

## Effect of carbonate ions on pyrite (FeS<sub>2</sub>) dissolution

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*Key words.* – Pyrite, Oxidation, Carbonate pH buffer, FTIR, Redox

*Abstract.* – Neutralization by carbonate of acidification generated by pyrite (FeS<sub>2</sub>) oxidation was investigated by both solution (iron and sulfur speciation, pH and Eh) and solid (FT-IR) characterizations. Batch dissolution experiments were carried out in contact with atmospheric oxygen (20 %) in four different bicarbonated solutions ([NaHCO<sub>3</sub>]=10<sup>-3</sup>, 1,12.10<sup>-2</sup>, 10<sup>-1</sup> and 1 mol/L). Five different contact duration were selected : 6 hours, 1, 3, 8 and 30 days. Ferrous carbonate complexes (FeOHCO<sub>3</sub><sup>-</sup> and Fe(CO<sub>3</sub>)<sub>2</sub><sup>2-</sup>) tend to maintain iron in solution (up to 152.2 µmol/L in [NaHCO<sub>3</sub>]=1 mol/L solution) and to increase pyrite oxidation rate by preventing surface coating. Acidification is thus more intense in diluted and concentrated carbonate medium ([NaHCO<sub>3</sub>]=10<sup>-3</sup> and 1 mol/L) with respectively ΔpH=5.06 and ΔpH=1.99 at 30 days whereas pH remains buffered in [NaHCO<sub>3</sub>]=1.12.10<sup>-2</sup> and 0.1 mol/L solutions. Siderite appears to be the first solid precipitating, transforming into goëthite, oxyhydroxy ferric sulfate incorporating sulfite and thiosulfate, and then lepidocrocite. Sulfur chemistry controls the acidification observed. Thiosulfate is the first sulfoxyanion released in solution and its oxidation into sulfite then sulfate seems to be the key of acidification production. Thus, carbonate pH buffer properties seem to be limited and effective for moderated carbonate concentrations.

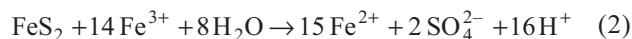
### Effet des ions carbonate sur la dissolution de la pyrite (FeS<sub>2</sub>)

*Mots clés.* – Pyrite, Oxydation, Carbonate, Tampon pH, FTIR, Redox

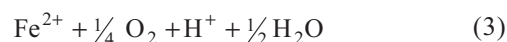
*Résumé.* – La neutralisation de l'acidité produite lors de l'oxydation de la pyrite (FeS<sub>2</sub>) par les carbonates a été étudiée par le couplage de l'approche des phases aqueuse (spéciations du fer et du soufre, pH et Eh) et solide (FT-IR). Des expériences de dissolution en batch ont été menées au contact de l'oxygène atmosphérique (20 %) en milieu bicarbonaté ([NaHCO<sub>3</sub>]=10<sup>-3</sup>, 1,12.10<sup>-2</sup>, 10<sup>-1</sup> et 1 mol/L). Cinq durées de dissolution ont été sélectionnées : 6 heures, 1, 3, 8 et 30 jours. Les complexes carbonates ferreux (FeOHCO<sub>3</sub><sup>-</sup> et Fe(CO<sub>3</sub>)<sub>2</sub><sup>2-</sup>) semblent maintenir le fer en solution (jusqu'à 152.2 µmol/L en milieu [NaHCO<sub>3</sub>]=1 mol/L) et augmenter la vitesse d'oxydation de la pyrite en évitant la précipitation d'oxydes ferriques. L'acidification est ainsi plus intense en milieu carbonaté dilué et concentré ([NaHCO<sub>3</sub>]=10<sup>-3</sup> et 1 mol/L) avec respectivement ΔpH=5.06 et ΔpH=1.99 à 30 jours alors que le pH demeure tamponné en solution [NaHCO<sub>3</sub>]=1.12.10<sup>-2</sup> et 0.1 mol/L. La sidérite est le premier solide formé, se transformant en goëthite, oxyhydroxyde ferrique sulfaté incorporant sulfites et thiosulfates, puis lépidocrocite. La chimie du soufre est à l'origine de l'acidification observée. Les thiosulfates sont les premiers sulfoxyanions relâchés en solution et leur oxydation en sulfite puis sulfate semble contrôler la production acide. La capacité tampon pH des carbonates semble être limitée pour des concentrations modérées.

