The composition of nanoparticulate mackinawite, tetragonal iron(II) monosulfide

David Rickard [a,*], A. Griffith [a], A. Oldroyd [a], I.B. Butler [a,b], E. Lopez-Capel [c], D.A.C. Manning [c], D.C. Apperley [d]

[a] *School of Earth, Ocean and Planetary Sciences, Cardiff University, Cardiff CF103YE, Wales, UK*
[b] *School of Geosciences, Grant Institute, The King's Buildings, West Mains Road, Edinburgh EH9, 3JW, UK*
[c] *School of Civil Engineering and Geosciences, University of Newcastle upon Tyne, Newcastle upon Tyne NE1 7RU, UK*
[d] *Department of Chemistry, University of Durham, Durham DH1 3LE, UK*

Abstract

The primary FeS precipitate formed from the reaction between Fe(II) and S(-II) in aqueous solutions at ambient temperatures and pressures is nanoparticulate stoichiometric mackinawite, $Fe_{1.00\pm0.01}S$. The material is not hydrated. It is probable that sedimentary mackinawite has this composition. Previous reports of mackinawite compositions of $Fe_{1\pm x}S$ are incorrect. Mackinawite dissolves in mineral acids to produce rhombic sulfur, the amount of sulfur formed being related to the acid concentration used. The formation of rhombic sulfur, which is not readily soluble in simple mineral acids, leads to poor total recoveries of Fe and S as well as to significant uncertainties in the precision of the analyses. The problem can be overcome by including a reducing agent, such as Ti(III) citrate, in the digestion procedure. Evaporative drying of the material leads to the formation of other contaminants which may be removed by intensive washing and re-suspension of the precipitate or long-term storage in low H_2O anoxic environments. Analyses of S(-II) and Fe sulfide species in sediments and natural waters containing FeS using digestion by mineral acids in the absence of a reducing agent are likely to be affected by these results.
© 2006 Elsevier B.V. All rights reserved.

Keywords: Mackinawite; FeS; Sulfide; Iron sulfide

1. Introduction

R.A. Berner (1962a) showed that the synthetic black iron(II) monosulfide phase produced by precipitation of Fe(II) salts with S(-II) in ambient aqueous systems has a tetragonal structure. It was a textbook-changing discovery. The standard high school chemistry curriculum at that time taught a sequential scheme of analysis that relied on the precipitation of sulfides, so that the black FeS precipitate was familiar to a significant fraction of the global scientific community. Berner showed that this phase was a major constituent of *hydrotroilite*, an older term for the black iron sulfide material of sediments. *Kansite*, originally defined by Meyer et al. (1958) as a corrosion product of steel pipes, also showed a tetragonal structure. In the geochemical literature this black iron(II) monosulfide precipitated from aqueous

---

* Corresponding author. Tel.: +44 2920874284.
 E-mail address: rickard@cardiff.ac.uk (D. Rickard).

solutions at low temperatures has been variously described as *hydrotroilite*, *kansite*, *precipitated FeS*, *amorphous FeS* or *disordered mackinawite*.

A case could be argued that Berner's (1962a) discovery was the last simple, widespread terrestrial mineral to be identified. Hundreds of minerals have been identified and characterised since but few, if any, with the abundance of mackinawite.

Mackinawite itself was formally defined as a mineral by Evans et al. (1964) from the Mackinaw Mine, Washington. Previously, Kuovo et al. (1963) had described a tetragonal iron sulfide from the Outokumpu Mine, Finland. In both of these occurrences, mackinawite was associated with a high temperature phase assemblage apparently related to the monosulfide-solid solution. Subsequently, mackinawite has been found commonly in these high temperature mineral associations. These ore mackinawites often include substantial concentrations of other metals such as Cr, Ni, Co and Cu. Indeed, mackinawite was the main Ni ore mineral in the Hitura Ni mine in Finland. Much of the original information about the composition of mackinawite derived from well-crystalline mackinawites from these high temperature ores.

Typically, the X-ray powder diffraction (XRPD) spectra of FeS_m display no distinct Bragg reflections apart from a broad, low intensity hump around 5 Å. This has been interpreted by some workers to indicate that the phase is amorphous. Wolthers et al. (2003) used low angle X-ray powder diffraction (LAXRPD) to show that synthetic Fe(II) monosulfide precipitated from aqueous solutions at low temperature is not amorphous but displays a tetragonal mackinawite structure. We refer to this synthetic material throughout as FeS_m. Michel et al. (2005) used paired distribution function analysis of XRD collected at the Advanced Photon Source and concluded that the initial precipitate showed only minor relaxation compared to the bulk material. They also found that drying did not induce significant structural changes. Neutron scattering analysis (Watson et al., 2000) of a synthetic mixture of greigite and mackinawite also showed the presence of 2 nm nanoparticles. Ohfuji and Rickard (2006) showed that the first precipitated FeS_m was in the form of plates elongated along the *c*-axis ranging in length from 3 to 10.8 nm and in thickness from 2 to 5.7 nm with a mean size of 5.6×3 nm. The smallest particles are more equidimensional 3×2 nm in size. They measured the structure with high resolution electron diffraction and showed that the precipitated material showed a 3% relaxation compared to the bulk and the freeze-dried material a 1% relaxation. They also showed that the material displayed

various structural flaws consequent on its nanoparticulate size. The studies of Michel et al. (2005) and Ohfuji and Rickard (2006) confirmed the original conclusions of Lennie et al. (1995) that precipitated FeS shows long-range ordering. Both studies also noted that the absence of XRD reflections resulted from the reduced coherence length of the nanoparticles. This means that XRPD methods routinely used to examine the material give no pattern or show a broad peak around 5 Å and explains why some previous workers assumed that it was amorphous.

Based on Kornicker's (1988) finding that drying changes the physical properties of mackinawite, Morse et al. (1987) suggested that disordered mackinawite may be a hydrate. Lattice expansion relative to crystalline mackinawite was interpreted by Wolthers et al. (2003) as possibly being caused by intercalation of water molecules between the tetrahedral sheets of the mackinawite structure but they noted that lattice relaxation due to small crystallite size might also contribute to the expansion.

The composition of mackinawite is not well constrained. The best results have been obtained from electron probe microanalyses analyses of larger mackinawite crystals from the ore associations. However, these materials are characterised by substantial concentrations of other metals. The result appears to be a non-stoichiometric metal excess composition often written as $Fe_{1+x}S$ but better written as $(Fe,M)_{1+x}S$, where M is another metal such as Ni, Co or Cr. A detailed Rietveld investigation of the structure of synthetic crystalline mackinawite by Lennie et al. (1995) showed that any vacancy occupancy or surplus Fe occupancy was below the detection limit of the method. This means that the Fe/S ratio of pure mackinawite should closely approach one. The results are in contrast to previous reported analyses of synthetic mackinawite. Berner (1962b) and Rickard (1969) found $Fe_{0.91}S$. Sweeney and Kaplan (1973) reported compositions between $Fe_{1.09}S$ and $Fe_{1.15}S$. Ward (1970) reported a range between $Fe_{0.995}S$ and $Fe_{1.023}S$. Rickard (1997) reported $Fe_{1.04}S$. The largest crystals of synthetic mackinawite are prepared by reaction of α-Fe (in the form of iron wire) with bisulfide solutions. Lennie et al. (1997) reported an average Fe/S ratio of 0.99 ± 0.02 for three such crystals using EDAX measurements in a TEM.

The purpose the investigation reported in this paper is to resolve the issue of mackinawite composition. Many published reports about mackinawite simply omit any compositional data and rely on XRPD for identification. The reason appears to be the problems of getting reproducible analytical results. We address this problem

by deconvoluting problems of mackinawite digestion from problems of mackinawite analyses.

