

# Effects of CH<sub>4</sub> and CO<sub>2</sub> on the sulfidization of goethite and magnetite: an *in situ* Raman spectroscopic study in high-pressure capillary optical cells at room temperature

MENGHAN WANG<sup>1,2</sup>, I-MING CHOU<sup>3</sup>, WANJUN LU<sup>1,\*</sup> and BENEDETTO DE VIVO<sup>2</sup>

<sup>1</sup> Department of Marine Science and Engineering, China University of Geosciences, Wuhan 430074, China

\*Corresponding author, e-mail: luwanjuncug@126.com

<sup>2</sup> Dipartimento di Scienze della Terra, dell'Ambiente e delle Risorse, Università di Napoli Federico II, 80134 Napoli, Italy

<sup>3</sup> Laboratory for Experimental Study Under Deep-sea Extreme Conditions, Sanya Institute of Deep-sea Science and Engineering, Chinese Academy of Sciences, Sanya 572000, China

**Abstract:** Reactions of goethite and magnetite with sulfide solutions under CH<sub>4</sub> and/or CO<sub>2</sub> atmospheres were monitored *in situ* with Raman spectroscopy in the high-pressure capillary optical cells (HPOCs) at room temperature. Isolated systems were created in the enclosed HPOCs for the study of the mineral–solution interactions to prevent oxidation during the experiments. We observed that iron (oxyhydr)oxide minerals were inert to sulfide solution under CH<sub>4</sub> atmosphere, and that the addition of CO<sub>2</sub> to this system triggered the sulfidization reactions and produced iron monosulfide; mackinawite was identified in the solid phase immersed in the solution after six hours and pyrrhotite in the solid phase exposed to the vapor phase after 5 days. Mackinawite formed in the aqueous phase was metastable, and dissolved after about 10 days. The observed sulfidization of iron (oxyhydr)oxide minerals was through a replacement reaction rather than a dissolution–precipitation process.

**Key-words:** goethite; magnetite; sulfidization; sulfidation; mackinawite; pyrrhotite; methane; carbon dioxide; Raman spectroscopy.

## Introduction

Iron sulfide minerals include a diverse group of solids, many of which play the key roles in low-temperature marine environments and in biogeochemical processes (Canfield *et al.*, 1992, 2000; Schoonen, 2004; Rickard & Luther, 2007). Pyrite is the most abundant iron sulfide mineral on the Earth's surface layer (Haese *et al.*, 1998; Li *et al.*, 2011; Morgan *et al.*, 2011), followed by mackinawite and greigite, whereas troilite and pyrrhotite are less abundant (Rickard & Luther, 2007).

Various valences of iron sulfide minerals commonly appear at the transition depth between the iron-oxide reduction zone and the sulfate reduction zone in marine sediments. Sulfidization of iron oxides was considered to be the main process forming iron sulfides in these sediments, and the conversion rate from oxide to sulfide minerals was related to the various crystal structures of the iron oxide minerals (Poulton *et al.*, 2004). However, large discrepancy of reaction rate exists between studies (Canfield *et al.*, 1992; Poulton *et al.*, 2004), and this discrepancy was assumed to result from different interstitial compositions and geochemical environments. For example,

organoclastic iron sulfides reflect high concentrations of S and Fe in pore water (Haese *et al.*, 1997), whereas methanotrophic iron sulfides indicate high concentrations of methane and carbon dioxide in pore water (Sassen *et al.*, 2004; Lim *et al.*, 2011; Wehrmann *et al.*, 2011).

The reaction mechanisms of iron sulfide minerals have been extensively studied (Luther, 1991; Wang & Morse, 1995; Wilkin & Barnes, 1996; Morse & Wang, 1997; Rickard, 1997; Theberge & Luther, 1997; Morse, 1999; Poulton *et al.*, 2004). Most of these studies investigated the reactions between sulfide solution and synthesized iron monosulfide minerals. The sol-gel approach (Wang & Morse, 1995) was used to simulate anoxic sediment and successfully synthesized crystalline pyrite. The freeze-drying method was used (Rickard, 1997) to protect FeS from oxidation during the kinetics study of pyritization. Another group of studies showed the controlling factors and reaction kinetics for the bulk reductive dissolution of iron (oxyhydr)oxides (Dos Santos Afonso & Stumm, 1992; Yao & Millero, 1996; Poulton, 2003; Poulton *et al.*, 2004). Recently, Raman spectroscopy was used to identify and characterize the conversion of iron sulfide minerals (Bourdoiseau *et al.*, 2008, 2011).

The main obstacle in the study of iron sulfide minerals is their extreme sensitivity to oxygen (Csákbérenyi-Malasics *et al.*, 2012). In this study, a high-pressure capillary optical cell (HPOC) was used to prevent oxidation of these minerals during experiments. Also, *in situ* monitoring of reactions allowed us to reveal the processes and the controlling factors for the transformation of these minerals.

## Materials and methods

### Syntheses of the starting iron (hydroxyl)oxide and iron monosulfides

Goethite and magnetite were synthesized from the following reagent-grade compounds (greater than 98.5 % purity):  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ , KOH,  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ,  $\text{KNO}_3$  and  $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ , purchased from Sinopharm Chemical Reagent Co., Ltd.  $\text{CH}_4$  and  $\text{CO}_2$  were purchased from Air Products and Chemicals, Inc. USA, with purities of more than 99.99 %.

Goethite and magnetite were synthesized following the procedures of Schwertmann & Cornell (2007a and b). To achieve pure goethite, 100 mL of  $\text{Fe}(\text{NO}_3)_3$  solution was poured into a 2 L polyethylene flask, followed by rapid addition of 180 mL solution of KOH with constant stirring. Immediately after the precipitation of the red-brown two-line ferrihydrite, the suspension was diluted to 2 L with distilled water in a closed polyethylene flask and stored at 70°C for 60 h. The preparation was carried out in a polyethylene vessel instead of a glass bottle, because silicate glass dissolves considerably in strong alkaline solution. During the heating stage (at 70°C), the voluminous, red-brown suspension of ferrihydrite was converted to a compact yellow-brown precipitate of goethite. At the end, the reaction vessel was removed from the oven and the goethite precipitate was centrifuged, washed, and dried.

