■■■ 論文 Effects of Cations on the Pyrite Dissolution with Fe(III) Ions near pH 2*

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The effects of cations including alkaline, alkaline earth, and transition metal ions on the pyrite dissolution with Fe(III) ions near pH 2 were studied by solution analysis and X-ray photoelectron spectroscopy (XPS). The results showed that Na⁺, K⁺, Ca(II), Mg(II), Ni(II), Zn(II), and Cd(II) ions had no effect, whereas Pb(II), and Ba(II) ions precipitated sulfate ions released from the pyrite; Cu(II) ions suppressed the release of Fe and S species from the pyrite. Pyrite is a soft base by HSAB theory but soft and moderate acids such as Cd(II), Ni(II), and Zn(II) did not adsorb significantly, leading to the absence of suppression. This suggests that the effect of other cations on pyrite dissolution with Fe(III) ions is not always explained by HSAB theory. After dissolution in the presence of Cu(II) ions, Cu(I) species, very similar to Cu(I) in Cu₂Se, were formed on pyrite. It was presumed that Cu(II) ions were preferentially adsorbed at active sites of pyrite-S over Fe(III) ions and reduced to Cu(I) species becoming stabilized on the pyrite, and leading to the suppression of pyrite dissolution.

KEY WORDS : Pyrite, HSAB Theory, Oxidative Dissolution, Cu(II) Ions, Cu(I) Species, Active Sites of Pyrite-S

1. Introduction

Pyrite (FeS₂) occurs widely in coal seams, sulfide deposits and other formations and the interaction between pyrite and cations involved in adsorption and oxidation/reduction have been of interest. Studies on the adsorption or reduction of toxic ions on pyrite have suggested that pyrite has the potential to remove toxic ions such as Hg(II), As(III, V), and Cr(VI) ions from waste water (Brown, et al., 1979; Jean, et al., 1986; Zouboulis, et al., 1993; 1995). Studies on interface reactions of Au-complexes/pyrite are related to the geochemical aspects in concentrating noble metals with pyrite functioning as a reductant (Hyland, et al., 1989; Bancroft, et al., 1990). In mineral processing, knowledge of the interaction between pyrite and Cu(II) ions, an activator in froth flotation of sulfide, is useful and often indispensable (Voigt, et al., 1994; Perry, et al., 1984). Pyrite has unique surface properties and further study of surface reactions is required.

Pyrite weathering is considered to be the main reason for acid mine drainage (e. g., Singer, et al., 1970), and geochemical studies of pyrite oxidation at ambient temperatures have been reported since the 1960s (e. g., Garrels, et al., 1960; Goldhaber, 1983). Direct oxidants to pyrite in natural environments are mainly Fe(III) ions and oxygen, and Fe(III) ions are known to be stronger oxidants of pyrite than oxygen (McKibben, et al., 1986). The reaction of pyrite with Fe(III)

ions in acid solutions has been conventionally expressed as
$$\text{FeS}_2 + 14\text{Fe}^{3+} + 8\text{H}_2\text{O} = 15\text{Fe}^{2+} + 2\text{SO}_4^{2-} + 16\text{H}^+ \quad \dots\dots\dots (1)$$

however, an additional reaction,

is also taking place in parallel with reaction (1), resulting in the nonstoichiometric release of Fe ions and sulfate ions (Sasaki, et al., 1994a; 1995a; 1995b).

We have been studying factors suppressing pyrite weathering by Fe(III) ions around pH 2, and found that some anionic ligands to Fe(III) ions such as oxalate and phosphate ions suppress pyrite dissolution by Fe(III) ions (Sasaki, et al., 1995b). Secondary mineral formation such as jarosite compounds (MFe₃(SO₄)₂(OH)₆, where M is a monovalent cation) also has this function (Konno, et al., 1991; Sasaki, et al., 1993). The Fe(II) ions are released according to reactions (1) and (2), so the effect of Fe(II) ions on reaction (1) is also of interest. The results suggested that initially added Fe(II) ions delay the pyrite dissolution by Fe(III) ions due to the preferential adsorption of Fe(II) ions over Fe(III) ions at active S-sites on pyrite (Sasaki, et al., 1996).