Knowledge of mackinawite composition is fundamental to understanding all aspects of its role in the natural environment. Mackinawite is thought to be a significant component in the biogeochemical cycles of sulfur and iron (Berner, 1970). It has been suggested that mackinawite plays an important role on controlling the concentrations of aqueous Fe(II) and S(-II) in anoxic sedimentary systems (e.g. Bagander and Carman, 1994) and it has been supposed to constitute a substantial reservoir in sedimentary sulfur isotope systematics (e.g. Neretin et al., 2004). It is also likely to control aqueous Fe(II) and S(-II) in sanitary landfill systems (e.g. Ulrich et al., 2003). The sorption of dissolved species onto mackinawite has been related to the both the sequestration of materials in sediments (e.g. Luther et al., 1980) and toxicity. Indeed, it is thought to be a key component of the simultaneously extracted metals—acid volatile sulfide (SEM-AVS) protocol for environmental toxicity estimations (e.g. DiToro et al., 1990). Mackinawite has been identified as a component of diverse biological systems, such as magnetotactic bacteria (Posfai et al., 1998) and even contributing to the formation of iron sulfide scales on vent gastropods (Waren et al., 2003). It

has been implicated in the iron-sulfur world hypothesis of the origin of life (Russell and Hall, 1997).

2. Methods

2.1. Experimental

Experiments 5–26 (Table 1) were mainly aimed at resolving the FeS_m dissolution problem. The aims of this group of experiments were (1) to establish a repeatable method for the analysis of FeS_m and (2) to investigate the reasons for the problems of FeS_m analytical repeatability in this study and previously published reports. A second series of experiments were aimed at (1) determining if FeS_m is a hydrate and (2) to determine the composition of FeS_m.

All processes involving FeS_m were carried out in an N_2-filled MBraun Labmaster anoxic chamber with O_2 levels maintained at less than detectable levels (<1 ppmv). All reagents used were of analytical grade and were used without further purification. Solutions were prepared with deionised 18.2 MΩ cm water (MilliQ), purged with O_2-free grade N_2 for 1 h (D2 water). Ti(III) citrate was prepared by adding 5 ml 15% $TiCl_3$ to 50 ml 0.2 M Na citrate buffered to pH=7 with

Table 1
Summary of experimental methods used to assess digestion and analytical methodology

Exp.	Reactant	Anti-oxidant	Run time	Cold HCl	Hot HCl		Hot CrCl₂	S(-II) analysis		Fe(II) analysis	
				6 M	1.2 M	6 M		Titration	Colorometric	HCl	CrCl₂
5	FeS	None	Overnight	y					y	y	
6	FeS	None	Overnight	y			y		y	y	y
7	Pyrrhotite	None	Overnight				y		y		y
8	Pyrrhotite	None	Overnight			y			y	y	
9	Mackinawite	None	Overnight	y			y		y		y
10	Pyrrhotite	None	Overnight			y		y		y	
11	FeS	None	Overnight			y		y		y	
12	FeS	None	Overnight			y		y		y	
13	FeS	None	Overnight			y		y		y	
14	FeS	None	Overnight				y	y			y
15	FeS	None	Overnight		y			y		y	
16	FeS	None	Overnight		y			y		y	
17	FeS	None	Overnight		y			y		y	
18	FeS	None	Overnight		y			y		y	
19	FeS	None	Overnight		y			y		y	
20	FeS	Zn acetate	Overnight		y			y		y	
21	FeS	Ti(III) citrate	Overnight		y			y		y	
22–36	FeS	Ti(III) citrate	2.5 h		y			y		y	

FeS: freeze-dried precipitated, nanocrystalline FeS_m; mackinawite: microcrystalline FeS_m; pyrrhotite: Acros Organics™ 99.9% monoclinic pyrrhotite. S(-II) analyses: titration—back titration of Cu(II) with EDTA; colorometric—back titration of Cu(II) with NH_3; Fe(II) analyses: HCl—ferrozine method on HCl digestion; CrCl₂—ferrozine method CrCl₂ digestion after HCl digestion. Experiments 22–36 were performed on differentially dried FeS. S(-II) collected in $ZnCl_2$ and S(-II) from ZnS analysed with methylene blue (see text).

Na$_2$CO$_3$ (Zehnder and Wuhrmann, 1976; Rickard, 1997).

FeS$_m$ was made by reacting equimolar (NH$_4$)$_2$Fe (SO$_4$)$_2$·6H$_2$O and Na$_2$S·9H$_2$O. The ammonium salt was used because it reduces the rate of oxidation of Fe(II) in aqueous solution. The effect of the degree of washing was investigated although this is difficult to describe quantitatively. Thus, samples for analysis were *un-washed* (the filtered product was freeze-dried directly), *partially washed* (the filtered product was washed with D2 water during filtration on the original filter before freeze-drying) or *washed* (the filtered sample was re-suspended in 100 ml D2 water, shaken for 5 min and filtered. This process was repeated three times).

The material was freeze-dried and disaggregated into a fine powder using a pestle and mortar, transferred into a glass bottle which was wrapped in aluminum foil to prevent a static charge. Since there has been some discussion about the effects of freeze-drying on the material, as described above, the FeS$_m$ was freeze-dried for various lengths of time, up to 23 days.

The dissolution apparatus is shown in Fig. 1. It is modified from a design used by Newton et al. (1995) for the analysis of pyrite in sediments. The apparatus was assembled inside the anoxic chamber. Two CuCl$_2$ traps
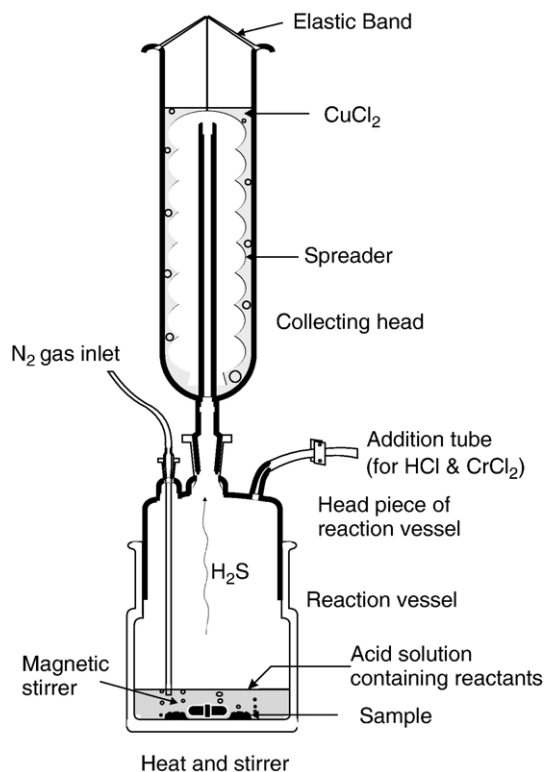
Table 2
Digestion procedures for FeS$_m$

Exp.	Reagent	Method
5	Cold 6 N HCl	Digestion in 20 ml 6 M HCl at room temperature
6,7,9,14	Hot CrCl$_2$	Digestion in 20 ml of 1 M CrCl$_2$ at 60 °C
11,12,13,23	Hot 6 N HCl	Digestion in 20 ml 6 M HCl at 60 °C
15–20	Hot 1.2 N HCl	Digestion in 20 ml 1.2 M HCl at 60 °C
21a	Hot HCl + Ti(III)	Digestion in 20 ml 6 M HCl or 1.2 M HCl with the addition of 5 ml of Ti(III) citrate

(containing 0.1 M CuCl$_2$, standardised against a 0.1 M EDTA standard solution) were used to collect evolved H$_2$S. Once inside the anoxic chamber, the bottom of the glassware was covered with either (1) 5 ml ethanol or (2) 2.5 ml Ti(III) citrate, to prevent the FeS$_m$ from sticking to the sides of the glassware and to wet the solid. The FeS$_m$ was spooned onto tiered aluminum foil using a metal spatula, the weight was recorded, and the sample was then added into the reaction vessel. A further 2.5 ml Ti(III) citrate was added to those digestions where this reagent was used, the glassware was sealed and taken out of the anoxic chamber. Two CuCl$_2$ traps (containing 0.1 M CuCl$_2$, standardised against a 0.1 M EDTA standard solution) were used to collect evolved H$_2$S. The CuCl$_2$ traps were attached to the reaction vessel and O$_2$-free nitrogen was passed through the apparatus at a rate of one bubble per second.

