2\text{S}_g$, $\sum[\text{Fe(II)}]$ is independent of pH and reaction (3) does not describe FeS solubility. Likewise the proportion of S(-II) in solution as $\{\text{H}_2\text{S}\}$ decreases logarithmically and the dominant S(-II) species becomes HS^- . The mean value of $\log \sum[\text{Fe(II)}]$ for this data set is -5.7 .

The pH independence means that protons cannot be involved in the overall reaction stoichiometry and reactions (1) and (3) do not determine the dissolved Fe(II) concentration. Davison et al. (1999) found the same pH-independent behaviour above pH 6 when they made measurements in the same range of $p\text{H}_2\text{S}_g$. These results show that no significant dependence of the solubility of FeS_m on S(-II) concentration is observed in the neutral to alkaline pH range. $\log[\text{Fe}^{2+}]$ tends to a constant value around -5.7 ± 0.27 over the whole range of $\sum[\text{S(-II)}]$ from 10^{-4} to 10^{-1} M , and pH (5.5–9.7) accessed in this study. This result was carefully checked to ensure that this was not an analytical detection limit problem. Linear standardisation curves for $[\text{Fe(II)}]$ were obtained down to 10^{-8} M or 2 magnitudes below the platform value. The filtration system was also examined. Wolthers et al. (2003) had found particles down to 2 nm in size in FeS precipitates and Ohfuji and Rickard (2006) showed that FeS_m produced in a similar manner to that in the present report, had an average size of 4 nm. However, the use of a 0.1 M NaCl matrix in our experiments caused sufficient flocculation of the FeS particles such that they were quantitatively retained on a 0.45 μm filter within experimental error. Filter passing FeS_m particles would increase the apparent $\sum[\text{Fe(II)}]$ in a non-systematic manner. The results confirm that the errors resulting from filter-passing particles were within the experimental uncertainty (Fig. 3). Successive filtrations down to 0.02 μm revealed no significant trend and standard precipitates were quantitatively retained.

The absence of a solubility dependence on S(-II) means that free H_2S or HS^- cannot be involved in the overall

process. The overall dissolution process in neutral to alkaline environments is then



where $\text{Fe}_n\text{S}_n \text{ aq}$ is an uncharged species or cluster with an Fe:S ratio of 1 (Buffle et al., 1988; Theberge and Luther, 1997). This is consistent with the results of the voltammetric analyses of the solutions.

From these experimental data, n in $\text{Fe}_n\text{S}_n \text{ aq}$ cannot be determined. However, the data can be treated by representing $\text{Fe}_n\text{S}_n \text{ aq}$ as the monomer FeS^0 . This is conventionally referred to in the chemical literature as the *intrinsic solubility* of the phase.

The intrinsic solubility of FeS_m (reaction (6)) may be expressed as

$$\log K_0(\text{FeS}_m) = \{\text{FeS}^0\} \quad (7)$$

The constant $\sum[\text{Fe(II)}]$ value in alkaline solutions suggests both that Eq. (7) describes the dissolution of FeS_m in these environments and that we can assume $[\text{FeS}^0] \approx \sum[\text{Fe(II)}]$. Since FeS^0 is a neutral species, $\gamma(\text{FeS}^0) \rightarrow 1$ and $\sum[\text{Fe(II)}] \approx \{\text{FeS}^0\}$, $\log K_0(\text{FeS}_m) = -5.7$.

Since $\log K_{sp,2}^*(\text{FeS}_m) = -3.5$, the equilibrium constant for the reaction.



$$\log K_2^*(\text{FeS}^0) = 2.2.$$

Note that Eq. (8) suggests that FeS^0 is in equilibrium with Fe^{2+} , and the voltammetry of the solution containing FeS^0 separated from FeS_m by filtration shows a small Fe(II) peak (Fig. 2) consistent with this interpretation.