To produce pure magnetite, 80 g of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  was dissolved in 560 mL of deionized water (previously flushed with  $\text{N}_2$ ) in a 1 L glass beaker, which was closed with an air-tight plastic lid with holes for gas inlet and a thermometer. The beaker was placed in a water bath (*i.e.*, a 3 L beaker filled with water at 90°C), with a thermometer in place and connected to an  $\text{N}_2$  gas inlet for purging the sample chamber. Once the desired temperature was reached, 240 mL of an oxygen-free solution containing 6.46 g of  $\text{KNO}_3$  and 44.9 g of KOH was added dropwise for approximately five minutes. The obtained solution was heated at 100°C for another half to one hour, and then cooled overnight to room temperature. The black precipitate was washed and dried. No protection against air oxidation was needed once the black precipitate was formed.

In order to compare the Raman spectra of our experimental products with iron monosulfide minerals, these minerals were first produced by mixing  $\text{FeSO}_4$  solution with  $\text{Na}_2\text{S}$  solution, and the precipitates were immediately loaded in a fused-silica capillary tube followed by sealing

both ends of the tube with a hydrogen-oxygen flame to form a fused-silica capillary capsule (FSCC) (Chou *et al.*, 2008) to prevent oxidation. Note that the sulfide solution was prepared by dissolving 12 g of  $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$  in 100 mL of deionized water (previously flushed with  $\text{N}_2$ ) in a 100 mL volumetric flask.

### Experimental apparatus and procedures

A high-pressure capillary optical cell (HPOC) was used as the reaction chamber (Chou *et al.*, 2005; Lu *et al.*, 2006, 2008). The HPOC was made from a 15-cm long silica capillary tube (0.3 mm ID and 0.66 mm OD) and one end of the tube was sealed with a hydrogen-oxygen flame. Sulfide solution of 0.5 M was sucked into the tube, and several grains of iron oxide solids were loaded into the tube. After the solid and solution were centrifuged to the enclosed end, the open end of the tube was connected to a gas line. The tube and the gas line were evacuated and then loaded with methane, and this evacuation-gas loading procedure was repeated several times to remove residual air before loading the desired gas in the HPOC. The cell was then mounted on an X-Y-Z stage under a microscope for observation and Raman analyses of the sample. A schematic diagram of the *in situ* Raman spectroscopic measurement system is shown in Fig. 1. The room temperature was kept around 20°C. The pressure was read from a Setra 204D digital pressure transducer with a Datum 2000TM manometer (69 MPa full scale; accurate to 0.14 %). Seven experimental runs were performed with different initial conditions (Table 1).

### Characterization of iron minerals and *in situ* monitoring with Raman spectroscopy

Raman analyses were carried out with a Jobin Yvon-Horiba, high-resolution Raman spectrometer (LabRAM HR-800) equipped with a microscope and a Peltier-cooled charge coupled device (CCD) detector. Excitation was provided by an Nd:YAG laser (532.08 nm) and its power was adjusted between 1.94 and 0.07 mW on the outer wall of the HPOC in order to prevent excessive heating of the samples. The sample spot diameter was  $\sim 4 \mu\text{m}$  under a 50x objective lens. A grating of 600 gr/mm was used, and most of the spectra for the samples in the HPOC were collected in the wavenumber range 100–4000  $\text{cm}^{-1}$  to cover the bands of iron (oxyhydr)oxide and sulfide minerals,  $\text{CO}_2$ ,  $\text{CH}_4$ ,  $\text{H}_2\text{O}$ , S,  $\text{CO}_3^{2-}$ ,  $\text{HCO}_3^-$  and  $\text{SO}_4^{2-}$  (Table S1, freely available online as Supplementary Material linked to this article on the GSW website of the journal, <http://eurjmin.geoscienceworld.org/>). The spectra were recorded with a resolution of  $\sim 2 \text{ cm}^{-1}$ .

In our control run, Raman spectra of iron monosulfide precipitates from a mixture of  $\text{FeSO}_4$  solution and  $\text{Na}_2\text{S}$  solution were obtained. Repeatable bands near 250 and 310  $\text{cm}^{-1}$  resulted from the species of black iron-sulfide precipitates (Fig. 2).

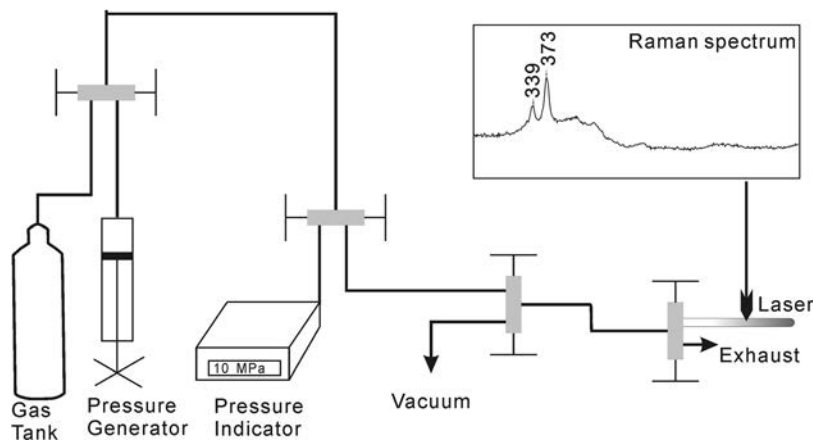


Fig. 1. A schematic diagram of the experimental set up for collecting *in situ* Raman spectra of the sample in a high-pressure optical cell (HPOC). The example Raman spectrum was derived from pyrrhotite, which was converted from magnetite exposed to a CH<sub>4</sub>-CO<sub>2</sub> vapor phase in the presence of a sulfide solution (for detail, see text).