In experiments 5–21, various digestion procedures were investigated (Table 2). Typically, the FeS solution was then heated to 60 °C and stirred using a magnetic hotplate, 20 ml of deoxygenated 50% v/v HCl was added via the sample tube using a syringe. In experiments 6, 7, 9 and 14, the digested solution was sub-sampled with a syringe and a PEEK™ tubing needle before CrCl$_2$ was added.

The apparatus was usually left for 2.5 h to react. However, we examined prolonged overnight digestion in experiments 21 and 22. The overnight digestions did not prove any advantages and the 2.5 h digestion time was found to be optimal for the method. After 2.5 h, the H$_2$S was flushed from the system and precipitated as CuS.

After 2.5 h, the magnetic hotplate was turned off and the O$_2$-free N$_2$ gas supply stopped. The CuCl$_2$ traps were filtered into a 250 ml conical flask using Whatman number 1 filter paper and washed three times with D2 water. The Cu solution was made up 200 ml with D2 water and split into two equal 100 ml volumes, which were reacted with 70 ml of pH 5.5 buffer (1 M Na acetate), and

Fig. 1. Apparatus used for FeS$_m$ digestions.

five drops of Glycine Cresol red (*o*-cresolsulfonphthalein) indicator, which were then titrated with Fischer™ 0.1 M standard volumetric EDTA solution.

2.2. Chemical analyses

2.2.1. Sulfide analysis

In our system, we had relatively large concentrations of S(-II) and the conventional methylene blue method (Cline, 1969) and its derivatives are inappropriate. Analyzing the Cu remaining in solution in the traps had some advantages in that it did not include a further dissolution stage. In experiments 5–9, we also analyzed S(-II) colorometrically by back titration of the non-precipitated Cu. 1 ml of Cu solution from the H_2S traps was added to 50% NH_3 and the adsorbance measured with the Perkin Elmer Lambda 2 UV–VIS spectrophotometer at a wavelength of 600 nm. We found this method less precise than the EDTA titration.

We investigated replacing $CuCl_2$ in the H_2S traps with Zn acetate and used the methylene blue method to analyze the S(-II) in the precipitated ZnS in experiment 23. The recovery and reproducibility was less than using the $CuCl_2$ traps.

2.2.2. Iron analysis

The Fe solutions were washed into a 200 ml volumetric flask with MilliQ water and Fe was analysed by the ferrozine method (Stookey, 1970). 1 ml of this solution, 3 ml of 1.2 M Na acetate buffer (pH 4.5), 1 ml 0.5% $NH_2OH \cdot HCl$ and 1 ml 5×10^{-3} M Ferrozine® (the monosodium salt of 3-(2-pyridyl)-5,6-bis(4-phenylsulfonic acid)-1,2,4-triazine) were pipetted into a 50 ml volumetric flask and made up to the mark with MilliQ water. The Fe concentration was determined by measuring adsorbance at a wavelength of 562 nm Perkin Elmer Lamda 2 spectrophotometer against a blank and comparing with a standard curve.

2.2.3. Elemental analysis

In order to check for the presence of elements other than Fe and S in the precipitates, analyses of the material were also made with ThermoElemental X-series ICP-MS, JY Horiba Ultima-2 ICP-OES and an analytical SEM based on a Cambridge Instruments (LEO) S360 with an Oxford Instruments INCA ENERGY (EDX) X-ray analysis system and INCA WAVE (WDX) wavelength dispersive X-ray spectrometer.

2.2.4. Ion chromatography

Ion chromatography was used to analyse for anions other than sulfide. The sample was weighed into a sample tube, suspended in 10 ml of water and shaken for a couple of minutes. It was then filtered and the filtrate analysed on the DIONEX DX-80 Ion Analyser using a carbonate/bicarbonate eluent.

2.2.5. Solid-state NMR

NMR spectra of the freeze-dried FeS_m samples were investigated at the UK ESPRC Solid State NMR Centre at Durham University, UK. The samples were heat sealed in glass ampoules under vacuum which were packed with a blank into the rotors. The samples were spun directly in the ampoules without opening after 48 h in the ampoule. The solid-state NMR work was carried out using a Varian Unity Inova spectrometer operating at 299.82 MHz for 1 H. Spectra were recorded using a direct-polarisation pulse sequence and magic-angle spinning. Sample spin-rates of approximately 3 kHz were used along with a 5 s recycle delay between pulses. Spectral referencing was with respect to tetramethylsilane.

2.2.6. Thermogravimetric analysis (TGA)

TGA of the FeS_m samples were carried out on a Thermo Analysis Instruments SDTQ 600. Ceramic crucibles were placed on the TGA instrument, tarred to zero and then the sample added under N_2 gas, where appropriate. The furnace was slid over the samples and they were heated under a nitrogen atmosphere. For comparison, some samples were weighed and heated in air. The samples were run on a series of heating programs ranging over durations from 6 to 420 min and from room temperature to 180 °C. The temperature was ramped up to 40°C and then stepped in 10°C intervals to either 110 °C or 180 °C. The FeS_m results were compared with runs with Acros Organics™ 99.9% monoclinic pyrrhotite. Samples were routinely checked before and after TGA runs by XRPD, using a Phillips PW1710 automated X-ray powder diffractometer equipped with a GTP Engineering low range environmental chamber and operated at operated at 35 kV, 40 mA, Cu-Kα radiation.

2.2.7. Thermogravimetric-mass spectrometry (TGA-MS)

TGA-MS measurements were carried out using a Netzsch TG-209 by coupling the TG-cDTA system connected via through an adapter head in the Netzsch TG-209 gas outlet via and a 200 °C heated capillary to a Netzsch Aeolos QMS 403C quadrupole mass spectrometry system (*m/z* range 10–300). Samples were loaded into alumina crucibles (sample mass approximately 20 mg) under argon as a precaution to prevent oxidation. The experimental conditions were: heating rate of 30 °C min^{-1} from 20 to 500 °C, under flowing helium (50 cm³

min^{-1}), Al_2O_3 crucible, with an approximate sample mass of up to 20 mg. For MS analysis, the evolved gas was sampled and analyzed by the mass spectrometer throughout the course of the heating process. Mass/charge (m/z) values from 10 to 300 were collected. The number of m/z signals selected gave a temporal resolution of 10 s corresponding to a temperature change of approximately 2 °C. The signals were exported to the NETZSCH software for analysis versus temperature. In order to compare the relative intensity of m/z peaks for different samples, the signals from the QMS were normalised to the total intensity.