4.3. Model

The experimental data summarized in Table 1 and plotted in Fig. 3 are based on $\log K_{sp,1}^*(\text{FeS}_m) = 3.5$ and $\log K_0(\text{FeS}_m) = -5.7$. The model solubility of FeS_m is compared with the experimental values in Fig. 4. Including FeSO_4^0 , FeCl^+ and FeOH^+ in the model, using the constants in the GWB database, does not improve the fit of the observed data. Davison et al. (1999) noted that the reported stability constant for FeHS^+ of ca. $10^{5.2}$ (Zhang and Millero, 1994; Luther et al., 1996) seemed too high for their FeS_m solubility data and these results concur with this conclusion. Including $\log K(\text{FeHS}^+) = 5.2$ into the model results in FeSH^+ appearing to become the dominant dissolved Fe(II) species in the experimental solutions between pH 4 and 6.5. This would reduce $\log\{\text{Fe}^{2+}\}$ in this pH region, a feature which is not observed in this study (Fig. 3). The reason for the conflict between the solubility experiments and the electrochemical measurements of the stability constant is unknown. Davison et al. (1999) suggested that $\text{Fe}(\text{SH})_2$, which had been proposed as a kinetic reaction intermediary in FeS_m formation by Rickard (1995), was the dominant species in neutral to alkaline conditions.

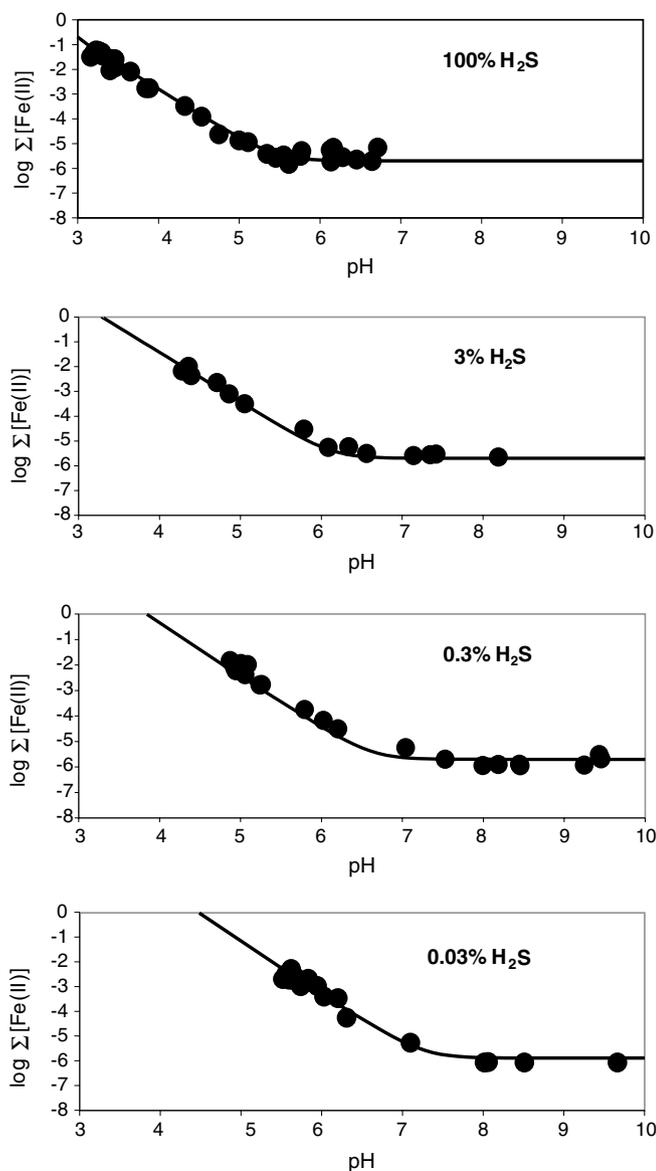


Fig. 4. Plot of $\log \Sigma[\text{Fe(II)}]$, the logarithm of the total dissolved Fe(II) concentration versus pH for systems with the H_2S gas concentration ranging between 0.03% and 100%. The experimental data are compared with the model data which are indicated by the solid curves.

However, this would imply that FeS_m solubility in this region is dependent on $p\text{H}_2\text{S}_g$, which is inconsistent with these results. Luther et al. (1996) found no evidence for $\text{Fe}(\text{SH})_2$ being a major species in sulfidic solutions containing Fe(II) and these results are consistent with this conclusion. A number of other Fe(II) sulfide clusters and complexes have been reported in the literature, including polymeric varieties. However, no evidence for these species was found in this experimentation and the experimental results closely accord with the simple model where only Fe^{2+} and FeS^0 dominate. The presence of one or more of these other species in the experimental solutions produces uncertainties which are within the experimental errors.