## INTRODUCTION

Pyrite (FeS<sub>2</sub>) is the most widespread metal sulfide at the surface of Earth. Observed in a variety of geological environments, pyrite is generally associated with coalfields and ores including zinc, copper, gold, silver, lead, uranium etc. Exposure to air of iron sulfides in mining waste and ore tailings generates acid drainage producing dramatic environmental damages (pH as low as 2 and presence of heavy metals). The main oxidizing agents, present in natural aquatic systems, are O<sub>2</sub> and Fe(III). The overall reactions of pyrite with oxygen and Fe(III) are usually expressed by reactions 1 and 2 respectively :



Oxidation of one mole of pyrite produces two moles of sulfuric acid (Eqn. 1). But the oxidation by oxygen of Fe(II) in Fe(III) can either keep up the pyrite oxidation according to reactions 2 and 3, leading to a self-sustained reaction, or raise the acidification by ferric hydroxide precipitation according to equation (4) :



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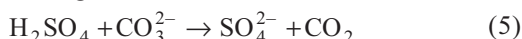
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Through its two oxidation states, iron appears firstly as an oxidation product ( $\text{Fe}^+$ ), and then after oxidation by  $\text{O}_2$ , as an oxidant ( $\text{Fe}^{3+}$ ). Approaches in preventing pyrite from oxidation are numerous. One may eliminate dissolved  $\text{Fe(III)}$  from waste pore waters, block access of atmospheric  $\text{O}_2$  to pyrite surfaces by coating, or neutralize acid production by alkaline materials such as limestones or phosphates [Evangelou, 1995]. Among them, carbonate is often used according to reaction 5 :



Literature concerning pyrite oxidation studies by FTIR is very sparse. When data exist [Donato *et al.*, 1993; Evangelou, 1995; Evangelou *et al.*, 1998], they are focused on spectral region  $900\text{--}1\,500\text{ cm}^{-1}$ , only representative of sulfur and carbonate species, and do not take into account absorption bands at  $400\text{--}900\text{ cm}^{-1}$  relative to iron species.

In this work we examined the carbonate ions pH buffer properties during pyrite oxidation. Both solution (speciation, pH and Eh) and solid characterizations (FT-IR) were used to ensure a complete understanding of the reactional paths.

## EXPERIMENTS AND METHODS

Sulfur speciation and analysis were performed by ionic chromatography (Dionex analyzer DX4500 using IonPac<sup>®</sup> AS14 analytical column and AG14 guard column in  $[\text{Na}_2\text{CO}_3]=3.5\text{ mmol/L} + [\text{NaHCO}_3]=1\text{ mmol/L}$  eluent). Iron was analyzed by furnace atomic absorption spectrometry (UNICAM 939,  $\lambda=248.3\text{ nm}$ ). Electrochemical parameters (pH and Eh) were followed after calibration (5 pH buffers and 1 Eh buffer) with a glass pH electrode (Radiometer #XG250) and a Pt electrode (Radiometer #XR110), each one being coupled with a calomel reference electrode (Radiometer #REF451) connected to an ionometer (Radiometer #PHM250). Solid characterization was carried out with FT-IR spectroscopy. 1 mg of sample powder (standard samples and oxidized pyrites) was mixed with 100 mg of KBr (FTIR grade, Aldrich) dried at  $40^\circ\text{C}$ . FTIR spectra (spectral region :  $400\text{--}4\,000\text{ cm}^{-1}$ ) were obtained with a Brüker Vector 22 spectrophotometer. Four hundred scans with a resolution of  $4\text{ cm}^{-1}$  were collected. Identification of different absorption bands on oxidized pyrite surfaces, was obtained after constitution of a FTIR data basis from sulfur and iron reference compounds of representative oxidation products susceptible to be observed. Hence, three spectral domains of interest are exploited in this study : iron environment (oxides, hydroxides and oxyhydroxides) at  $400\text{--}900\text{ cm}^{-1}$  whereas information concerning sulfur species is at  $1\,000\text{--}1\,200\text{ cm}^{-1}$  (except for the pyrite S-S vibration located at  $415\text{ cm}^{-1}$ ), sulfite ( $\text{SO}_3^{2-}$ ) and thiosulfate ( $\text{S}_2\text{O}_3^{2-}$ ) ions respectively at  $632$  and  $671\text{ cm}^{-1}$ . Carbonate ( $1\,300\text{--}1\,500\text{ cm}^{-1}$ ) and OH stretching ( $2\,500\text{--}4\,000\text{ cm}^{-1}$ ) define the other two spectral regions.

Pyrite from Spain (Logroño) was used in this study. Cubic samples were first dipped into concentrated hydrochloric acid (37 %) during several hours to eliminate any oxidation products present at the mineral surface. The pyrite was then introduced in a glove box ( $p(\text{H}_2\text{O})$  and  $p(\text{O}_2)$  both inferior to 1 vpm) and rinsed with acetone. The mineral was ground in an agate mortar and sifted with ethanol

(grain sizes in the  $50\text{--}150\text{ }\mu\text{m}$  fraction). Pyrite was then washed in ultra-sonic bath to remove any fine particles adhering to the grains surface. These two operations were repeated until the ethanol after ultrasonic-bath was clear. Samples were kept in a glove box for drying until experiments.