Here we report on the effect of alkaline, alkaline earth, and transition metal cations on the oxidative dissolution of pyrite by Fe(III) ions around pH 2 by solution and XPS analysis.

2. Experimental

2.1 Pyrite

Pyrite was supplied from the Yanahara mines (Japan), ground in a tungsten carbide ball mill (Fritsch Co. Ltd., P-5, Germany), and sieved to collect the 38-75 μm size fraction. The purity is around 98.2 %, and composition details were

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reported elsewhere (Sasaki, 1994; Sasaki, et al., 1994b).

The samples were pretreated individually prior to each dissolution experiment to establish a well defined surface of the stoichiometric composition, as reported previously (Sasaki, et al., 1994a).

The specific surface area after the pretreatment was determined for each dissolution experiment by the $N_2(g)$ adsorption BET method with a Quantasorb QS-13 (Yuasa Ionics Co. Ltd.) using a QS-300 cell for small area measurements, and it was $0.40 \pm 0.060 (\pm 1\sigma) m^2 g^{-1}$.

2 · 2 Dissolution experiments

Dissolution experiments were carried out in a batch reactor with an impeller and a G2 glass ball filter for N_2 bubbling. All assemblies were made of glass and rinsed with diluted HNO_3 before use to avoid iron contamination. When other cations, M^{m+} , with a higher M^{m+}/M^{n+} standard redox potential ($E^0_{M^{m+}/M^{n+}}$, $m > n$) than $0.771 V (= E^0_{Fe^{3+}/Fe^{2+}})$, coexist with pyrite in a solution containing $Fe(III)$ ions, the M^{m+} ions may function as an oxidant to pyrite similar to the $Fe(III)$ ions. Cations with $E^0 < 0.771 V$ were selected for the present investigation, and the concentrations were as shown in Table 1. Reagents were of analytical grade (AR) : Nos. 1–19, $FeCl_3 \cdot 6H_2O$; No. 2, $NaCl$; No. 3, KCl ; No. 4, $MgCl_2 \cdot 6H_2O$; Nos. 5–6, $NiCl_2$; Nos. 7–8 and 20, $ZnCl_2 \cdot 2H_2O$; Nos. 9–10 and 21, $CdCl_2 \cdot 2H_2O$; Nos. 11–12, $CaCl_2 \cdot 2H_2O$; Nos. 13–14, $Pb(COOH)_2 \cdot 3H_2O$; Nos. 15–17, $BaCl_2 \cdot 2H_2O$; Nos. 18–19 and 22, $CuCl_2 \cdot 2H_2O$. The initial pH of the solutions was adjusted to near 2 using super special grade (SSG) HCl and SSG $NaOH$.

Prior to each experiment, the solution was deaerated by

Table 1 Details of dissolution experiments and properties of the introduced cations.