The model data are calculated according to the equation

$$\begin{aligned} \log \Sigma[\text{Fe(II)}] &= \log\{\text{Fe}^{2+}\} + \log\{\text{FeS}^0\} \\ &= \log K_{\text{sp},1}^*(\text{FeS}_m) - \log\{\text{H}_2\text{S}\} - 2\text{pH} \\ &\quad + \log K_0(\text{FeS}^0) \end{aligned} \quad (9)$$

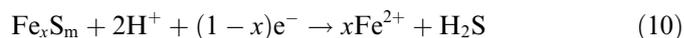
which is a combination of Eqs. (2) and (7). The model, which uses the experimentally derived values of $\log K_{\text{sp},1}^*(\text{FeS}_m) = 3.5$ and $\log K_0(\text{FeS}_m) = -5.7$, closely describes the solubility of FeS_m at 23 °C for pH 3–10 and $\log \Sigma[\text{S(-II)}] = -1$ to -5 (Fig. 4).

4.4. Effects of FeS_m composition

The balance of published evidence suggests that the composition of crystalline mackinawite is close to FeS (Lennie et al., 1995). It should be also noted that, in relatively alkaline environments (e.g., $\text{pH} \geq 9.5$), alkaline Fe(II) sulfides may be formed (Rickard, 1969) which might contribute to the experimental uncertainties observed in some runs at high pH.

The first FeS_m precipitate to be isolated in solutions at $\text{pH} < 9.5$ has been shown to be nanoparticulate with a modified mackinawite structure (Wolthers et al., 2003; Oh-fuji and Rickard, 2006). Morse et al. (1987) and Kornicker (1988) proposed that the material is probably hydrated and Wolthers et al. (2003) found that this suggestion was not inconsistent with their structural data. However, they also noted that similar structural effects could be caused by lattice relaxation effects in non-hydrated nanoparticles. Experimentally it is not currently possible to obtain a direct chemical analysis of the FeS_m composition at the point of precipitation, since drying and filtration take time. Most of the least aged material measured is up to 20 min old. The kinetics of FeS_m crystal growth are presently unknown. In this experimentation it took 2–6 h for the reaction to approach equilibrium, which was defined as a reduction in the change in pH to less than 0.02 pH units per hour. Wolthers et al. (2003) showed that the material grew in size and became similar structurally to bulk mackinawite within this time period.

If the material analysed is non-stoichiometric Fe_xS_m , reaction (1) becomes



and

$$\begin{aligned} \log K_{\text{sp},1}^*(\text{Fe}_x\text{S}_m) &= x \log\{\text{Fe}^{2+}\} + \log\{\text{H}_2\text{S}\} + 2\text{pH} \\ &\quad + (1-x)\text{pe} \end{aligned} \quad (11)$$

For constant $\{\text{H}_2\text{S}\}$ and pe , a plot of pH versus $\log\{\text{Fe}^{2+}\}$ gives a slope of $-2/x$. Analyses of the experimental data for experiments in which $\{\text{H}_2\text{S}\}$ is approximately constant (e.g., $\text{pH} < 4$, $p\text{H}_2\text{S}_g \approx 0.1$ MPa) shows a slope slightly less than -2 , suggesting $x \approx 0.98$. However, the experimental data are insufficiently precise to define this stoichiometry. All that can be concluded is that the FeS_m non-stoichiometry

is relatively small, since large non-stoichiometries would be readily detectable in the slope.

4.5. Transition from pH-dependent to pH-independent dissolution

At the point of transition, the total dissolved Fe(II) concentration in equilibrium with FeS_m is made up of equal proportions of Fe^{2+} and FeS^0 . So that, from Eqs. (2) and (7),

$$\log K_{sp,1} = \log K_0(\text{FeS}_m) + \log\{\text{H}_2\text{S}\} - 2\log\{\text{H}^+\} \quad (12)$$

This means that, at the transition point, $(\log\{\text{H}_2\text{S}\} + 2\text{pH})$ is constant equal to the difference between $\log K_{sp,1}$ and $\log K_0(\text{FeS}_m)$. The locus of these points is plotted on Fig. 5 for total dissolved S(-II) concentrations between 100 mM and 1 μM . The computation for $\log\sum[\text{S(-II)}]$ involves γ_{HS^-} and therefore the plot is dependent on ionic strength. However, the dependence is relatively weak and the plot broadly limits the boundary between the two dissolution regimes. Of course, it must be emphasised that this is a dominance diagram: the two dissolution processes occur through pH– $\log\sum[\text{S(-II)}]$ space and the boundary merely indicates where $\{\text{FeS}^0\}$ and $\{\text{Fe}^{2+}\}$ are equal. Since $\{\text{FeS}^0\}$ is fixed at $10^{-5.7}$, the locus defines a total dissolved Fe(II) activity of 4×10^{-6} . In most natural systems with ionic strengths up to 0.7, this means a concentration of about 1–4 μM total dissolved Fe(II).