Table 1. Initial conditions and final products of experiments.

| Run No. | Gas                                    |                                        | Na <sub>2</sub> S solution |             | Iron oxide | Location | Products (solids)   | pH <sup>1</sup> | pE <sup>1</sup> |
|---------|----------------------------------------|----------------------------------------|----------------------------|-------------|------------|----------|---------------------|-----------------|-----------------|
|         | CH <sub>4</sub> partial pressure (MPa) | CO <sub>2</sub> partial pressure (MPa) | Concentration (M)          | Length (cm) |            |          |                     |                 |                 |
| 1       | 10                                     | 0                                      | 0.5                        | 3.14        | Goethite   | Liquid   | –                   | 12.8            | –11.5           |
| 2       | 10                                     | 0                                      | 0.5                        | 1.12        | Goethite   | Gas      | –                   | 12.8            | –11.5           |
| 3       | 0.7                                    | 6.3                                    | 0.5                        | 0.5         | Magnetite  | Gas      | Pyrrhotite, Sulfur  | 5.8             | –2.5            |
| 4       | 0.7                                    | 6.3                                    | 0.5                        | 2.27        | Magnetite  | Gas      | Pyrrhotite, Sulfur  | 5.9             | –2.7            |
| 4       | 0.7                                    | 6.3                                    | 0.5                        | 2.27        | Magnetite  | Liquid   | Mackinawite, Sulfur | 5.9             | –2.7            |
| 5       | 3.2                                    | 3.8                                    | 0.5                        | 0.92        | Goethite   | Liquid   | Mackinawite, Sulfur | 6.1             | –2.9            |
| 6       | 0.7                                    | 6.3                                    | 0.5                        | 1.14        | Goethite   | Liquid   | Mackinawite, Sulfur | 5.8             | –2.5            |
| 7       | 0.7                                    | 6.3                                    | 0.5                        | 1.21        | Goethite   | Liquid   | Mackinawite, Sulfur | 5.8             | –2.5            |
| 8       | 0.5                                    | 4.5                                    | 0.5                        | 1           | –          | –        | Sulfur              | 5.9             | –2.7            |

<sup>1</sup> Calculated by using PHREEQC 2.18.3 with the initial conditions listed in this Table.

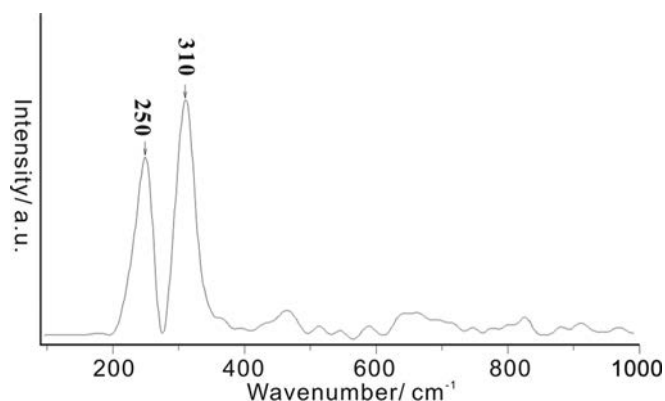


Fig. 2. Raman spectra of the instantaneous precipitate produced by mixing FeSO<sub>4</sub> solution and Na<sub>2</sub>S solution. Repeatable Raman bands at ~250 cm<sup>-1</sup> and 310 cm<sup>-1</sup> resulted from iron sulfide precipitates.

## Results

Experimental results, together with their initial conditions, are listed in Table 1. Goethite was reacted with Na<sub>2</sub>S solution under CH<sub>4</sub> gas (run nos. 1 and 2) and under a CH<sub>4</sub>-CO<sub>2</sub> gas mixture (run nos. 5, 6, and 7). Magnetite was reacted with a CH<sub>4</sub>-CO<sub>2</sub> gas mixture (run nos. 3 and 4). An additional run (no. 8) was performed to illustrate the effect of CO<sub>2</sub> to the system.

### Goethite and Na<sub>2</sub>S solution under CH<sub>4</sub> atmosphere

In run no. 1, goethite was immersed in the solution near the sealed end of the cell (Fig. 3), whereas in run no. 2, it was exposed to the vapor phase (Fig. S1 in Supplementary Material). Raman spectra of the samples were collected

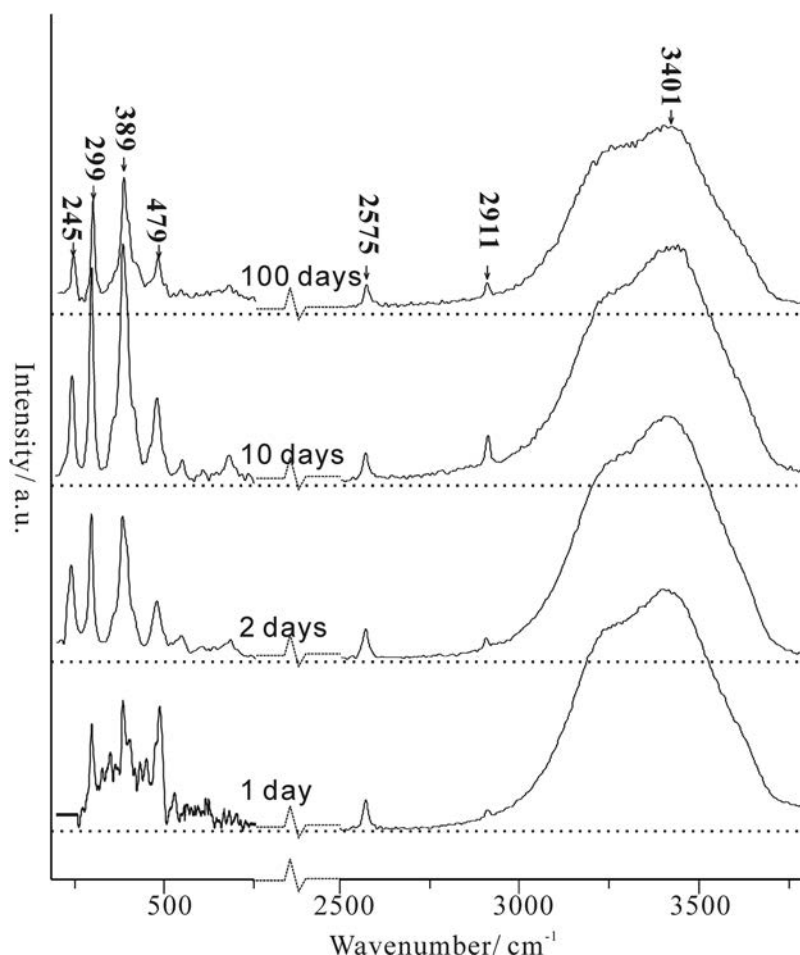


Fig. 3. Raman spectra of the sample in run no. 1 collected *in situ* at various time, showing the coexistence of goethite and sulfide solution for up to 100 days under 10 MPa of methane pressure at 20°C with no reaction detected. The peaks indicated in the top spectrum are for water (3401  $\text{cm}^{-1}$ ), aqueous methane (2911  $\text{cm}^{-1}$ ), dissolved sulfide ions (2575  $\text{cm}^{-1}$ ) and goethite (246  $\text{cm}^{-1}$ , 298  $\text{cm}^{-1}$ , 387  $\text{cm}^{-1}$  and 482  $\text{cm}^{-1}$ ).