Experiments were run as batch experiments in Teflon<sup>®</sup> reactors in contact with atmospheric oxygen (20 %) at room temperature (typically between  $20$  and  $25^\circ\text{C}$ ). Agitation by an orbital shaker guaranteed continuous homogeneity of the solution. The water to solid ratio was of  $150\text{ mL.g}^{-1}$ . Time course began with pyrite introduction in the solution. Dissolution experiments were carried out in four different bicarbonated solutions  $[\text{NaHCO}_3] = 10^{-3}, 1, 12.10^{-2}$  (chosen to represent a clayey groundwater),  $10^{-1}$  and  $1\text{ mol/L}$  (Merck #6329). Five different contact durations were selected : 6 hours, 1, 3, 8 and 30 days allowing us to follow and identify the formation sequence of different oxidation products. The final samples were kept in glove box before FT-IR analysis. Solution samples were filtered and immediately analyzed for sulfur and stored in glove box for iron.

## RESULTS

### Speciation and solution

Sulfur speciation is seen in two main species : thiosulfate ( $\text{S}_2\text{O}_3^{2-}$ ) and sulfate ( $\text{SO}_4^{2-}$ ), and occasionally sulfite ( $\text{SO}_3^{2-}$ ). Thiosulfate can represent up to 85 % of dissolved sulfur (fig. 1). If we consider total sulfur concentration as the pyrite oxidation apparent rate, the more carbonated is the solution, the more dissolved is pyrite (fig. 2). Total sulfur concentration is about  $2\text{ mmol/L}$  at 30 days in a diluted medium ( $[\text{NaHCO}_3]=10^{-3}\text{ mol/L}$ ), whereas in more carbonated medium ( $[\text{NaHCO}_3]=0.1$  and  $1\text{ mol/L}$ ) concentration rises up to  $7\text{ mmol/L}$ . Time evolutions of iron concentration show two different trends depending on carbonate concentration (fig. 3). The same trend as illustrated by sulfur is observed. Iron concentration raises with carbonate concentration up to  $1\,52.2\text{ }\mu\text{mol/L}$  at 8 days ( $[\text{NaHCO}_3]=1\text{ mol/L}$ ). In less carbonated media, iron concentrations become insignificant

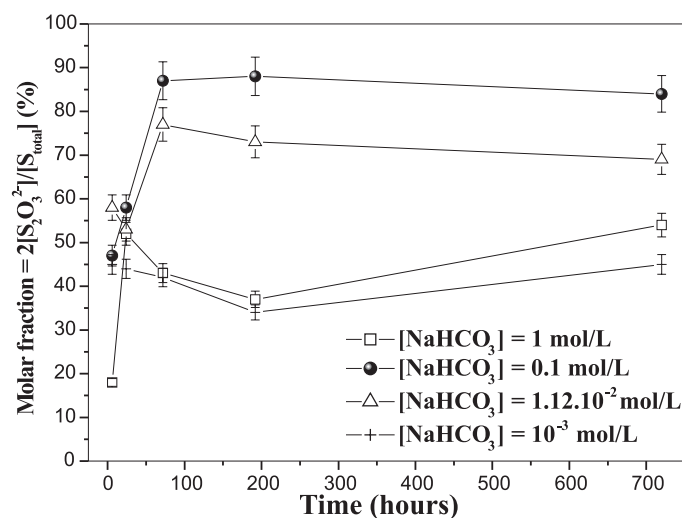


FIG. 1. – Thiosulfate evolution in carbonated media versus time.  
FIG. 1. – Evolution temporelle des ions thiosulfate en milieu carbonaté.

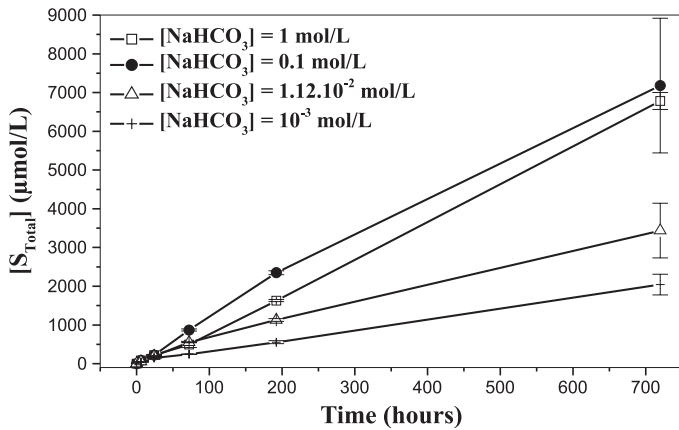


FIG. 2. – Total sulfur concentration evolution in carbonated media versus time.