4.6. Comparison with previous work

The differences in measured solubility constants of the pH-dependent reaction between this study ($K_{sp,2} = 10^{-3.5}$), Benning et al. (2000, $K_{sp,2} = 10^{-3.8}$), Berner (1967,

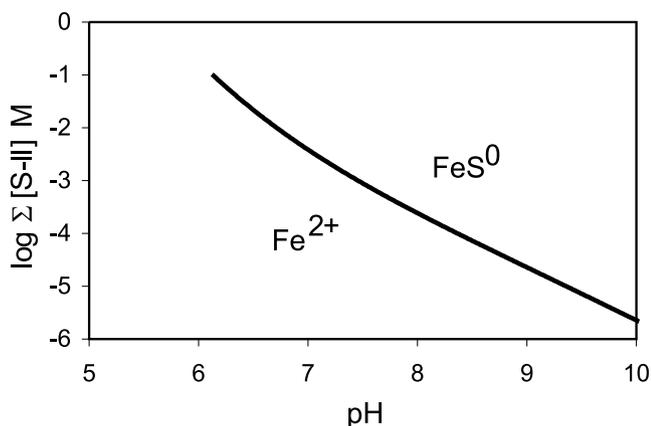


Fig. 5. Plot of locus of transition points between pH-dependent dissolution of FeS_m , producing dominant Fe^{2+} , and pH-independent dissolution with dominant FeS^0 , in terms of the logarithm of the total dissolved sulfide concentration and pH, between a $\sum[\text{S(-II)}] = 100 \text{ mM}$ and the lower limit of 1 μM , where insufficient S(-II) is present for FeS^0 to be stable. The data is approximately correct for a range of ionic strengths encompassing both fresh and marine waters.

$K_{sp,2} = 10^{-2.95}$) and Davison et al. (1999, $K_{sp,2} = 10^{-3.0}$), appear to be consistent with the different experimental methods used. In this study and that of Benning et al. (2000), FeS_m was precipitated by adding OH^- to an acid solution of Fe(II) and S(-II) and its solubility measured. In the case of Berner (1967) and Davison et al. (1999), FeS_m was precipitated and its solubility was measured by acid dissolution. The dissolution methods give higher solubility constants ($K_{sp,2} = 10^{-3.0}$ and $10^{-2.95}$) than the precipitation methods ($K_{sp,2} = 10^{-3.5}$ and $10^{-3.8}$). It is oversimplistic to describe the acid dissolution approach as measuring the dissolution of FeS_m and the alkali addition method as measuring the precipitation of FeS_m . In both cases it is assumed that a reversible equilibrium is reached at the point of cessation of OH^- or H^+ addition.

There appears to be nothing intrinsically wrong with either experimental approach. As mentioned above, the OH^- addition is advantageous for penetrating more alkaline systems experimentally but otherwise the measurement systems are similar. However, at the same S(-II) concentration in the pH-dependent regime, the continuous dissolution approach results in a higher total dissolved Fe(II) than the continuous precipitation method by a factor of 3. This appears to be far greater than the uncertainties in the Fe(II) analyses.

Unfortunately, previous reports of FeS_m solubility only include very basic information on the actual nature of the precipitate involved. Berner (1967) and Davison et al. (1999) refer to “amorphous FeS ” which, as shown by Wolthers et al. (2003) probably means it was nanoparticulate. However, it also means that there is no information about the structure of the phase and, in the absence of any analyses of the composition of the material, a direct comparison with this study is not possible with any certainty. It seems unlikely that incipient oxidation is a cause of the differences in measured solubilities. Greigite, Fe_3S_4 , is more stable and therefore less soluble than mackinawite, according to the single, pioneering report by Berner (1967). The transformation of mackinawite to greigite appears to be facile, involves a solid state oxidation of part of the mackinawite-Fe(II) to Fe(III) and may involve auto-oxidation with H_2O as well as more conventional oxidation by molecular O_2 (Rickard and Morse, 2005). However, HRTEM analyses by Ohfuji and Rickard (2006) of FeS_m similar to that used in this study showed no evidence for greigite interlayers in the mackinawite structure as has been observed in biogenic materials by Posfai et al. (1998).