daily for more than 60 days. In run no. 1, peak positions and intensities of goethite (245, 299, 389, and 479  $\text{cm}^{-1}$ ) remained constant, indicating that no reaction occurred. This was also supported by the appearance of the goethite in the cell, showing no obvious changes in either shape or color. Similarly, in run no. 2, Raman spectra and appearance of goethite that was exposed to the methane gas phase remained the same without obvious changes (Fig. 3). Our results showed that goethite did not react with sulfide solution under  $\text{CH}_4$  atmosphere.

#### **$\text{Na}_2\text{S}$ solution under $\text{CO}_2$ - $\text{CH}_4$ atmosphere**

In run no. 8, no iron oxides were added to be exposed to either aqueous or vapor phase, and only sodium sulfide solution was exposed to the  $\text{CO}_2$ - $\text{CH}_4$  atmosphere (Supplementary Figure S2). As soon as the high-pressure  $\text{CO}_2$ - $\text{CH}_4$  (gas) (5 MPa) was loaded into the HPOC, the reaction started and produced sulfur and unknown organic compounds with strong fluorescence. Raman spectroscopic analyses showed that sulfur was produced in both

aqueous and vapor phases (Supplementary Figure S3). Organic compounds produced by the reactions of FeS,  $\text{H}_2\text{S}$ , and  $\text{CO}_2$  at elevated temperature were also reported by Heinen & Lauwers (1996). However, because the nature of these compositions was difficult to determine based on our *in situ* Raman analyses, the exact chemical reactions involved were not formulated.

#### **Iron minerals (goethite or magnetite) and $\text{Na}_2\text{S}$ solution under $\text{CO}_2$ - $\text{CH}_4$ atmosphere**

When the medium was a mixed  $\text{CO}_2$ - $\text{CH}_4$  gas, sulfide ions in the aqueous phase reacted with both magnetite (run no. 4) and goethite (run nos. 5, 6, and 7; Figs. 4 and 5) to form mackinawite, sulfur, and organic products as described in run no. 8. On the other hand, when magnetite was exposed to the vapor phase (run nos. 3 and 4), instead of mackinawite, pyrrhotite was produced (Figs. 6 and 7) together with sulfur. No observations were made for goethite exposed to the vapor phase in this study, but will be made in the near future.

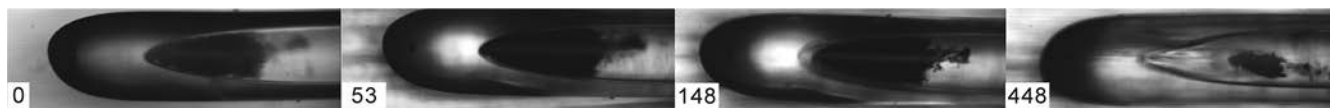


Fig. 4. Images of goethite in a HPOC for run no. 5 under  $\text{CH}_4\text{-CO}_2$  pressure from 0 to 448 h. Iron sulfide minerals appeared before 53 h, and the intensity of Raman signals decreased after 53 h and became undetectable at 448 h, indicating the dissolution of the newly formed iron sulfides.

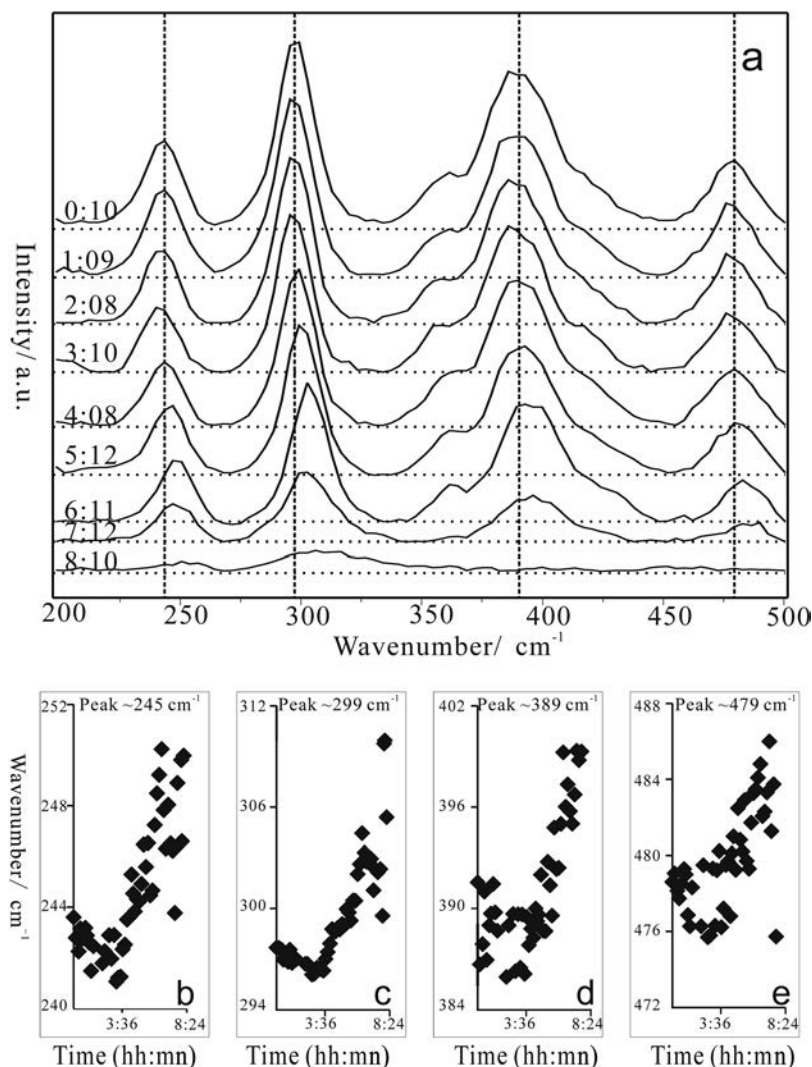


Fig. 5. *In situ* Raman spectra for the solid phases in run no. 7 for the first 8.2 h, showing the shift of the peak positions after 4.08 h and the reduction of the signals after 6.11 h. The shift of the peak positions at about 245, 299, 389, and 479  $\text{cm}^{-1}$  are shown in (b), (c), (d), and (e), respectively. The reversal points near 3:36 for all of these peaks indicate the transformation of goethite to mackinawite. The reduction of Raman signals after 6.11 h shown in (a) resulted from the dissolution of this newly formed mackinawite.