FIG. 2. – Evolution temporelle des concentrations en soufre total en milieu carbonaté.

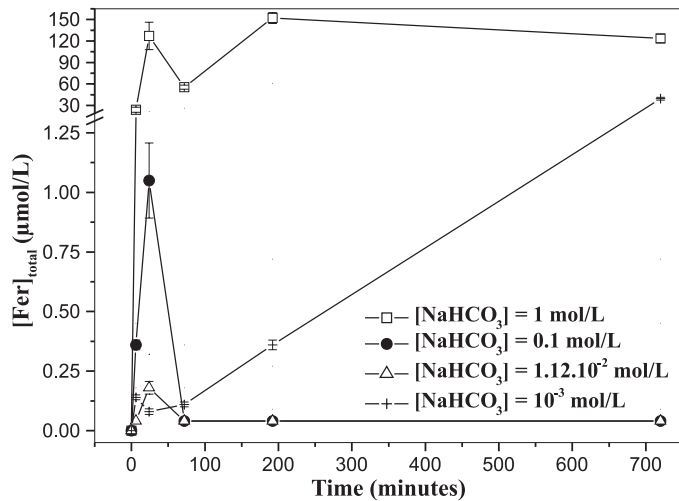


FIG. 3. – Total iron concentration evolution in carbonated media versus time.

FIG. 3. – Evolution temporelle des concentrations en fer total en milieu carbonaté.

with 1 μmol/L in the first dissolution stage ([NaHCO<sub>3</sub>] = 0.1 mol/L) decreasing to 0.18 μmol/L ([NaHCO<sub>3</sub>] = 1.12.10<sup>-2</sup> mol/L) and 0.1 μmol/L ([NaHCO<sub>3</sub>] = 10<sup>-3</sup> mol/L), except of the end of the experiment where concentration reaches 39.4 μmol/L. Acidification was followed by Eh and pH measurements (fig. 4A and B). An acidification is observed whatever carbonate concentration in the first stages of dissolution. pH decrease was observed in the diluted medium ([NaHCO<sub>3</sub>] = 10<sup>-3</sup> mol/L) and in alkaline solution ([NaHCO<sub>3</sub>] = 1 mol/L). The acidification is effective since the pH decreases dramatically (ΔpH=1.99 and 5.06 in [NaHCO<sub>3</sub>] = 1 and 10<sup>-3</sup> mol/L respectively). Eh remains rather constant close to 320 mV with a slight decrease. The only increase is observed for the diluted medium ([NaHCO<sub>3</sub>] = 10<sup>-3</sup> mol/L) with 200 mV up to 630.8 mV correlated to higher iron concentration and indicating an oxidation of ferrous ions into ferric ions.

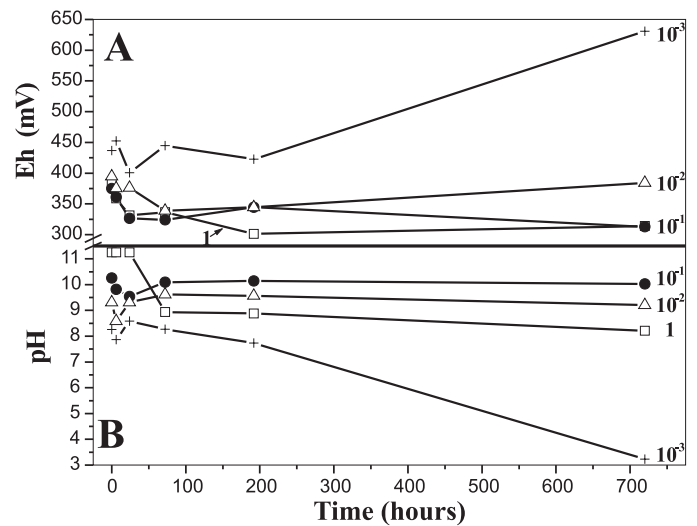


FIG. 4. – Eh (A) and pH (B) evolutions in carbonated media versus time. □ : [NaHCO<sub>3</sub>] = 1 mol/L; ● : [NaHCO<sub>3</sub>] = 0.1 mol/L; Δ : [NaHCO<sub>3</sub>] = 1.12.10<sup>-2</sup> mol/L; + : [NaHCO<sub>3</sub>] = 10<sup>-3</sup> mol/L.

FIG. 4. – Evolutions temporelles du Eh (A) et pH (B) en milieu carbonaté. □ : [NaHCO<sub>3</sub>] = 1 mol/L; ● : [NaHCO<sub>3</sub>] = 0.1 mol/L; Δ : [NaHCO<sub>3</sub>] = 1.12.10<sup>-2</sup> mol/L; + : [NaHCO<sub>3</sub>] = 10<sup>-3</sup> mol/L.