2.3. Uncertainty

The concentration of Fe(II) in the analyzed samples was measured using standard curves of adsorption versus concentration of Fe(II) in $(NH_4)_2Fe(SO_4)2 \cdot 6H_2O$ solutions. The square of the Pearson product moment correlation (R^2) for the ferrozine method was 0.9987 ($n=20$) and the standard error estimate was 6.15×10^{-8} M. The Fe sample was 1 ml from a 20 ml digestion volume made up to 50 ml total. The total Fe dissolved in a 50 mg sample of FeS_m was 32×10^{-3} g, so the analytical error of the method is 0.002%. The average standard deviation of Fe analyses in 14 sets of 4 repeated analyses of FeS_m samples was 2.56%. This is far greater than the uncertainty in the analyses themselves and therefore is mainly due to errors in the sampling and digestion procedures.

Sulfide analyses were made by back titration of Cu against EDTA. The 1 σ errors in Cu concentration were less than 0.01%. The EDTA solution was standardised by titration against $CuSO_4$. The 1 σ error in the EDTA solution was less than 0.01%. The precision of the sulfide analyses was determined by digestions and analyses of a Sigma-Aldrich™ standard 99.99% pure ZnS. The average analysed recovery of S(-II) was 99.51% ($n=4$) with a standard deviation of 0.86%. The average standard deviation of 4 repeated analyses of S in 14 FeS_m samples was 1.58%. This compares with the average S.D. of the S(-II) analyses of the ZnS standards, and we conclude that the digestion method for FeS_m is quantitative.

The absolute uncertainty is the square root of the sum of the squares of the absolute uncertainties of the individual measurements. The individual measurements are the analyses of Fe and S and the absolute uncertainty in the analysis of FeS, σ(FeS), is given by

$$\sigma_{(FeS)} = \sqrt{\sigma_{(Fe)}^2 + \sigma_S^2}$$

where $\sigma_{(Fe)}$ is the standard deviation of the Fe analyses and $\sigma_{(S)}$ is the standard deviation of the S analyses. In terms of the measured σ values, this means that $\sigma_{(FeS)}$ is 3% or ±0.03 in the mole ratio.

The precision of the FeS analyses can be estimated from the repeated analyses of the samples. The standard deviation of the mole ratio of Fe/S in 10 sets of 4 repeat analyses of FeS samples varied between 0.040 and 0.007 with an average of 0.027 which is similar to the calculated absolute analytical uncertainty. The estimated uncertainty in the mole ratio of FeS is therefore generally 0.03 but the uncertainty for analyses of pure FeS_m samples decreases to ±0.01.

3. Results

3.1. Dissolution of FeS_m

Analytical results are summarised in Table 3. Dissolution of freeze-dried FeS_m in cold 6 N HCl gave a recovery of 52.25% (experiment 5). This was increased somewhat to 61.75% and 87.77% with $CrCl_2$ (experiments 6 and 14). No significant difference was found in the recovery from the nanoparticulate material or the microcrystalline material prepared electrolytically (experiment 9.). Three samples of freeze-dried FeS_m were dissolved in hot 6 N HCl (experiments 11, 12 and 13). The recovery varied between 51.96% and 91.09%. Note also that the standard deviation of repeated runs varied up to 13.07%. We conclude that dissolution of FeS_m in hot 6 N HCl or hot $CrCl_2$ gives irreproducible results with a significant, but variable, loss of material.

The problem appeared to be the sulfur analyses. We noted that, in some digestions, a black, fine-grained precipitate remained after digestion. We had assumed that this material was undigested FeS_m. However, XRPD analysis revealed that this material is rhombic sulfur. The formation of sulfur during the digestion means that the sulfide analysis would be underestimated. Once formed, sulfur is difficult to digest by inorganic methods.

The production of sulfur appeared to be erratic and we investigated whether the use of relatively strong acid would cause local pH lows in the reaction vessel resulting in sulfur formation. We made a series of digestions with a more dilute acid, hot 1.2 N HCl (experiments 15–20). The results showed improved recovery between 82.52% and 99.68% with standard deviations between 2.01% and 5.37%. However, the results overall were disappointing. For 21 digestions of 6 different samples, the average recovery was just

Table 3
Results of FeS$_m$ digestions

Exp.	Digestion type	n	FeS	Fe		S		Total		Fe/S	
			mg	wt.%	S.D.	wt.%	S.D.	wt.%	S.D.	Mole ratio	S.D.
5	Cold 6 N HCl	4	164	35.25	7.59	17.00	2.94	52.25	6.13	1.23	0.37
6	Hot CrCl$_2$	4	209	40.00	2.16	21.75	2.06	61.75	2.36	1.06	0.13
9	Hot CrCl$_2$	2	66	52.00	2.83	12.00	1.41	64.00	4.24	2.49	0.16
11	Hot 6 N HCl	4	77	36.59	1.51	15.36	0.55	51.95	2.05	1.36	0.01
12	Hot 6 N HCl	2	67	49.64	7.77	26.18	6.26	75.82	13.96	1.08	0.04
13	Hot 6 N HCl	4	63	60.38	2.29	30.71	5.95	91.09	6.92	1.12	0.32
14	Hot CrCl$_2$	4	52	53.14	1.60	34.64	2.31	87.77	2.90	0.88	0.06
15	Hot 1.2 N HCl	4	47	55.52	2.46	27.00	0.96	82.52	2.91	1.18	0.06
16	Hot 1.2 N HCl	4	53	56.64	1.72	34.18	3.65	90.82	5.34	0.95	0.07
17	Hot 1.2 N HCl	2	53	58.23	0.97	36.00	1.28	94.23	2.01	0.92	0.03
18	Hot 1.2 N HCl	3	62	60.67	0.73	35.88	5.16	96.55	4.73	0.98	0.16
19	Hot 1.2 N HCl	4	54	59.50	2.35	40.18	0.87	99.68	2.96	0.85	0.03
20	Hot 1.2 N HCl	4	50	54.51	2.90	33.06	3.21	87.57	5.48	0.95	0.06
21a	Hot 6 N HCl+Ti(III)	2	54	54.40	0.80	29.61	0.63	84.01	0.17	1.05	0.04
21b	Hot 1.2 N HCl+Ti(III)	2	52	54.59	0.84	30.41	1.05	85.00	1.10	1.00	0.06
22a	Hot 6 N HCl+Ti(III)	2	47	56.11	3.45	35.32	3.01	91.43	6.46	0.91	0.02
22b	Hot 1.2 N HCl+Ti(III)	2	49	56.95	1.35	37.82	2.57	94.77	3.92	0.86	0.04

91.45% and the standard deviation was 7.23%. This equates to an average composition of Fe$_{0.979}$S with a standard deviation of 0.128 (i.e. Fe$_{0.851}$S to Fe$_{1.107}$S). That is, the analytical results are so imprecise that it is not possible to determine whether the FeS$_m$ is Fe-rich (i.e. Fe$_{1+x}$S) or Fe-poor (i.e. Fe$_{1-x}$S). We assumed that the problem with sulfur formation during the digestion was not resolved by using a more dilute acid, although it was somewhat ameliorated.

We suppressed the formation of sulfur by the addition of Ti(III) citrate. We had shown previously (Rickard, 1997) that Ti(III) citrate did not interfere significantly with sulfide analyses and, as noted above, our controls during this investigation confirmed this conclusion. We tried Ti(III) citrate with both hot 1.2 N HCl (experiments 21b and 22b) and with hot 6 N HCl (experiments 21a and 21b). The results showed no significant difference

in the recovery but no sulfur was observed to form during the process.

3.2. Analysis of FeS

The analyses of the material with ICP-MS, ICP-OES and analytical SEM showed no significant concentrations of elements other than Fe and S. Of course, oxygen and hydrogen are not readily analyzable by these methods. However, the results show that the FeS does not contain significant amounts of N, which might be expected from NH$_3$ derived from the (NH$_4$)$_2$Fe (SO$_4$)$_2$·6H$_2$O used in the synthesis, Na (from the Na$_2$S), Cl (from the HCl in the dissolution), Ti or C (from Ti citrate).