#### Sulfidization of goethite and mineral dissolution

The transition process from goethite to iron monosulfide was clearly indicated by the evolution of Raman spectra in the changes of the number of peaks, peak heights, and peak positions. In Fig. 5(a), *in situ* Raman spectra for the solid phases in run no. 7 are shown for the first 8.2 hours. It shows the shift of the peak positions after 3 h 36 min and the decrease of the signals after 6.11 hours. The shifts of the peak positions at about 245, 299, 389, and 479  $\text{cm}^{-1}$  are shown in Fig. 5(b)–(e), respectively. The reversal points

near 3 h 36 min for all of these peaks indicate the transformation of goethite to mackinawite. This is in agreement with Bourdoiseau *et al.* (2011), who reported the peak shifts at 251 and 306  $\text{cm}^{-1}$  corresponding to the formation of mackinawite. Also, Bourdoiseau *et al.* (2008) reported the shift of peak positions from 283 ( $\pm 1$ )  $\text{cm}^{-1}$  to 297 ( $\pm 1$ )  $\text{cm}^{-1}$ , and from a symmetric to an asymmetric peak. In our control run, repeatable bands near 250 and 312  $\text{cm}^{-1}$  were observed for the species of black iron-sulfide precipitates (Fig. 2).

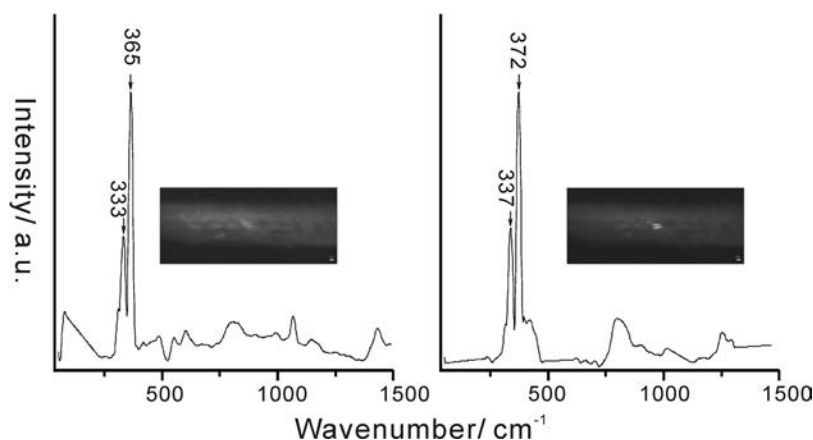


Fig. 6. Raman spectra of iron sulfide minerals in run no. 3. Peaks at  $\sim 333\text{ cm}^{-1}$  and  $\sim 365\text{ cm}^{-1}$  left, or  $337\text{ cm}^{-1}$  and  $\sim 372\text{ cm}^{-1}$  right indicate the occurrence of pyrrhotite. The white sample spot became brighter after being excited by laser.

The reduction of Raman signals after 6.11 h as shown in Fig. 5(a) was the result from the dissolution of this newly formed mackinawite. This process may take more than 10 days, depending on how far away goethite was from the vapor-aqueous phase boundary; the farther away from the interface, the slower the reaction, indicating that the reaction was regulated by the mass transfer of  $\text{CO}_2$  from the gas into the sulfide solution.

In comparative observations, goethite showed no obvious change in more than 30 days when it was loaded in pure water with 5 MPa of  $\text{CH}_4\text{-CO}_2$  as a medium gas without sulfide ions in the aqueous phase.

#### *Minerals exposed to the vapor phase*

Pyrrhotite, a thermodynamically stable iron sulfide, was produced when the synthesized magnetite was exposed to the  $\text{CH}_4\text{-CO}_2$  vapor phase.

Raman spectra databases were checked to identify products of run nos. 3 and 4 (Table S2). Spectra of these databases were obtained from various natural minerals or synthetic material, and disturbances of lattice defects or drop-in were also reflected on the various peaks for the same minerals/material. In our case, the primary peaks of the experimental products were at  $335 (\pm 2)$  and  $369 (\pm 4)\text{ cm}^{-1}$ , indicating the presence of pyrrhotite rather than pyrite (Table 2).

## Discussion

### Effect of $\text{CO}_2$

Iron oxides were thermodynamically stable with low solubility coefficients: their  $K_{\text{sp}}$  ranged from  $10^{-37}$  to  $10^{-44}$  (Schwertmann, 1991). Dissolved hydrogen sulfide could reductively dissolve iron (oxyhydr)oxides (Dos Santos Afonso & Stumm, 1992; Yao & Millero, 1996; Poulton, 2003; Poulton *et al.*, 2004) to produce dissolved Fe (II) ions and elemental sulfur. The rate of reaction was found highly dependent upon pH of the solution, with a

maximum oxidation rate at pH near 7 for goethite (Yao & Millero, 1996).

Under methane atmosphere, the pH of solution was 12.8 based on geochemical simulation (Table 1). At such pH condition, if any reductive dissolution of iron oxides occurred, the rate would be extremely low, as indicated by the observed stability of solids in solution for over 100 days. When  $\text{CO}_2$  partially replaced  $\text{CH}_4$ , the pH of the solution decreased because of dissociation of dissolved  $\text{CO}_2$ . The ultimate pH of the solution was in the range 5.8–6.1, which was close to the optimal condition for the dissolution of iron oxides. The change of pH could explain the different phenomena observed under different atmospheres in this study.