No.	Foreign cations			pH		E^0 *2 / V	K_{sp} *2 for sulfate /(mol dm ⁻³) ²
	M ⁿ⁺	[M ⁿ⁺] /mmol dm ⁻³	HSAB*1	initial	final		
[Fe(III)] = 5 mmol dm ⁻³							
1	-	-	-	2.09	1.91	+0.771 (Fe ³⁺ + e ⁻ = Fe ²⁺)	
2	Na ⁺	75	HA	2.01	1.86		
3	K ⁺	75	HA	2.00	1.91		
4	Mg ²⁺	5	HA	2.09	1.91		
5	Ni ²⁺	5	MA	2.02	1.92	-0.250 (Ni ²⁺ + 2e ⁻ = Ni)	
6	Ni ²⁺	15		2.05	1.93		
7	Zn ²⁺	5	MA	2.00	1.93	-0.763 (Zn ²⁺ + 2e ⁻ = Zn)	
8	Zn ²⁺	15		2.00	1.91		
9	Cd ²⁺	5	SA	2.02	1.87	-0.403 (Cd ²⁺ + 2e ⁻ = Cd)	
10	Cd ²⁺	15		2.02	1.87		
11	Ca ²⁺	5	HA	2.02	1.93	-2.866 (Ca ²⁺ + 2e ⁻ = Ca)	10 ^{-4.62}
12	Ca ²⁺	15		2.05	1.90		
13	Pb ²⁺	1	MA	1.96	1.85	-0.126 (Pb ²⁺ + 2e ⁻ = Pb)	10 ^{-7.79}
14	Pb ²⁺	5		2.05	1.91		
15	Ba ²⁺	0.5	HA	2.06	1.91	-2.906 (Ba ²⁺ + 2e ⁻ = Ba)	10 ^{-9.96}
16	Ba ²⁺	1		2.07	1.92		
17	Ba ²⁺	5		2.08	1.92		
18	Cu ²⁺	5	MA	2.04	1.90	+0.538 (Cu ²⁺ + Cl ⁻ + e ⁻ = CuCl) +0.521 (Cu ⁺ + e ⁻ = Cu) +0.337 (Cu ²⁺ + 2e ⁻ = Cu) +0.153 (Cu ²⁺ + e ⁻ = Cu ⁺)	
19	Cu ²⁺	15		2.06	1.93		
[Fe(III)] = 0 mmol dm ⁻³							
20	Zn ²⁺	15		2.06	2.06		
21	Cd ²⁺	15		2.06	2.06		
22	Cu ²⁺	15		2.06	2.06		

*1 HA: hard acid; MA: moderate acid; SA: soft acid

*2 refer to Smith, et al., 1976.

bubbling N_2 gas ($> 99.999\%$) for more than 1 h, and the dissolved oxygen in the deaerated solution was measured to be lower than 1 ppm. Then, 2.00 g of the just pretreated pyrite powder was added to 200 cm³ of solution. Dissolution experiments were carried out for 72 h under the N_2 bubbling condition at room temperature. The temperature was not controlled due to the small changes ($23 \pm 2^\circ C$) during the experiments. Solution pH was also not controlled, as it is reported that pH does not affect dissolution rate in the pH 0 to 2 range (McKibben, et al., 1986). At intervals, 1 cm³ of supernatant was pipetted off and filtrated with a 0.20 μm pore membrane filter for solution analysis. The total Fe concentration and $Fe(II)$ ion concentration were determined by the 1, 10-phenanthroline method and the total S concentration by ICP-AES (SEIKO Co. Ltd., SPS 1200). Around pH 2 dissolved S species are sulfate ions (Moses, et al., 1991). The sampled solution was diluted with 0.01 mol dm⁻³ SSG HCl . After the dissolution experiments, the residue was separated by filtration using a 0.20 μm pore membrane filter and stored in a N_2 purged desiccator for XPS analysis.

2 · 3 XPS measurements

Chemical species on the surface of the pyrite were analyzed by XPS with an ESCALAB Mk II (V. G. Scientific). The samples were pressed onto copper foil on a holder and introduced into the spectrometer. For measurements of the Cu 2p spectra, carbon tape was used in place of copper foil. After evacuating to better than 10^{-5} Pa within 15 min, the sample was transferred into an analyzer chamber of better than 5×10^{-8} Pa and cooled below 150 K, then irradiated with $Al K\alpha$ X-ray (15 kV, 10 mA). For the measurements of the spectra for chalcopyrite ($CuFeS_2$) and pyrite (FeS_2) in Nos. 15–17 (with adsorption of Ba species on pyrite surface), $Mg K\alpha$ X-ray (15 kV, 10 mA) was also used to avoid interference by Auger peaks. The binding energies, E_B , were calibrated with $E_B[Au 4f_{7/2}] = 84.0$ eV. Under these conditions, $Cu(II)$ clusters on zeolite was not reduced to $Cu(I)$ with a significant rate by X-ray irradiation (Konno, 1993).