### FT-IR observations

FT-IR spectra are very rich whatever the carbonate concentration, with the exception of 10<sup>-3</sup> mol/L and in a less extent 1.12.10<sup>-2</sup> mol/L. We only present spectra for 1 and 0.1 mol/L (fig. 5A and 5B).

Sulfates, observed in all spectra, are associated with ferrous (606 cm<sup>-1</sup> ν<sub>4</sub>, 985 cm<sup>-1</sup> ν<sub>1</sub>, 1 084 cm<sup>-1</sup> ν<sub>3</sub>), ferric iron (998 cm<sup>-1</sup> ν<sub>1</sub>, 1 043 and 1 167 cm<sup>-1</sup> ν<sub>3</sub> degenerated) and occasionally with both iron oxidation states (1 019 cm<sup>-1</sup>). Iron is controlled by carbonate and oxygen. Siderite is present in [NaHCO<sub>3</sub>] = 0.1 and 1 mol/L media (745 cm<sup>-1</sup> ν<sub>4</sub>, 866 cm<sup>-1</sup> ν<sub>2</sub> and 1413 cm<sup>-1</sup> ν<sub>3</sub>) and tends to transform into hydroxide and oxyhydroxide such as goëthite (623, 780, 800 880 and 893 cm<sup>-1</sup> : α-FeOOH) which are present in all media, but in a smaller amount in diluted alkaline solution. Goëthite shows sulfate (1 350 and 1 395 cm<sup>-1</sup>) and carbonate adsorption (694, 849, 1 435 cm<sup>-1</sup>) but is known to be unstable in carbonated medium when pH is above 10, and to transform into lepidocrocite (γ-FeOOH : 485 cm<sup>-1</sup> with a significant OH<sup>-</sup> band shift towards 3 200 cm<sup>-1</sup>) for long duration experiments. Vibration bands at 687, 702 and 800 cm<sup>-1</sup>, are indicative of a chemical environment Fe-O-H oxyhydroxy ferric sulfate type including carbonate and sulfate. The crystallographic structure is very close to akaganeite (β-FeOOH) [Schwertmann and Cornell, 1991]. This mineral (ideal formula Fe<sub>8</sub>O<sub>8</sub>(OH)<sub>6</sub>SO<sub>4</sub>) is found in waste pore waters downstream of pyrite mines, when amounts of Fe<sup>+</sup> and SO<sub>4</sub><sup>2-</sup> are significant. Lines at 632 and 667 cm<sup>-1</sup> are characteristic of sulfoxyanions such as sulfite (observed by X-ray photoelectron spectroscopy) [Descostes, 2001] and thiosulfate (ν<sub>3</sub> à 671 cm<sup>-1</sup>) incorporated in the crystallographic structure previously depicted. This mineral seems to be present in the more concentrated media, while another green colored ferric oxyhydroxide (δ-FeOOH, 915 cm<sup>-1</sup>) [Nauer *et al.*, 1985] appears in the other studied solutions. From a chemical