However, the possible effects of  $\text{CO}_2$  was not only limited to the change of pH of the solution. As shown in run no. 8,  $\text{CO}_2$  itself could also react with sulfide solution and produce elemental sulfur and organic compounds. These products were similar to those produced by the reductive dissolution of iron oxides and may potentially change the iron oxides surface condition, which was believed to be one of the key factors of reductive dissolution (Dos Santos Afonso & Stumm, 1992; Yao & Millero, 1996; Poulton, 2003; Poulton *et al.*, 2004).

### Reaction mechanism

A widely accepted model of reductive dissolution of iron oxides toward hydrogen sulfide was proposed by Dos Santos Afonso & Stumm (1992). The reaction scheme could be summarized as 1) reduction of Fe (III) to Fe (II); 2) release of Fe (II); and 3) formation of FeS (for detailed descriptions, see Supplementary materials A). In other words, this reaction was a dissolution-precipitation process. This scheme had been adopted and proved in experiments of bulk reactions (Yao & Millero, 1996; Poulton, 2003; Poulton *et al.*, 2004) (Supplementary materials A).

However, the result in run no. 7 presented a different pathway. In the first stage, iron (oxyhydr)oxides changed to FeS. Alteration of Raman bands did not indicate any

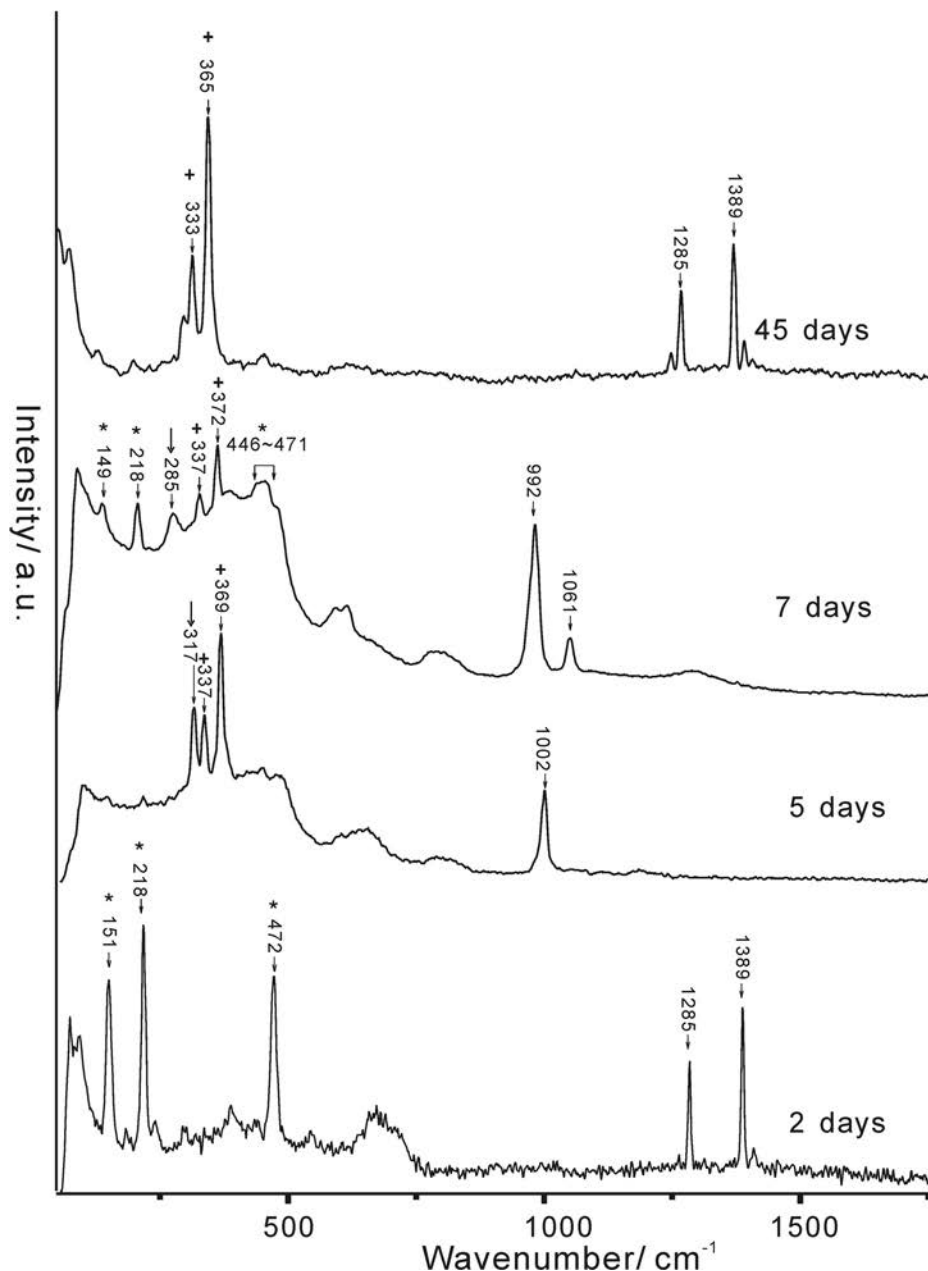


Fig. 7. Raman spectra collected from the iron sulfide minerals exposed to the vapor phase in run no. 4. Peaks at 333 (or 336)  $\text{cm}^{-1}$  and 369 (or 372, 365)  $\text{cm}^{-1}$  indicate the formation of pyrrhotite. Bands of  $\sim 101 \text{ cm}^{-1}$ ,  $\sim 148 \text{ cm}^{-1}$ ,  $216 \text{ cm}^{-1}$  and  $460 \text{ cm}^{-1}$  are related to elemental sulfur. Bands at  $317 \text{ cm}^{-1}$  (5 days) and  $285 \text{ cm}^{-1}$  (7 days) are corresponding to metastable iron minerals. Peaks of elemental sulfur are marked by stars (\*), those for pyrrhotite by plus signs (+), and those for metastable sulfide minerals by arrows ( $\leftarrow$ ). The Raman peaks at  $1285$  and  $1389 \text{ cm}^{-1}$  are from  $\text{CO}_2$  in the vapor phase, and those near  $1020 \text{ cm}^{-1}$  from a thin film of aqueous phase, indicating the presence of bicarbonate ions.

signal of reductive dissolution (Fig. 5); a slight change in the shapes of solids occurred, but no major dissolution of minerals was observed (Fig. 4). In the second stage, FeS dissolved in the aqueous phase. Therefore, replacement-dissolution rather than dissolution-precipitation process was possibly the mechanism for the reaction between goethite and sulfide solution observed in this study.