We stored FeS$_m$ which had been freeze-dried for 6 days, for periods between 6 and 23 days in the N$_2$-

Table 4
Effect of storage of freeze-dried FeS$_m$

	Storage days	n	Fe		S		Total		Fe/S	
			wt.%	S.D.	wt.%	S.D.	wt.%	S.D.		S.D.
27	6	4	45.71	6.82	26.91	4.12	72.62	10.52	0.98	0.08
28	7	2	49.51	8.97	29.93	4.38	79.44	13.29	0.95	0.04
29	8	4	46.50	1.54	28.03	0.46	74.52	1.93	0.95	0.02
30	9	4	50.75	0.57	30.58	0.79	81.33	0.88	0.95	0.03
31	12	4	56.10	1.62	32.88	0.72	88.98	1.51	0.98	0.04
32	14	4	56.10	1.62	32.88	0.72	88.98	1.51	0.98	0.04
33	16	4	57.79	0.47	33.85	0.74	91.64	0.66	0.98	0.03
34	19	4	61.00	0.85	34.82	0.47	95.82	0.72	1.01	0.02
35	21	4	61.84	0.41	35.55	0.21	97.40	0.47	1.00	0.01
36	23	4	63.55	0.42	36.16	0.17	99.71	0.51	1.01	0.01

filled MBraun Labmaster 130 anoxic chamber with O_2 levels maintained at less than detectable levels (<1 ppmv) and H_2O at less than 100 ppm (Table 4). These experiments showed that the recovery increased systematically from 72.62% to 99.08% after 23 days. This standard deviation is within the analytical error. The results listed in Table 4 show: (1) the accuracy of the analyses increases asymptotically with time as indicated by the totals; (2) the precision of the analyses increases asymptotically with time as indicated by the standard deviations. The results plateau out after 19 days storage and show that the composition of the material is $Fe_{1.00}S$ with a standard deviation ($n=12$) of 0.015.

However, solid-state NMR analyses of the FeS_m showed no signal. The results suggested that no significant H_2O was present in any of the samples. The complete lack of signal can also be a result of line-broadening due to electronic interaction. The electronic properties of mackinawite are not well defined. It is expected to show unusual electronic properties because of its structure but no actual measurements have been made. Therefore, it is possible that some electronic effect was masking an H_2O signal.

The results of TGA analyses of FeS_m are summarised in Table 5. Although a weight loss was observed, there is little evidence to support the hypothesis that this weight loss was due to H_2O. Runs done on the pyrrhotite standard showed no phase changes up to 180 °C and a maximum 0.3% weight loss, even when the sample was loaded in air. The small weight loss is consistent with evaporation of surface water resulting from adsorption of atmospheric H_2O during storage. Heating the FeS_m to 180 °C resulted in a phase change to greigite and a greater weight loss. However, there was no difference in weight loss between FeS_m samples dried for 4 or

Table 5
The results of TGA analyses of FeS_m and pyrrhotite (Acros Organics™ 99.9% monoclinic pyrrhotite)

	Sample	Freeze-dried (days)	Atmosphere	Heating time (min)	Temp. (°C)	Wt. loss (%)
37	FeS_m	4	Air	6	110	3.5
38	FeS_m	4	Air	10	180	4
39	FeS_m	18	Air	6	110	4
40	FeS_m	18	Air	10	180	4
41	FeS_m	18	Air	12	110	5
42	FeS_m	18	Air	120	180	17
43	FeS_m	18	N_2	12	110	5
44	FeS_m	18	N_2	120	180	17
45	FeS_m	18	N_2	420	180	13
46	Pyrrhotite	0	Air	12	110	0.3
47	Pyrrhotite	0	Air	120	180	0.15

Table 6
Effect of washing FeS precipitates showing the effect of sulfate on the totals and the reproducibility of the analyses

	Sample	Fe (wt.%)	S (wt.%)	(Fe+S) (wt.%)	SO_4 (wt.%)	Total (wt.%)
Unwashed	37a	37.02	28.17	65.19	29.71	94.90
	37b	43.41	32.01	75.42	25.35	100.77
	37c	36.88	29.34	66.22	27.02	93.24
	Average	39.10	29.84	68.94	27.36	96.30
	S.D.	3.73	1.97	5.63	2.20	3.95
Washed	38a	60.74	34.77	95.51	4.01	99.52
	38b	59.95	36.34	96.29	3.11	99.40
	Average	60.35	35.56	95.90	3.56	99.46
	S.D.	0.56	1.11	0.55	0.63	0.08

18 days. The weight loss of the FeS_m samples in runs up to 110 °C, where there was no major phase change, was between 3.5% and 5%, independent of whether the samples were exposed to air before being heated and independent of the sample drying time. The weight began to decrease from 40 °C, which again suggests that it is not structural H_2O that is being lost.

In order to confirm this, TGA-MS analyses of the samples were made. The mass spectra showed small distinct m/z peaks at 48 and 64 and no evidence for the characteristic H_2O peaks (m/z 18). This confirms that the small weight loss of the TGA is not water and that significant H_2O does not occur in FeS_m. The m/z peaks at 48 and 64 would be equivalent to SO and SO_2, respectively, suggesting that sulfur oxides were included in the material. The peak at 64 is also consistent with S_2 and might be expected through phase changes in heating FeS_m to 500 °C (although this is less likely as m/z 32 was not observed).

Ion chromatograph analyses (Table 6) demonstrated that the dried precipitates contained substantial and variable contents of sulfate. We found that the sulfate could be removed by washing. Simple washing, as described above, removed part of the sulfate but intensive washing, involving re-suspension of the

Table 7
Composition of FeS_m from six analyses of well-washed precipitates with no measurable included sulfate

	Fe (wt.%)	S (wt.%)	Total (wt.%)	Composition
39	63.04	37.4	100.44	$Fe_{0.97}S$
40	61.47	36.51	97.98	$Fe_{0.97}S$
41	62.01	35.47	97.48	$Fe_{1.00}S$
42	62.33	35.99	98.32	$Fe_{0.99}S$
43	65.04	37.55	102.59	$Fe_{0.99}S$
44	62.62	36.64	99.26	$Fe_{0.98}S$
Average $n=6$	62.75±1.24	36.59±0.80	99.35±0.02	$Fe_{0.98±0.02}S$

precipitate in D2 H$_2$O three times removed almost all the sulfate.

The analyses of well-washed freeze-dried FeS$_m$ produce reproducible analyses with totals approaching 100 wt.%. The composition of analyses of six samples from two syntheses (Table 7) show a composition Fe$_{0.98 \pm 0.02}$S. The result of the well-washed samples are similar to those of the samples stored for at least 19 days.

4. Discussion

4.1. Nature of FeS$_m$

The FeS$_m$ investigated in this experimentation is similar to the FeS$_m$ characterised by Wolthers et al. (2003) and imaged by Ohfuji and Rickard (2006). This material is precipitated directly from aqueous solution and has the form of nanoparticulate FeS$_m$. Wolthers et al. (2003) and Michel et al. (2005) showed that drying precipitated FeS$_m$ preserves the initial structure, although Ohfuji and Rickard (2006) demonstrated a small (ca. 2%) shrinkage in the cell dimensions. The freeze-drying technique used by Wolthers et al. (2003) and Ohfuji and Rickard (2006) is the same as that used in the present experimentation. Wolthers et al. (2003) showed that putting the freeze-dried material back into solution resulting in the crystallisation process continuing. That is, the freeze-drying process stops the further evolution of the material. The FeS$_m$ investigated in this experimentation is about the most primitive form that can be investigated by conventional means. By the time synthesis, filtration and freezing is completed the material is about 20 min old. In this experimentation, we routinely continued the freeze-drying process for 6 days—but the material is still 20 min old FeS$_m$. Subsequent aging of this FeS$_m$ took place at room temperature in an anoxic atmosphere in the presence of <100 ppm water vapour. The results showed that FeS$_m$ continued to develop in this environment up to 20 days.