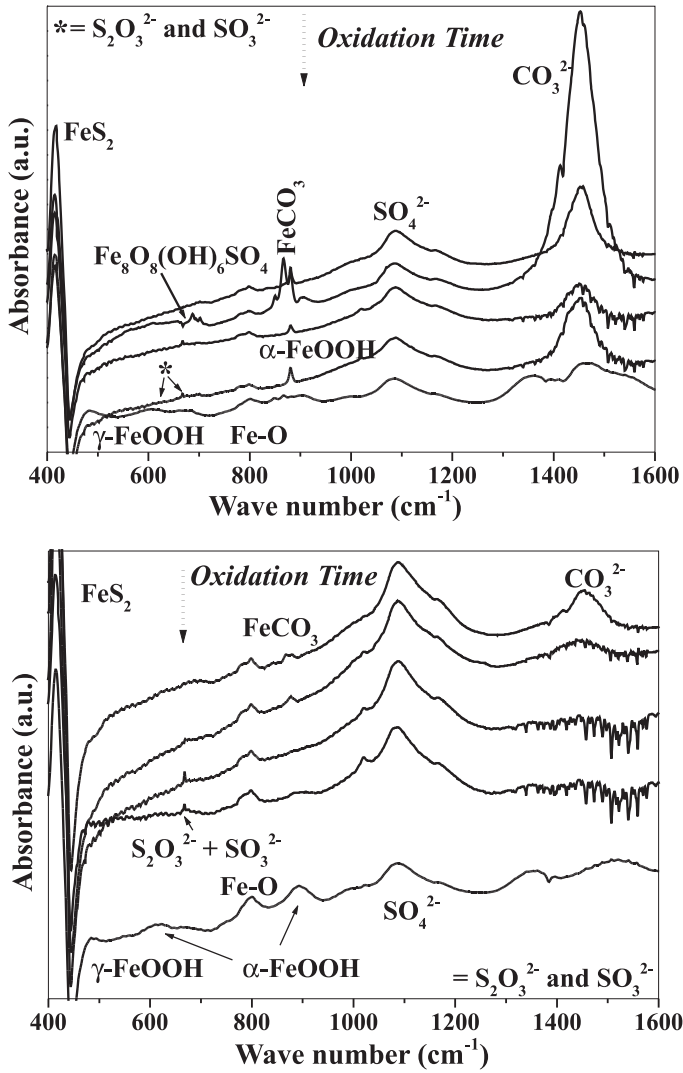


FIG. 5. – FT-IR spectra of oxidized pyrites. (A) : [NaHCO<sub>3</sub>] = 1 mol/L; (B) [NaHCO<sub>3</sub>] = 0.1 mol/L; oxidation duration increases from top to bottom (6h, 1d, 3d, 8d and 30d).  
 FIG. 5. – Spectres FT-IR de pyrites oxydées. (A) : [NaHCO<sub>3</sub>] = 1 mol/L; (B) [NaHCO<sub>3</sub>] = 0.1 mol/L; le temps d'oxydation augmente de haut en bas (6h, 1j, 3j, 8j et 30j).

point of view, these two minerals can be assigned to green rusts with a coexistence of Fe<sup>II</sup> Fe<sup>III</sup> S<sub>2</sub>O<sub>3</sub><sup>2-</sup> SO<sub>3</sub><sup>2-</sup> CO<sub>3</sub><sup>2-</sup> and OH<sup>-</sup> [Simon *et al.*, 1998].

In [NaHCO<sub>3</sub>]=1 mol/L, carbonates evolve at 30 days into carboxylate (COO<sup>-</sup>) and carbonyl (C=O) groups (1 560 and 1 800 cm<sup>-1</sup>) [Evangelou, 1995]. Carbon is able to form also S-C-S groups near 1 019 cm<sup>-1</sup> [Laajalheto *et al.*, 1999 ; Cases *et al.*, 1989]. Nevertheless, it is very difficult to distinguish in a definitive way this vibration band since the spectral region is very rich in interferences.

**DISCUSSION**

Acidification during pyrite dissolution is more effective in diluted and concentrated carbonate media ([NaHCO<sub>3</sub>]=10<sup>-3</sup> and 1 mol/L). This result is accompanied by an apparent rise of dissolution rate (sulfur concentration) with carbonate concentration. One might suggest that alkaline pH tend

to inhibit pyrite dissolution by blocking access of the oxidizing agent (O<sub>2</sub>) to pyrite surfaces by coating and precipitating iron oxyhydroxides and carbonates [Nicholson *et al.*, 1988 and 1990]. This case occurs when moderately carbonated concentrated conditions are encountered. In diluted environments ([NaHCO<sub>3</sub>]=10<sup>-3</sup> mol/L), carbonate is totally consumed by acidic pyrite dissolution. In these conditions, the carbonate system is not a pH buffer, and iron concentration reaches 39.4 μmol/L as pH goes down to pH=3.23. At higher concentrations ([NaHCO<sub>3</sub>]=1.12.10<sup>-2</sup> and 0.1 mol/L), pH remains constant whereas dissolution still goes on. In more concentrated medium ([NaHCO<sub>3</sub>]=1 mol/L), pH remains buffered in the first stages, but from 3 to 30 days, acidification is observed (ΔpH=2). This acidification is illustrated by a high dissolution rate and iron enrichment by a factor 10<sup>4</sup> compared with [NaHCO<sub>3</sub>]=1.12.10<sup>-2</sup> mol/L medium. Ferrous iron carbonate complexes (FeOHCO<sub>3</sub><sup>-</sup> and Fe(CO<sub>3</sub>)<sub>2</sub><sup>2-</sup>) are involved to explain such concentration and dissolution rates. Figure 6 illustrates the distribution of ferrous carbonate complexes as a function of pH and HCO<sub>3</sub><sup>-</sup> activity (ionic strength corrections have been taken into consideration using Specific Interaction Theory during calculation) [see Vitorge, 1995, Lemire *et al.*, 2001 for further details and Descostes, 2001 for thermodynamic data]. Thus, iron remains in solution under FeOHCO<sub>3</sub><sup>-</sup> and Fe(CO<sub>3</sub>)<sub>2</sub><sup>2-</sup> forms when high carbonate concentrations are encountered ([NaHCO<sub>3</sub>]=0.1 and 1 mol/L). It has to be pointed out that initial HCO<sub>3</sub><sup>-</sup> concentration is not always equal to sodium concentration since basic properties of carbonates (H<sub>2</sub>CO<sub>3</sub> / HCO<sub>3</sub><sup>-</sup>) have to be considered. As pH increases, bicarbonate (HCO<sub>3</sub><sup>-</sup>) concentration decreases while carbonate (CO<sub>3</sub><sup>2-</sup>) concentration increases. These complexes were already mentioned to describe metallic iron dissolu-