The surface composition of components 1 and 2 described as a mole ratio, n_1/n_2 , was calculated according to eq(3) :

$$n_1/n_2 = (I_1/s_1)/(I_2/s_2) \quad \dots\dots\dots (3)$$

where s is a sensitivity factor including escape depth of electrons, and I is an intensity by area where the contribution from X-ray satellite peaks was subtracted by computer calculation. Correction for the surface contamination layer was not carried out since the C 1s peak intensity was always very low. Details of the data analysis were described elsewhere (Konno, et al., 1991). The relative sensitivity factor between Cu 2p_{3/2} and S 2p was experimentally determined by using a fresh chalcopyrite surface cleaved in argon, $CuSO_4 \cdot 5H_2O$ (analytical grade of Kanto Chemicals) and $CuSCN$ (practical grade of Wako Chemicals). The chalcopyrite was natural mineral, supplied from the Sayama mines (Japan), and of purity $\sim 98\%$, based on the chemical composition and XRD patterns. The splitting between the Cu 2p_{3/2} and Cu 2p_{1/2} peak is large enough to take the intensity by area of Cu 2p_{3/2} peak independently. Further, oxygen Auger peaks do not interfere with

Table 2 Relative sensitivity factors, s_S/s_{Cu} , between S 2p and Cu 2p_{3/2}.

Compounds	$s_S/s_{Cu\ 2p_{3/2}}$
CuSO ₄	0.117
CuSCN	0.116
CuFeS ₂	0.114
Average	0.11 ₆

Cu 2p_{3/2} peak. The relative sensitivity factor, $s_{S\ 2p}/s_{Cu\ 2p_{3/2}}$, was estimated to be 0.11₆ as shown in Table 2, the value is comparable to 0.13 calculated from empirical factors reported by Briggs, et al (1990). The relative sensitivity factors between other elements and S were calculated from empirical factors (Briggs, et al., 1990), since precisely quantitative discussion was not important as described below.

Fig. 1 Effect of Na⁺, K⁺, and Mg(II) ions on (a) $\Delta x_S(t)$ and (b) $\Delta x_{Fe(II)}(t)$. Symbols: ●, No. 1; ○, No. 2; △, No. 3; □, No. 4. See Table 1 for experimental details.

3. Results

3.1 Effect of foreign cations excluding Cu(II) ions

As reported elsewhere (Sasaki, et al., 1994a; 1995a), there is preferential dissolution of iron species in pyrite, so that both S and Fe species must be considered when examining the dissolution behavior. The dissolved amount of i species per unit initial surface area of pyrite at a dissolution time, t , is expressed as $\Delta x_i(t)$ in mmol m⁻², where i indicates total S or Fe(II) ions. Oxidative dissolution curves of total S and Fe(II) ions from pyrite by Fe(III) ions in a HCl solution without foreign cations (No. 1) are shown with solid circles in Figs. 1–8. The $\Delta x_S(t)$ and $\Delta x_{Fe(II)}(t)$ increased with t , but the mole ratio did not agree with the stoichiometry from reaction (1). It is evident that the oxidative dissolution of pyrite by Fe(III) ions does not proceed by reaction (1) alone. In the present work, the total S and Fe(II) ion amounts released were used as parameters, but total Fe was not used due to its small change (Sasaki, et al., 1994a; 1995a; 1996).

The effect of Na⁺ and K⁺ ions was examined (Nos. 2–3) but there was no suppression as shown in Fig. 1. The scatter in Fig. 1 is due to low concentrations and is not significant for the discussion below. As Fe(II) ions suppress the dissolution of pyrite (Sasaki, et al., 1996), several divalent metal ions including Mg(II), Ni(II), Zn(II), and Cd(II) were tested (Nos. 4–10). However, they did not suppress the dissolution of pyrite in the presence of Fe(III) ions (Figs. 1–4) even at [Ni(II)], [Zn(II)], or [Cd(II)] = 15 mmol dm⁻³ (Figs. 2–4). In the absence of Fe(III) ions, no dissolution was observed (Nos. 20–21 in Figs. 3–4), indicating that these three ions cannot dissolve pyrite. Further, the amount of metal ions adsorbed on the pyrite surface was the same with pyrite dissolved and undissolved. For an example with 15 mmol dm⁻³ Cd(II) ion addition (Nos. 10 and 21), the mole ratio, n_{Cd}/n_S , on pyrite after dissolution experiments with or without Fe(III) ions was around 0.01 as shown in Table 3. The values were similar with