4.2. Dissolution of FeS$_m$

The problem with the determination of the chemical composition of FeS$_m$ centers on the deconvolution of the problems caused by digestion procedures and the uncertainties intrinsic to the composition of the material itself. Our observation that the black material remaining after some digestions is not remnant FeS$_m$ but rhombic sulfur explains much of the problem with the conventional acid digestion procedure. These experiments were also performed in strict anoxic atmospheres with O$_2$ levels below detection (1 ppmv). Even the freeze-drying

was carried out within sealed vessels taken from the anoxic chamber, attached to the manifold of an already evacuated and purged freeze-dryer and opened to that vacuum. After drying the freeze-drier was purged and flooded with O$_2$-free N$_2$, the sample sealed off and then removed from the manifold and passed back into the anoxic chamber. This means that the formation of rhombic sulfur is not caused by O$_2$-oxidation of the material. The reasons for the formation of S(0) are indicated in Fig. 2. This conventional equilibrium diagram approximates to the conditions experienced in the experimental system during the dissolution of FeS$_m$. The area of rhombic sulfur stability is clearly coincident with these conditions. The addition of Ti(III) citrate reduces the Eh such that S(0) is no longer stable and does not form. The diagram also suggests that decreasing the acid concentration would reduce the span of S(0) stability zone increasing the chance of S(0) not forming. However, as can be seen from the diagram, this effect is likely to be minor which is consistent with our experimental observations. Varying acid concentrations do not give reproducible digestions.

Intuitively, it would be thought that iron(II) monosulfides dissolve quantitatively in mineral acids. In fact, this is not the case. We recovered 84.50% Fe and S from pyrrhotite dissolution in hot 6 N HCl (experiment 10, Table 1). The Fe/S ratio was 1.252. This iron-rich result from Fe$_{1-x}$S indicates that the error in the pyrrhotite analyses is largely a result of the formation of rhombic
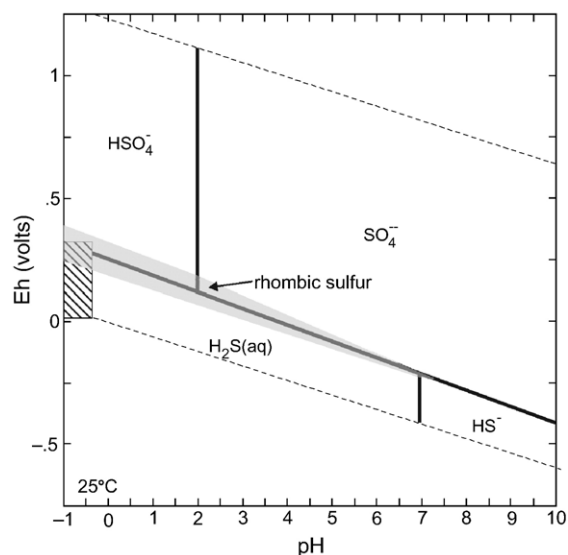

Fig. 2. Conventional pH–Eh equilibrium diagram for sulfur species at 25 °C and 1 atm pressure. The conditions of the FeS$_m$ dissolution environment are hatched (total S=0.03 M, HCl=6 M) and range down to the presence of Ti(II) citrate with Eh→0 V at pH<0. Computed with GWB Act 2.

sulfur and a consequent underestimate of the S(-II) content of the material.

Again, it would be conventionally assumed that nanoparticulate mackinawite would dissolve more readily than crystalline pyrrhotite because of the increased in free energy provided by the enhanced surface area. In fact, this is not the case. Nanoparticulate mackinawite can give recovery rates as low as 52% (experiment 11) with hot 6 N HCl. In other words, the reaction to form sulfur may be more efficient in the hot acid digestion reaction of the nanoparticulate material. This appears to be a kinetic effect, since the influence of an increase of the temperature between 25 and 60 °C on the equilibrium diagram (Fig. 2) is experimentally insignificant.

The fact that mackinawite, even in its nanoparticulate form, is not quantitatively soluble in mineral acids is implied in the reports of Polushkina and Sidorenko (1963), Cornwell and Morse (1987), and Allen and Parkes (1995). Cornwell and Morse (1987) analyzed wet FeS-S and corrected for water contents by weight loss on drying at 65 °C overnight. They reported 100% recovery in hot and cold HCl between 1.0 and 6.0 N for FeS-S and $100 \pm 4\%$ recovery for mackinawite-S, except for cold 1 N HCl which only recovered 92%. However, the Fe content is not reported and the recovery efficiency appears to have been measured against a theoretical stoichiometric composition for mackinawite and FeS. Polushkina and Sidorenko (1963) and Allen and Parkes (1995) found that only $81 \pm 3\%$ of the iron(II) monosulfide was recovered in hot 6 M HCl digestions over 1 h and $104 \pm 14\%$ recovered in cold 6 M HCl digestions over 1 h.

The observation and identification of sulfur as a product of the acid dissolution of FeS_m even in O_2-free atmospheres is interesting. The results suggest that simple acid dissolution of natural materials in the absence of a reducing agent is likely to produce erratic results and that this effect is likely to be enhanced in acid dissolutions in the presence of air. The problem is that sulfur, once formed, will not easily be digested and the resulting analysis will provide an underestimate of the sulfide content of the material. This means that the totals of Fe and S(-II) analyses will also not approach 100% for this material and it is not possible to estimate the contribution of the varying amounts of sulfur formation. In terms of sediments, of course, any sulfur formed artefactually by the acid dissolution process will contribute finally to the pyrite analysis (Morse and Rickard, 2004).

Cornwell and Morse (1987) noted that the recovery efficiency of FeS-S from dried FeS_m was less than that of wet FeS_m. This seems to be a general observation.

The reasons are unknown. We have noted that dried FeS_m has a strong static charge and it may be that this contributes to a difficulty in wetting the sample. We overcame this by the use of Al-foil.

4.3. Hydration of FeS_m

There are at least three possible types of water present in FeS_m precipitated from aqueous solution: (1) interparticle water, which should be readily removed on drying, (2) surface adsorbed water, which may not be as labile as the interparticle water, and (3) structural water, which is water held between the Fe–Fe sheets in the mackinawite structure. Much of the reported evidence for H_2O in FeS_m is circumstantial, even if it is often persuasive. The fundamental mechanism of the formation of FeS_m from aqueous solution involves the expulsion of H_2O (Rickard, 1995) and, intuitively, one might expect some part of this H_2O to be trapped in the rapidly forming initial precipitate. However, the results of our analyses clearly demonstrate that H_2O is not present as structural H_2O in FeS_m. FeS_m is not a hydrate. Although Michel et al. (2005) could find no significant differences between dried FeS_m, precipitated FeS_m and the bulk material within the precision of their method, Ohfuji and Rickard (2006) clearly showed by direct observation that drying resulted in a tightening of the FeS_m lattice by ca. 2% and that the resultant material had lattice dimensions which were ca. 1% larger than those of the bulk material. This result is consistent with the trends in Wolthers et al.'s original analyses although rather smaller. Kornicker's (1988) original observation that drying changes the physical properties of the material may therefore have some basis in fact.