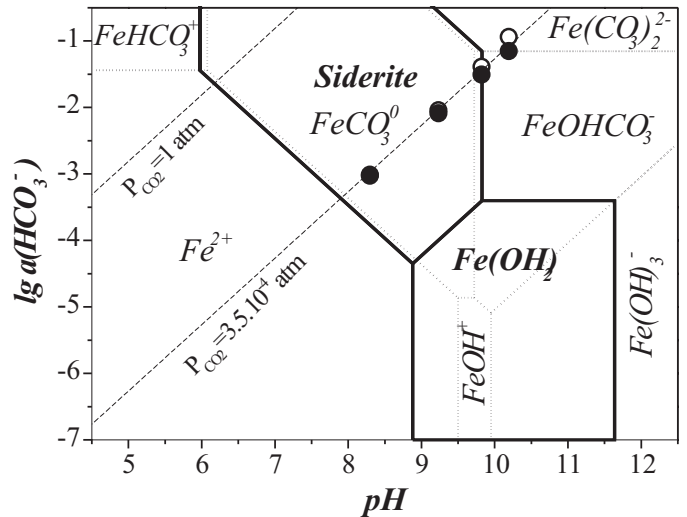


FIG. 6. – Distribution diagram for Fe(II) solid compounds (bold lines and font) and aqueous species (dotted lines and italics) as a function of pH and bicarbonate activity (a(HCO<sub>3</sub><sup>-</sup>)), plotted using the thermodynamic data taken from Descostes [2001]. Experimental conditions are converted to activities (white points) by using the SIT formula [Vitorge, 1995; Lemire *et al.*, 2001] from molar concentrations (black points).  
 FIG. 6. – Diagramme de distribution des composés solides (lignes et police en gras) et des espèces aqueuses du Fe(II) (lignes pointillées et police en italique) en fonction du pH et de l'activité en bicarbonate (a(HCO<sub>3</sub><sup>-</sup>)) établie en utilisant les données thermodynamiques de Descostes [2001]. Les conditions expérimentales sont converties en activité (points blancs) en utilisant la formule de la SIT [Vitorge, 1995 ; Lemire *et al.*, 2001] à partir des concentrations molaires (points noirs).

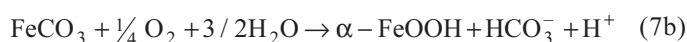
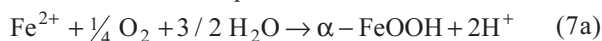


tion in carbonated medium [Legrand *et al.*, 2000]. Iron remains in solution and prevents surface from coating. In the first pyrite dissolution stages, siderite and ferrous carbonated complexes are formed according to equations 6a, 6b and 6c

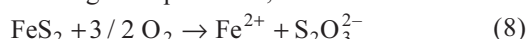


Chemical modelling is under progress to confirm this hypothesis since  $\text{CO}_2$  accumulation can generate also an acidification despite the precautions taken for guaranteeing a continuously homogeneous solution and equilibrated with atmosphere.

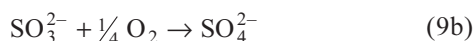
Ferrous iron and siderite are unstable in oxidising conditions and tend to transform into goëthite which in its turn is destabilized into lepidocrocite :



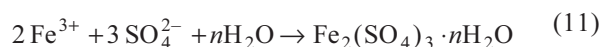
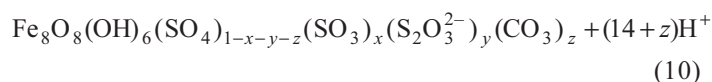
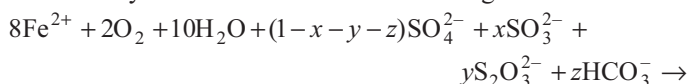
Sulfur chemistry is more complex with three redox aqueous species (thiosulfate, sulfite and sulfate). Nevertheless, acidification mainly depends on aqueous sulfur chemistry. The first sulfoxyanion released in solution is thiosulfate, according to equation 8,



Whereas further sulfur oxidation into sulfite and sulfate leads to acid production,



These two aqueous species can finally be incorporated in solid oxidation products such as oxyhydroxy ferric sulfate and hydrated ferric sulfate according to :



Thus acidification can be controlled, but thiosulfates are known to be corrosive agents [Marcus and Protopopoff, 1997].