Fig. 2 Effect of Ni(II) ions on (a) $\Delta x_S(t)$ and (b) $\Delta x_{Fe(II)}(t)$. Symbols: ●, No. 1; ○, No. 5; △, No. 6. See Table 1 for experimental details.

Fig. 3 Effect of Zn(II) ions on (a) $\Delta x_S(t)$ and (b) $\Delta x_{Fe(II)}(t)$. Symbols: ●, No. 1; ○, No. 7; △, No. 8; □, No. 20. See Table 1 for experimental details.

Fig. 4 Effect of Cd(II) ions on (a) $\Delta x_S(t)$ and (b) $\Delta x_{Fe(II)}(t)$. Symbols: ●, No. 1; ○, No. 9; △, No. 10; □, No. 21. See Table 1 for experimental details.

Table 3 Mole ratio, n_M/n_S , on the pyrite surface after dissolution experiments. See Table 1 for experimental details.

No.	$I_M/I_{S\ 2p}^{*1}$	$s_{S\ 2p}/s_M$	n_M/n_S	Reference
M = Cd $3d_{5/2}$				
		0.15 ₄		*2
10	0.067		0.01 ₀	
21	0.079		0.01 ₂	
M = Ba $3d_{5/2}$				
		0.068		*2
15	0.385		0.026	
16	0.568		0.038	
17	0.509		0.035	
M = Cu $2p_{3/2}$				
		0.11 ₆		Present work (Table 2)
19	1.04		0.12 ₁	
22	1.42		0.16 ₅	

*1 contribution from the surface sulfate species were excluded.

*2 cited from the Photoelectron and Auger Energies compiled by C. D. Wagner (1990).

Fig. 5 Effect of Ca(II) ions on (a) $\Delta x_S(t)$ and (b) $\Delta x_{Fe(II)}(t)$. Symbols: ●, No. 1; ○, No. 11; △, No. 12. See Table 1 for experimental details. **Fig. 6** Effect of Pb(II) ions on (a) $\Delta x_S(t)$ and (b) $\Delta x_{Fe(II)}(t)$. Symbols: ●, No. 1; ○, No. 13; △, No. 14. See Table 1 for experimental details. **Fig. 7** Effect of Ba(II) ions on (a) $\Delta x_S(t)$ and (b) $\Delta x_{Fe(II)}(t)$. Symbols: ●, No. 1; ○, No. 15; △, No. 16; □, No. 17. See Table 1 for experimental details.

other ions and concentrations, and indicate that there is no interaction with Fe(III) ions in the adsorption of these ions on pyrite.

The effect of Ca(II), Pb(II), and Ba(II) ions (Nos. 11–17) which form insoluble or little soluble compounds with sulfate are shown in Figs. 5–7. Here Ca(II) ions did not show any effect, while with Pb(II) and Ba(II) ions $\Delta x_S(t)$ decreased and $\Delta x_{Fe(II)}(t)$ was unaffected. The $\Delta x_S(t)$ decreased with increasing initial concentration of these ions, except at $[Ba(II)] \geq 1 \text{ mmol dm}^{-3}$, where $\Delta x_S(t)$ was unchanged.