However, we show that the analytical results can be misleading. The analytical totals of synthetic FeS_m can be both erratic and very much less than 100 wt.%. Elemental analysis shows that no other elements other than Fe, S, O and H are present in the material and XRD shows no other crystalline phase. We also found, oddly, that long-term storage of FeS_m in a relatively dry anoxic atmosphere resulted in a steady increase in the analytical totals with time. This increase is coincident with a steady approach of the Fe/S ration to 1.0. All these features might suggest, as Kornicker (1988) originally suggested, that FeS_m is a hydrate.

In fact, our results show conclusively that FeS_m is not a hydrate. We found no evidence of water in freeze-dried FeS_m with either NMR or TGA-MS and the TGA weight loss was also not consistent with an FeS hydrate. It is fairly obvious that H_2O will be present in wet FeS_m, both as intraparticle water and as water adsorbed on the

FeS_m surface. But both forms of water are readily removed by freeze-drying.

Our youngest FeS_m is 20 min old. Therefore it is possible that H_2O is contained in the first formed condensed FeS phase and is rapidly expelled (within 20 min). However, the dimension of the 20 min phase has been shown to include FeS_m particles as small as 2 nm in size, equivalent to just 150 FeS molecules, and it seems unlikely that a smaller condensed phase including structural water occurs. As pointed out by Luther and Rickard (2005), the main difference between the aqueous FeS clusters that form in solution prior to the nucleation of the solid phase, and the solid phase itself is a discontinuous increase in density. The increase in density results essentially from the expulsion of H_2O in the nucleation of FeS_m.

4.4. Composition of FeS_m

The mackinawites analysed from the ore parageneses may contain large amounts of metal ions other than Fe (II) and are uniformly non-stoichiometric with a metal-rich composition $(Fe,M)_{1+x}S$ where M represents metals like Ni, Cu, Co and Cr. By analogy with pyrite, the reported non-stoichiometry is probably more closely related to the incorporation of other metals rather than intrinsic structural parameters.

Both synthetic and natural mackinawites formed by the reaction between Fe reactants and S(-II) from aqueous solutions around ambient temperatures and pressures are essentially pure FeS phases, with limited to negligible contents of other metals. Indeed, reports of other metals in these materials are probably the results of the admixture of discrete nanoparticulate metal sulfides rather than true solid solutions.

The problem has been that previously reported chemical analyses of these precipitated mackinawites have not produced analytical results that can be robustly interpreted in terms of composition. Thus, for example, in the case of the hot acid digestions, the ca. 80% recovery would place a considerable uncertainty on the computed composition of the FeS_m well outside the generally accepted range of non-stoichiometries. In the case of the cold acid digestions, the $\pm 14\%$ standard deviation of the recovery suggests a range between 90% and 118% recovery. The result is a spread of analyses over 28%, which means a lack of reproducibility of the analyses. The 28% recovery range seems to be consistent with the reported spread of FeS_m compositions in the literature and the range extends from S-deficient to S-excess compositions. It is noteworthy that 6 repeated analyses with hot 6 N HCl (experiments 12

and 13) gave apparent analyses which were consistently Fe-rich with formulations between $Fe_{1.083}S$ and $Fe_{1.124}S$. The cause of this apparent Fe-enrichment was the underestimation of the S(-II) content due to sulfur formation. The results are similar to $Fe_{1.1}S$ sometimes reported in the literature. e.g. Sweeney and Kaplan (1973).

In the present investigation, we have been able to deconvolute the effects of digestion chemistry and we can therefore determine the composition of pure mackinawite with a relatively high precision. Our results show that well-washed freeze-dried FeS_m has a composition indistinguishable from $Fe_{1.0}S$. We also show that FeS_m aged in an essentially anhydrous anoxic atmosphere at room temperature will also display a stoichiometric $Fe_{1.0}S$ composition. The 1σ analytical uncertainty in the analysis of the aged material is 0.01 giving a composition of $Fe_{1.00 \pm 0.01}S$. The 1σ analytical uncertainty in the well-washed material is 0.02 and the composition is $Fe_{0.98 \pm 0.02}S$.

In our experimental system, the FeS_m precipitates included substantial sulfate from the $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$ used in the synthesis. We found no equivalent concentrations of any counter ion, such as Na^+ in the material. Furthermore, the sulfate-containing phase did not appear on any XRD analysis and therefore is not a well-crystalline material. The most interesting result was that storage in an anhydrous anoxic atmosphere resulted in the disappearance of the sulfate contaminant over 19 days. These observations suggest that the sulfate was a form of H_2SO_4 which was produced during the initial drying of the FeS precipitate on evaporation of the sulfate solution remaining after the removal of Fe(II) (as FeS_m) from the $(NH_4)_2Fe(SO_4)_2$ solution. The phase diagram for H_2SO_4 is complex and several phases are possible. H_2SO_4 hydrates were probably crystallised out first on initial evaporation followed by the formation of anhydrous H_2SO_4 on freeze-drying. Anhydrous H_2SO_4 has a melting point of 10.4 °C so that the crystalline form would be stable during freeze-drying. At room temperature, it would be in liquid form and would therefore not appear on conventional XRD analyses even if it did not evaporate completely. Storage of FeS_m for extended time periods in a low H_2O atmosphere at temperatures > 10 °C simply gradually removed the H_2SO_4 as a vapour. Increasing the H_2O content, by thorough washing and repeated resuspension in excess H_2O, dissolved it. The presence of H_2SO_4 is unlikely to have had any other significant affect on the analyses through, for example, acid dissolution of the FeS_m. The only stage in the process where any component could be lost from the system was during the addition of FeS_m to the reaction vessel in the

anoxic cabinet prior to sealing. During this stage, the added solvent was either ethanol or Na_2CO_3-buffered Ti (III) citrate, neither of which would release significant quantities of strong acid on reaction with H_2SO_4 in the FeS_m.

It is probable that the anions from any Fe salt used in the synthesis of FeS_m would also appear in the product on evaporation of the aqueous solution. The problem here is that other Fe salts are often difficult to control in terms of Fe oxidation and this introduces a further error.

5. Conclusions

We conclude that the FeS formed at ambient temperatures from aqueous solutions is stoichiometric $Fe_{1.0}S$ and has a mackinawite structure. Our results explain previous reports by Berner (1962b), and Polush-kina and Sidorenko (1963), Rickard (1969), Ward (1970), Sweeney and Kaplan (1973), Cornwell and Morse (1987), Allen and Parkes (1995), Rickard (1997) and Lennie et al. (1997). They are consistent with structural observations by Lennie et al. (1997), Wolthers et al. (2003), Michel et al. (2005) and Ohfuji and Rickard (2006).

Previous reports of mackinawite non-stoichiometry have been caused by:

- The inclusion of other metals in natural mackinawites from ore associations.
- The problem of acid dissolution of FeS_m which can result in the formation of significant but erratic amounts of sulfur.
- The formation of other salts during evaporative drying of FeS_m.

We show that FeS_m is not a hydrate. Previous reports of possible structural water in FeS_m are due to the features listed above.

The behavior of FeS_m on acid dissolution is of some concern in environmental studies. In many published reports of the acid volatile sulfide (AVS) content of sediments, only the S(-II) fraction is analysed. Our results suggest that these analyses, if performed in the absence of a reducing agent, are likely to underestimate the acid volatile sulfide content and to give poor reproducibility. The rhombic sulfur formed artefactually during such a digestion may contribute to the pyrite sulfur pool, if a sequential chromic acid digestion is performed on the solid material remaining after digestion in mineral acids. We also note that the exposure of the material to air at any stage during acid digestion is likely to enhance the problem. The underestimation of the AVS-S content of sediments and natural waters will contribute a degree of uncertainty to the simultaneously extracted metal-AVS (SEM-AVS) method of estimating potential toxicity of trace metals in the environment.