## CONCLUSION

Carbonate pH buffer properties during pyrite oxidation were examined. Both solution (speciation, pH and Eh) and solid characterization (FT-IR) were used to ensure a complete comprehension of the reactional paths. Iron is controlled by carbonate and oxygen. Siderite appears to be the first solid precipitating, transforming into goëthite, oxyhydroxy ferric sulfate incorporating sulfite and thiosulfate, and finally lepidocrocite. Acidification during pyrite dissolution is more effective in diluted and concentrated carbonate medium ( $[\text{NaHCO}_3^-] = 10^{-3}$  and 1 mol/L) whereas pH remains buffered in  $[\text{NaHCO}_3^-] = 1.12 \cdot 10^{-2}$  and 0.1 mol/L solutions. Higher apparent dissolution rates are observed for higher carbonate contents. These results strongly illustrate the importance of ferrous iron carbonate complexes ( $\text{FeOHCO}_3^-$  and  $\text{Fe}(\text{CO}_3)_2^{2-}$ ) which tend to prevent surface from coating. Acidification mainly depends on aqueous sulfur chemistry by the oxidation of thiosulfate, first sulfoxyanion released in solution. In order to prevent from acidic pollution, one should be careful with the adjunction of alkaline materials and think of other materials such as limestone or phosphate. Further analyses by X-ray Photoelectron Spectroscopy and chemical modeling are in progress to understand the chemical evolution of the coating oxidation products.

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## References

- CASES J.M., de DONATO J.M., KONGOLO M. & MICHOT L. (1989). – An infrared investigation of amilxanthate adsorption by pyrite after wet grinding at natural and acid pH. – *Colloids and Surf.*, **36**, 323-338.
- DESCOSTES M. (2001). – Evaluation d’une perturbation oxydante en milieu argileux : mécanismes d’oxydation de la pyrite ( $\text{FeS}_2$ ). – Ph-D thesis, Denis Diderot, Paris.
- DONATO P., MUSTIN C., BENOIT R. & ERRE R. (1993). – Spatial distribution of iron and sulfur species on the surface of pyrite. – *Applied Surface Science*, **68**, 81-93.
- EVANGELOU V.P.B. (1995). – Pyrite oxidation and its control. – CRC Press, 295 p.
- EVANGELOU V.P.B., SETA A.K. & HOLT A. (1998). – Potential role of bicarbonate during pyrite oxidation. – *Environ. Sci. Technol.*, **32**, 2084-2091.
- LAAJALHETO K., LEPPINEN J., KARTIO I. & LAIHO T. (1999) – XPS and FTIR study of the influence of electrode potential on activation of pyrite by copper or lead. – *Colloids and Surf.*, **154**, 193-199.
- LEGRAND L., SAVOYE S. CHAUSSE A. & MESSINA R. (2000). – Study of oxidation products formed on iron in solutions containing bicarbonate/carbonate. – *Electrochimica Acta*, **46**, 111-117.
- LEMIRE R., FUGER J., NITSCHKE H., RAND M., SPAHIU K., SULLIVAN J., ULLMAN W. & VITORGE P. (2001). – Chemical thermodynamics – 3 Chemical thermodynamics of neptunium and plutonium. – Elsevier, Paris OCDE AEN, 845 p.
- MARCUS P. & PROTOPOPOFF E. (1997). – Thermodynamics of thiosulfate reduction on surfaces of iron, nickel and chromium in water at 25 and 300 °C. – *Corrosion Science*, **39**, 1741-1752.
- NAUER G., STRECHA P., BRINDA-KONOPIK N. & LIPTAY G. (1985). – Spectroscopic and thermoanalytical characterization of standard substances for the identification of reaction products on iron electrodes. – *J. Thermal Analysis*, **30**, 813-830.
- NICHOLSON R.V., GILLHAM R.W. & REARDON E.J. (1988). – Pyrite oxidation in carbonate-buffered solution : 1. Experimental kinetics. – *Geochim. Cosmochim. Acta*, **52**, 1077-1085.

- NICHOLSON R.V., GILLHAM R.W. & REARDON E.J. (1990). – Pyrite oxidation in carbonate-buffered solution : 2. Rate control by oxide coatings. – *Geochim. Cosmochim. Acta*, **54**, 395-402.
- SCHWERTMANN U. & CORNELL R.M. (1991). – Iron oxides in the laboratory : preparation and characterization. – Editions VCH., Weinheim, 137 p.
- SIMON L., REFAIT P. & GENIN J.M. (1998). – Transformation of Fe(II)-Fe(III) hydroxysulphite into hydroxysulphate green rusts. – *Hyperfine Interactions*, **112**, 217-220.
- VITORGE P. (1995). – Neptunium en solution carbonate concentrée réductrice<sup>o</sup> : bibliographie pour l'OCDE-AEN-TDB. – Rapport CEA-BIB-246, 95 p.