Different primary conditions and reaction scale may lead to different results. The solubility of amorphous FeS

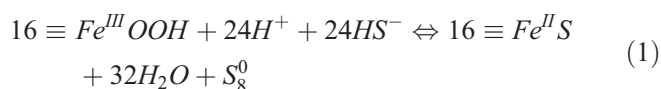
(s) is dependent on  $[\text{S}^{2-}]$  (sulfide ion concentration). In more acidic solutions, solubility is also pH dependent, while in neutral or alkaline solutions it is pH independent (Rickard, 2006). For bulk reactions,  $[\text{S}^{2-}]$  and pH were controlled as constant values in previous studies, where the FeS (s) formed was either entirely dissolved in more acidic solution (Dos Santos Afonso & Stumm, 1992) or partially dissolved in less acidic solution (Yao & Millero, 1996; Poulton, 2003; Poulton *et al.*, 2004). In such cases,

Table 2. Raman peak positions of iron sulfide minerals produced in experiments.

| Run No. | Raman peak position of stable minerals (cm <sup>-1</sup> ) |     | Raman peak position of metastable minerals (cm <sup>-1</sup> ) |
|---------|------------------------------------------------------------|-----|----------------------------------------------------------------|
| 3       | 333                                                        | 363 |                                                                |
| 3       | 337                                                        | 372 |                                                                |
| 4       | 337                                                        | 369 | 317                                                            |
| 4       | 337                                                        | 372 | 285                                                            |
| 4       | 333                                                        | 365 |                                                                |

reductive dissolution was easily considered as the first step of the reaction because solid FeS was not always present. On the other hand, in our experiments in HPOC, [S<sup>2-</sup>] and pH changed progressively due to the diffusion of CO<sub>2</sub>; when the pH of the solution satisfied the requirement of iron reduction, sulfide replacement occurred, and as the pH of the solution around the solids decreased due to more dissolved CO<sub>2</sub>, FeS dissolved gradually. Thus, a possible mechanism can be schematically represented by the following reaction sequence.

#### (I) Sulfide replacement:

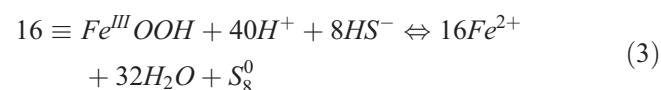


where  $\equiv$  represents iron surface complex (see Supplementary materials A).

#### (II) FeS dissolution:



Equations (1) and (2) can be combined:



such that the solid FeS does not appear in the net reaction.

## Conclusion

The processes of sulfidization of goethite and magnetite in Na<sub>2</sub>S solution under CH<sub>4</sub>/CO<sub>2</sub> atmospheres were observed in high-pressure capillary optical cells (HPOCs) and characterized *in situ* with Raman spectroscopy at room temperature. No obvious sulfidization reactions were observed when the assemblages were under CH<sub>4</sub> pressure. However, the addition of CO<sub>2</sub> to the sample assemblages promoted the sulfidization reaction. The main product was elemental sulfur and mackinawite when goethite or magnetite was immersed in the Na<sub>2</sub>S solution, and pyrrhotite was produced when magnetite was exposed to the vapor phase; no observations were made for goethite exposed to the vapor phase. The produced mackinawite was not stable and

dissolved gradually. The addition of CO<sub>2</sub> decreased the pH of the solution and initialized the reaction. The mechanism of reaction between iron (oxyhydr)oxides and sulfide ions was a replacement-dissolution rather than a reductive dissolution-precipitation process.

**Acknowledgements:** This work was partly supported by the National Sciences Foundation of China (No. 41176047, 41472218), the National Basic Research Program of China (No. 2009CB219503), the Program for New Century Excellent Talents in University by Ministry of Education (NCET-08-0830), the Knowledge Innovation Program (SIDSSE-201302), and the Hadal-trench Research Program (XDB06060100) of Chinese Academy of Sciences. This work is also a part of the Ph.D. Program of M. Wang with Università degli studi di Napoli Federico II (Italy).

## References

- Bourdoiseau, J.A., Jeannin, M., Sabot, R., Rémaizeilles, C., Refait, P. (2008): Characterisation of mackinawite by Raman spectroscopy: effects of crystallisation, drying and oxidation. *Corrosion Sci.*, **50**, 3247–3255.
- Bourdoiseau, J.A., Jeannin, M., Remazeilles, C., Sabot, R., Refait, P. (2011): The transformation of mackinawite into greigite studied by Raman spectroscopy. *J. Raman Spectrosc.*, **42**, 496–504.
- Canfield, D.E., Raiswell, R., Bottrell, S. (1992): The reactivity of sedimentary iron minerals toward sulfide. *Am. J. Sci.*, **292**, 659–683.
- Canfield, D.E., Habicht, K.S., Thamdrup, B. (2000): The Archean sulfur cycle and the early history of atmospheric oxygen. *Science*, **288**(5466), 658–661.
- Chou, I.M., Burruss, R.C., Lu, W.J. (2005): A new optical cell for spectroscopic studies of geologic fluids at pressures up to 100 MPa. in “Proceedings advances in high-pressure technology for geophysical applications”, J. Chen, Y. Wang, T.S. Duffy, G. Shen & L.F. Dobrzhinetskaya, eds. Elsevier, Amsterdam, 475–485.
- Chou, I.M., Song, Y., Burruss, R.C. (2008): A new method for synthesizing fluid inclusions in fused silica capillaries containing organic and inorganic material. *Geochim. Cosmochim. Acta*, **72**, 5217–5231.
- Csákerényi-Malasics, D., Rodriguez-Blanco, J.D., Kis, V.K., Rečnik, A., Benning, L.G., Pósfai, M. (2012): Structural properties and transformations of precipitated FeS. *Chem. Geol.*, **294**, 249–258.
- Dos Santos Afonso, M. & Stumm, W. (1992): Reductive dissolution of iron (III) (hydr) oxides by hydrogen sulfide. *Langmuir*, **8**, 1671–1675.
- Haese, R.R., Wallmann, K., Dahmke, A., Kretzmann, U., Muller, P.J., Schulz, H.D. (1997): Iron species determination to investigate early diagenetic reactivity in marine sediments. *Geochim. Cosmochim. Acta*, **61**, 63–72.
- Haese, R.R., Petermann, H., Dittert, L., Schulz, H.D. (1998): The early diagenesis of iron in pelagic sediments: a multidisciplinary approach. *Earth Planet. Sci. Lett.*, **157**, 233–248.