The nature of natural sedimentary mackinawite, however, remains largely unknown. It is relatively rarely observed directly in marine sediments (Rickard and Morse, 2005) and its analysis by classical chemical methods would prove difficult. The data in this investigation suggest that the initial phase is likely to be anhydrous, stoichiometric $Fe_{1.0}S_m$.

Acknowledgements

References

Allen, R.E., Parkes, R.J., 1995. Digestion procedures for determining reduced sulfur species in bacterial cultures and in ancient and recent sediments. In: Vairavamurthy, A., Schoonen, M.A.A. (Eds.), Geochemical Transformations of Sedimentary Sulfur. American Chemical Society, Washington, DC, pp. 243–259.

Bagander, L.E., Carman, R., 1994. In situ determination of the apparent solubility product of amorphous iron sulphide. Appl. Geochem. 9, 379–386.

Berner, R.A., 1962a. Tetragonal iron sulfide. Science 137, 669.

Berner, R.A., 1962b. Iron sulfides formed from aqueous solution at low temperatures and atmospheric pressure. J. Geol. 72, 293–306.

Berner, R.A., 1970. Sedimentary pyrite formation. Am. J. Sci. 268, 1–23.

Cline, J.D., 1969. Spectrophotometric determination of hydrogen sulfide in natural waters. Limnol. Oceanogr. 14, 454–458.

Cornwell, J.C., Morse, J.W., 1987. The characterization of iron sulfide minerals in marine sediments. Mar. Chem. 22, 193–206.

DiToro, D.M., Mahony, J.D., Hansen, D.J., Scott, K.J., Hicks, M.B., Mayr, S.M., et al., 1990. Toxicity of cadmium in sediments: the role of acid volatile sulfide. Environ. Toxicol. Chem. 9, 1487.

Evans Jr., H.T., Milton, C., Chao, E.C.T., Adler, I., Mead, C., Ingram, B., et al., 1964. Vallerite and the new iron sulfide, mackinawite. USGS Professional Paper 475-D, 64–69.

Kornicker, W.A., 1988. Interactions of divalent cations with pyrite and mackinawite in seawater and NaCl solutions. PhD Dissertation, Texas A&M University, unpublished.

Kuovo, O., Vuorelainen, Y., Long, J.V.P., 1963. A tetragonal iron sulfide. Am. Mineral. 48, 511–524.

Lennie, A.R., Redfern, S.A.T., Schofield, P.F., Vaughan, D.J., 1995. Synthesis and Rietveld crystal structure refinement of mackinawite, tetragonal FeS. Mineral. Mag. 59, 677–683.

Lennie, A.R., Redfern, A.T., Champness, P.E., Stoddart, C.P., Schofield, P.F., Vaughan, D.J., 1997. Transformation of mackinawite to greigite: an in situ X-ray powder diffraction and transmission electron microscope study. Am. Mineral. 82, 302–309.

Luther, G.W., Rickard, D., 2005. Metal sulfide cluster complexes and their biogeochemical importance in the environment. J. Nanopart. Res. 7, 389–407.

Luther, G., Meyerson, A., Krajewski, J., Aires, R., 1980. Metal sulfides in estuarine sediments. J. Sediment. Petrol. 50, 1117–1120.

Meyer, F.H., Riggs, O.L., .McGlasson, R.L., Sudbury, J.D., 1958. Corrosion of mild steel in H_2S environments. Corrosion 14, 109.

Michel, F.M., Antao, S.M., Chupas, P.J., Lee, P.L., Parise, J.B., Schoonen, M.A.A., 2005. Short- to medium-range atomic order and crystallite size of the initial FeS precipitate from pair distribution function analysis. Chem. Mater. 17, 6246–6255.

Morse, J.W., Rickard, D., 2004. Chemical dynamics of sedimentary acid volatile sulfide. Environ. Sci. Technol. 38, 131A–136A.

Morse, J.W., Millero, F.J., Cornwell, J.C., Rickard, D., 1987. The chemistry of hydrogen sulfide and iron sulfide systems in natural waters. Earth-Science Reviews 24, 1–42.

Neretin, L.N, Böttcher, M.E., Jørgensen, B.B., Volkov, I.I., Lüschen, H., Hilgenfeldt, K., 2004. Pyritization processes and greigite formation in the advancing sulfidization front in the Upper Pleistocene sediments of the Black Sea. Geochim. Cosmochim. Acta 68, 2081–2093.

Newton, R.J., Dean, S.H., Hatfield, S.P., Raiswell, D., 1995. An evaluation of the use of the chromous chloride reduction method for isotopic analysis of pyrite in rocks and sediments. Chem. Geol. 125, 317320.

Ohfuji, H., Rickard, D., 2006. High resolution transmission electron microscopic study on synthetic nanocrystalline mackinawite. Earth Planet. Sci. Lett. 241, 227–233.

Polushkina, A.P., Sidorenko, G.A., 1963. Melnikovite as a mineral species, Zapiski Vseross. Mineral. Obshch. 92, 547–554 (in Russian).

Posfai, M., Buseck, P.R., Bazylinski, D.A., Frankel, R.B., 1998. Reaction sequence of iron sulfide minerals in bacteria and their use as biomarkers. Science 282, 880–883.

Rickard, D., 1969. The chemistry of iron sulfide formation at low temperatures. Stockh. Contrib. Geol. 20, 67–95.

Rickard, D., 1995. Kinetics of FeS precipitation. 1. Competing reaction mechanisms. Geochem. Cosmochim. Acta 59, 4367–4379.

Rickard, D., 1997. Kinetics of pyrite formation by the H_2S oxidation of iron(II) monosulfide in aqueous solutions between 25 and 125 degrees C, the rate equation. Geochim. Cosmochim. Acta 61, 115–134.

Rickard, D., Morse, J., 2005. Acid volatile sulfide. Mar. Chem. 97, 141–197.

Russell, M.J., Hall, A.J., 1997. The emergence of life from iron monosulphide bubbles at a submarine hydrothermal redox and pH front. J. Geol. Soc. (Lond.) 154, 377–402.

Stookey, L.L., 1970. Ferrozine: a new spectrophotometric reagent for iron. Anal. Chem. 42, 779–781.

Sweeney, R.E., Kaplan, I.R., 1973. Pyrite framboid formation, laboratory synthesis and marine sediments. Econ. Geol. 68, 618–634.

Ulrich, G.A., Breit, G.N., Cozzarelli, I.M., Suflita, J.M., 2003. Sources of sulfate supporting anaerobic metabolism in a contaminated aquifer. Environ. Sci. Technol. 37, 1093–1099.

Ward, J.C., 1970. The structure and properties of some iron sulphides. Rev. Pure Appl. Chem. 175, 175–205.

Waren, A., Bengtson, S., Goffredi, S.K., van Dover, C.L., 2003. A hot-vent gastropod with iron sulfide dermal sclerites. Science 302, 1007.

Watson, J.H.P., Cressey, B.A., Roberts, A.P., Ellwood, D.C., Charnock, J.M., Soper, A.K., 2000. Structural and magnetic studies on heavy-metal-adsorbing iron sulphide nanoparticles produced by sulphate-reducing bacteria. J. Magn. Magn. Mater. 214, 13–30.

Wolthers, M., Van der Gaast, S.J., Rickard, D., 2003. The structure of disordered mackinawite. Am. Mineral. 88, 2007–2015.

Zehnder, A.J.B., Wuhrmann, K., 1976. Titanium(III)-citrate as a nontoxic oxidation-reduction buffering system for the culture of obligate anaerobes. Science 194, 1165–1166.