As shown by Rickard (1995), there is no discernable lag phase in the precipitation kinetics and thus significant supersaturation should not be involved in FeS_m nucleation. Therefore the difference in solubilities appears to be due to different properties of the material, with the FeS_m precipitated from acid solutions being more stable (and less soluble) than that precipitated from more alkaline solutions. Certainly, the mechanism of the precipitation reaction is pH dependent (Rickard, 1995), with Fe(II) reacting directly with H_2S in acid solutions to form FeS_m whereas the

similar reaction with HS^- involves the formation of an $\text{Fe}(\text{HS})_2$ intermediary.

Zhang et al. (2003) found that ZnS nanoparticles were sensitive to the nature of the medium. Analogous structural distortions were observed in FeS_m nanoparticles by Ohfuchi and Rickard (2006) and were inferred as potential explanations for the results of structural analyses of nanoparticulate FeS_m by Wolthers et al. (2003). It is possible therefore that the difference in results between the dissolution and precipitation experiments reflect the state of the nanoparticulate material. As noted by Luther and Rickard (2005), it cannot be assumed that nanoparticles behave simply as small samples of the bulk materials.

5. Implications

The effect of the model on dissolved Fe(II) activities in anoxic sulfidic environmental systems is illustrated in Fig. 6. At pH 8, for example, the concentration for dissolved Fe(II), in the form of FeS_{aq} , is some 3 magnitudes greater than the concentration of free hexaqua Fe^{2+} at millimolar concentrations of S(-II). Since $\sum[\text{S(-II)}] = [\text{H}_2\text{S}] + [\text{HS}^-] + [\text{FeS}^0]$, FeS_m dissolves at $\sum[\text{S(-II)}] \leq 10^{-5.7}$ M to form Fe^{2+} , FeS_{aq} as a dominant dissolved Fe(II) species is limited to environments with greater than micromolar total dissolved S(-II) concentrations. Note that as the concentration of $\sum[\text{S(-II)}]$ approaches $10^{-5.7}$ M, a progressively more significant part of the total dissolved sulfide is in the form of FeS_{aq} rather than free H_2S or HS^- .

The increased equilibrium solubility of FeS_m in neutral to alkaline environments is consistent with the observation by Rickard and Morse (2005) that FeS_m has not often been reported from direct observations of marine sediments. In contrast, aqueous FeS has been widely observed.

The idea that FeS_m is relatively insoluble in sulfidic sedimentary environments is an oversimplification. Compared with Fe solubility in oxic ocean water, the concentration of

dissolved Fe(II) in sulfidic systems in equilibrium with FeS_m is substantial. The data suggest that Fe(II) is transportable in solution at quite significant concentrations in sulfidic sediments in the presence of FeS_m , mainly in the form of an aqueous FeS species. This means that in the global Fe cycle, the transfer of Fe from a normal oxic oceanic environment to an anoxic sulfidic system with FeS_m may result in a sharp increase in the dissolved Fe concentration and a consequent increase in the transport of Fe within the system. The result contributes to the understanding of the formation of pyrite concretions in sediments (cf. Raiswell, 1982) and also suggests a flux of Fe from sulfidic sediments with FeS_m to more oxic overlying systems. However, the availability of the hexaqua Fe(II) ion itself, which may be significant biologically, may be correspondingly reduced in high sulfide systems (cf. Luther et al., 2001).

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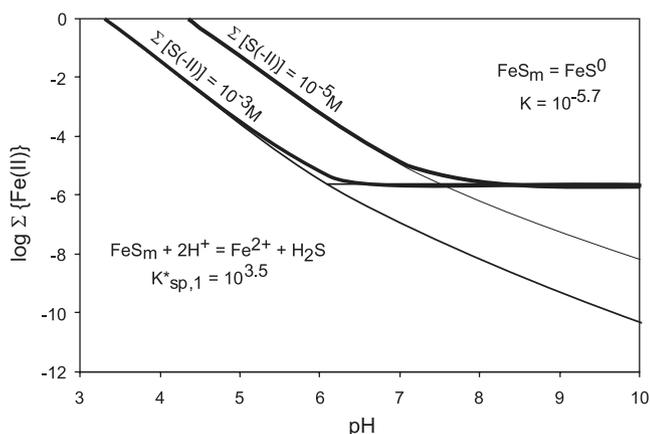


Fig. 6. Total activity of dissolved Fe(II) in equilibrium with FeS_m (bold lines) at 25 °C and total dissolved S(-II) concentrations, $\sum[\text{S(-II)}]$, of 10^{-3} and 10^{-5} M resulting from the Fe(II) activities of the pH-dependent and pH-independent reactions (fine lines).

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