The XPS measurements of pyrite after 72 h-dissolution in the presence of Ba(II) ions (Nos. 15–17) showed that the mole ratio of Ba(II) to S species excluding sulfate, n_{Ba}/n_S , increased with increasing Ba(II) concentration, but that n_{Ba}/n_S did not increase at $[Ba(II)] \geq 1 \text{ mmol dm}^{-3}$. As shown in Table 3, the values of n_{Ba}/n_S were larger than those of the other ions that did not show any effect of the dissolution of pyrite, such as Cd(II) ions. It indicates that Ba(II) ions may precipitate as insoluble sulfate but that the amount is very

small, since the S 2p peak for sulfate was too low to estimate the intensity accurately. Accordingly, Pb(II) and Ba(II) ions precipitate the sulfate released from pyrite, and do not suppress the pyrite dissolution. There was no effect of Ca(II), maybe due to the solubility of $CaSO_4$ as discussed below.

3 · 2 Effect of Cu(II) ions

The effect of Cu(II) ions on $\Delta x_S(t)$ and $\Delta x_{Fe(II)}(t)$ is shown in Fig. 8 (Nos. 18, 19 and 22). Addition of 5 mmol dm^{-3} Cu(II) ions (No. 18) decreased the initial dissolution rate of pyrite ($t < 10 \text{ h}$), but both $\Delta x_S(t)$ and $\Delta x_{Fe(II)}(t)$ reached values similar to those without addition of Cu(II) ions. The larger amount of Cu(II) ions (No. 19) clearly decreased both $\Delta x_S(t)$ and $\Delta x_{Fe(II)}(t)$. Without Fe(III) ions, both $\Delta x_S(t)$ and $\Delta x_{Fe(II)}(t)$ remained nearly zero (No. 22).

The XP-spectra of pyrite after 72 h-dissolution in the presence of 15 mmol dm^{-3} Cu(II) ions and 5 mmol dm^{-3} Fe(III) ions (No. 19) are shown in Fig. 9 (top). The peak at $E_B[Cu$

Fig. 8 Effect of Cu(II) ions on (a) $\Delta x_S(t)$ and (b) $\Delta x_{Fe(II)}(t)$. Symbols: ●, No. 1; ○, No. 18; △, No. 19; □, No. 22. See Table 1 for experimental details.

Fig. 9 XPS-spectra of (a) S 2p, (b) Fe 2p, (c) Cu 2p and (d) Cu LMM for pyrite after dissolution Nos. 19 (top) and 22 (bottom). Vertical bars indicate 1000 cps in (a) and (b), 500 cps in (c), and 100 cps in (d). The spectra were obtained by irradiation with Al K α X-ray (1486.6 eV; 15 kV, 10 mA).

Table 4 Binding energies, E_B , kinetic energies, E_K , and the auger parameter, α , in eV for some related elements and compounds, corrected by $E_B[\text{Au } 4f_{7/2}] = 84.0$ eV

Compounds	$E_B[\text{Cu } 2p_{3/2}]$	$E_K[\text{Cu LMM}]$	α	$E_B[\text{Fe } 2p_{3/2}]$	$E_B[\text{S } 2p_{3/2}]$	References
No. 19	931.7	918.0	1849.7	707.0	162.2	present work
No. 22	931.7	918.0	1849.7	707.0	162.2	present work
FeS ₂ * ¹	-	-	-	707.0	162.2	Konno, et al., 1991
FeS ₂ (Cu)* ²	932.5	917.2	1849.7	707.4	162.6	Voigt, et al., 1994
Cu	932.67	918.65	1851.32	-	-	*3
CuCl	932.4	915.6	1848.0	-	-	*3
Cu ₂ S	932.6	917.3	1849.9	-	161.7	Perry, et al., 1984
Cu ₂ Se	931.9	917.6	1849.5	-	-	*3
	932.3	917.8	1850.1	-	-	Romand, et al., 1978
CuFeS ₂ * ¹	932.3	917.8	1850.3	708.8	161.2	present work
CuCl ₂	934.4	915.5	1849.9	-	-	*3
CuS	932.4	917.9	1850.3	-	162.5	Perry, et al., 1984
	932.6	917.8	1850.4	-	-	Romand, et al., 1978
CuSe	932.4	918.4	1850.8	-	-	Romand, et al., 1978

*¹ with the fresh surface after cleaving in argon

*² activated FeS₂ by Cu(II) ions.