- Heinen, W. & Lauwers, A.M. (1996): Organic sulfur compounds resulting from the interaction of iron sulfide, hydrogen sulfide and carbon dioxide in an anaerobic aqueous environment. *Orig. Life Evol. Biosph.*, **26**, 131–150.
- Li, X., Cutter, G.A., Thunell, R.C., Tappa, E., Gilhooly Iii, W.P., Lyons, T.W., Astor, Y., Scranton, M.I. (2011): Particulate sulfur species in the water column of the Cariaco Basin. *Geochim. Cosmochim. Acta*, **75**, 148–163.
- Lim, Y.C., Lin, S., Yang, T.F., Chen, Y.-G., Liu, C.-S. (2011): Variations of methane induced pyrite formation in the accretionary wedge sediments offshore southwestern Taiwan. *Mar. Petrol. Geol.*, **28**, 1829–1837.
- Lu, W.J., Chou, I.M., Burruss, R.C., Yang, M.Z. (2006): In situ study of mass transfer in aqueous solutions under high pressures via Raman spectroscopy: a new method for the determination of diffusion coefficients of methane in water near hydrate formation conditions. *Appl. Spectrosc.*, **60**, 122–129.
- Lu, W.J., Chou, I.M., Burruss, R.C. (2008): Determination of methane concentrations in water in equilibrium with sI methane hydrate in the absence of a vapor phase by in situ Raman spectroscopy. *Geochim. Cosmochim. Acta*, **72**, 412–422.
- Luther, G.W. (1991): Pyrite synthesis via polysulfide compounds. *Geochim. Cosmochim. Acta*, **55**, 2839–2849.
- Morgan, B., Burton, E.D., Rate, A.W. (2011): Iron monosulfide enrichment and the presence of organosulfur in eutrophic estuarine sediments. *Chem. Geol.*, **296–297**, 119–130.
- Morse, J.W. (1999): Sulfides in sandy sediments: new insights on the reactions responsible for sedimentary pyrite formation. *Aquatic Geochem.*, **5**, 75–85.
- Morse, J.W. & Wang, Q.W. (1997): Pyrite formation under conditions approximating those in anoxic sediments.2. Influence of precursor iron minerals and organic matter. *Mar. Chem.*, **57**, 187–193.
- Poulton, S.W. (2003): Detection and removal of dissolved hydrogen sulphide in flow-through systems via the sulphidation of hydrous iron (III) oxides. *Environ. Technol.*, **24**, 217–229.
- Poulton, S.W., Krom, M.D., Raiswell, R. (2004): A revised scheme for the reactivity of iron (oxyhydr)oxide minerals towards dissolved sulfide. *Geochim. Cosmochim. Acta*, **68**, 3703–3715.
- Rickard, D. (1997): Kinetics of pyrite formation by the H<sub>2</sub>S oxidation of iron (II) monosulfide in aqueous solutions between 25 and 125°C: The rate equation. *Geochim. Cosmochim. Acta*, **61**, 115–134.
- (2006): The solubility of FeS. *Geochim. Cosmochim. Acta*, **70**, 5779–5789.
- Rickard, D. & Luther, G.W. (2007): Chemistry of iron sulfides. *Chem. Rev.*, **107**(2), 514–562.
- Sassen, R., Roberts, H.H., Carney, R., Milkov, A.V., DeFreitas, D.A., Lanoil, B., Zhang, C.L. (2004): Free hydrocarbon gas, gas hydrate, and authigenic minerals in chemosynthetic communities of the northern Gulf of Mexico continental slope: relation to microbial processes. *Chem. Geol.*, **205**, 195–217.
- Schoonen, M. (2004): Mechanisms of sedimentary pyrite formation. *Geol. Soc. Am. Spec. Pap.*, **379**, 117–134.
- Schwertmann, U. (1991): Solubility of dissolution of iron oxides. *Plant Soil.*, **130**, 1–25.
- Schwertmann, U. & Cornell, R.M. (2007a): Goethite, iron oxides in the laboratory. Wiley-VCH Verlag GmbH, Weinheim, 67–92.
- , — (2007b): Magnetite, iron oxides in the laboratory. Wiley-VCH Verlag GmbH, Weinheim, 135–140.
- Theberge, S.M. & Luther, G.W. (1997): Determination of the electro-chemical properties of a soluble aqueous FeS species present in sulfidic solutions. *Aquatic Geochem.*, **3**, 191–211.
- Wang, Q. & Morse, J.W. (1995): Laboratory simulation of pyrite formation in anoxic sediment, in “Geochemical transformations of sedimentary sulfur”, Vairavamurthy, M.A., & Schoonen, M.A.A., ed. Washington, DC, American Chemical Society Symposium Series 612, 206–223.
- Wehrmann, L.M., Templer, S.P., Brunner, B., Bernasconi, S.M., Maignien, L., Ferdelman, T.G. (2011): The imprint of methane seepage on the geochemical record and early diagenetic processes in cold-water coral mounds on Pen Duick Escarpment, Gulf of Cadiz. *Mar. Geol.*, **282**, 118–137.
- Wilkin, R.T. & Barnes, H.L. (1996): Pyrite formation by reactions of iron monosulfides with dissolved inorganic and organic sulfur species. *Geochim. Cosmochim. Acta*, **60**(21), 4167–4179.
- Yao, W.S. & Millero, F. (1996): Oxidation of hydrogen sulfide by hydrous Fe (III) oxides in seawater. *Mar. Chem.*, **52**, 1–16.

Received 4 February 2014

Modified version received 9 July 2014

Accepted 16 December 2014