*³ cited from the Photoelectron and Auger Energies compiled by C. D. Wagner (1990).

$2p_{3/2}] = 931.7$ eV is assigned to Cu(I), taking into account the absence of significant satellite peaks and the Auger parameter, $\alpha = 1849.7$ eV, calculated from $E_B[\text{Cu } 2p_{3/2}]$ and the E_K [Cu LMM]. The results are in agreement with those reported by Szargan, et al. (1992) and Voigt, et al. (1994). The possibility of a reduction of Cu(II) to Cu(I) on the pyrite surface

during the XPS measurements can be ignored as no satellite signals of Cu(II) were observed even at the first scan of the measurements. The formation of CuCl is a possibility because dissolution experiments were carried out in 10^{-2} mol dm⁻³ HCl solutions, but the Cu(I) species in Figs. 9(c)(d) (top) are not assigned to CuCl, since as shown in Table 4, the α value

for Cu(I) species on pyrite is significantly larger than that for CuCl (1848.0 eV), and similar to the Cu(I) species of Cu₂Se.

As shown in Figs. 9(c)(d), Cu(I) species were also observed on the control experiment No. 22 (bottom), and are identical to those of the top spectrum (No. 19). It suggests that the reduction of Cu(II) to Cu(I) species has no relation to the reaction of pyrite with Fe(III) ions.

The coverage of Cu(I) ions on the pyrite was estimated to be $n_{\text{Cu}}/n_{\text{S}} = 0.12_1$ and 0.16_5 for Nos. 19 and 22 (Table 3), very similar with and without Fe(III) ions.

4. Discussion

4 · 1 Effect of cations other than Cu(II) ions

Previously, we observed that Fe(II) ions suppress both $\Delta x_{\text{S}}(t)$ and $\Delta x_{\text{Fe(II)}}(t)$, and speculated that the suppression by Fe(II) ions was due to their preferential adsorption over Fe(III) ions to active sites of pyrite-S (Sasaki, et al., 1996). This is consistent with the idea of Moses, et al (1991). They attempted to explain the preferential adsorption of Fe(II) ions over Fe(III) ions to active sites of pyrite-S with the principle of hard and soft acids and bases (HSAB); Fe(II) ions are 'soft' acids and Fe(III) ions are 'moderate' acids and so Fe(II) ions are more active adsorbent to 'soft' bases of sulfides than Fe(III) ions. The Na⁺, K⁺, and Mg(II) ions did not suppress pyrite dissolution. Seemingly, this may also be explained by HSAB theory, since these ions are 'hard' acids and cannot adsorb preferential to Fe(III) ions. However, HSAB theory cannot be applied to the adsorption of Ni(II), Zn(II) and Cd(II) ions: these ions did not suppress the pyrite dissolution in spite of being 'moderate' or 'soft' acids. The present results suggest that the effect of foreign cations on the reactivity of pyrite with Fe(III) ions is not always explained by HSAB theory.

It is clear that Ba(II) or Pb(II) ions do not suppress reactions (1) and (2), since $\Delta x_{\text{Fe(II)}}(t)$ was not affected. From the data without foreign cations (solid circles in Figs. 1–8), the concentration of dissolved S species at $t \sim 34$ h is calculated to be about $0.72 \text{ mmol dm}^{-3}$. Considering the K_{sp} values (Table 1) and stability constants of hydroxyl- and chloride-complexes, the concentrations of divalent cations needed to precipitate 99 % of the dissolved sulfate are calculated as follows: $[\text{Ca(II)}] = 6.11 \text{ mol dm}^{-3}$, $[\text{Pb(II)}] = 4.33 \text{ mmol dm}^{-3}$, and $[\text{Ba(II)}] = 0.0255 \text{ mmol dm}^{-3}$. As shown in Figs. 5–7(a), addition of 1 mmol dm^{-3} Ba(II) ions finally decreased $\Delta x_{\text{S}}(t > 10 \text{ h})$ to ~ 15 % of that without addition (No. 16), and the addition of 5 mmol dm^{-3} of Pb(II) ions decreased $\Delta x_{\text{S}}(t > 10 \text{ h})$ to ~ 25 % (No. 14). Addition of 15 mmol dm^{-3} of Ca(II) ions did not affect $\Delta x_{\text{S}}(t)$ (No. 12). These results are parallel to the values of K_{sp} . Sulfate minerals formed in Nos. 11–17 possibly correspond to gypsum (CaSO₄), anglesite (PbSO₄) and barite (BaSO₄), which occur as secondary minerals in sulfide-rich tailings (Jambor, et al., 1994). The present results also indicate that sulfate minerals may have been formed in the aqueous phase, not on the surface of the pyrite.

4 · 2 Effect of Cu(II) ions

As reported previously (Sasaki, et al., 1995b), we

estimated that the SO₄²⁻/pyrite S standard redox potential, $E^0_{\text{SO}_4^{2-}/\text{pyrite S}}$, would be between 0.27 V and 0.34 V, using oxidants having different E^0 values. The cations discussed in part 4 · 1 cannot act as oxidants to pyrite due to their lower E^0 as shown in Table 1. The Cu(II)/CuCl standard redox potential, $E^0_{\text{Cu(II)}/\text{CuCl}}$ ($= +0.538\text{V}$) is higher than $E^0_{\text{SO}_4^{2-}/\text{pyrite S}}$, while the lowering of $E^0_{\text{Cu(II)}/\text{CuCl}}$ caused by ligand effects is not large as the stability constant of Cu(II)-Cl complex is $\log K = 0.4$ at 25 °C (Smith, et al., 1976). Therefore, Cu(II) ions should oxidize pyrite, as:

However, Cu(II) ions do not oxidize pyrite (Fig. 8 (No. 22)), and CuCl was not observed by XPS (Fig. 9 and Table 4). The K_{sp} of CuCl is 3.2×10^{-7} at 25 °C, and CuCl would be detected by XPS, if it is present. This suggests that reaction (4) did not occur on the pyrite surface, but that another redox reaction took place between the Cu(II) ions and pyrite.

The Cu(I) species on pyrite (Fig. 9(c)(d)) are very similar to Cu(I) species in Cu₂Se (Table 4). Szargan, et al. (1992) and Voigt, et al. (1994) speculated that the surface Cu(I) species are $[\text{Cu}^+\text{S}_2^-]$ formed by Cu filling in the Fe sites left vacant by oxidation, as:

This implies that pyrite-S reduces the adsorbed Cu(II) to Cu(I). As the coverage of Cu(I) is about 0.17, there would be some change in the S 2p spectra due to the surface S₂²⁻ group. This was not observed, however (Fig. 9(a) bottom). This discussion has not specified the source of electron. There is a possibility that free electrons from the bulk pyrite took part, as pyrite is an *n*-type semiconductor. When the pyrite is dissolved by Fe(III) ions, the number of vacant Fe-sites in FeS₂ must be much larger than without Fe(III) ions, but the Cu(I) coverage was very similar (Table 3) with and without dissolution of Fe(II) ions from pyrite (Nos. 19 and 22 in Fig. 8). The results here are inconsistent with Voigt, et al. (1994) that $[\text{Cu}^+\text{S}_2^-]$ species easily adsorb on vacant Fe sites. This indicates the possibility, that, preferential to Fe(III) ions, Cu(II) ions adsorbed to active "S-sites" of pyrite not on vacant Fe sites.

The suppression of pyrite dissolution by Fe(II) ions takes place as Fe(II) ions are preferentially over Fe(III) adsorbed on active sites of pyrite-S (Sasaki, et al., 1996). A similar mechanism may work for Cu(II) ions, but there are differences between Cu(II) and Fe(II) ions in the degree of suppression and electron transfer. The addition of very small amounts of Fe(II) ions (0.5 mmol dm^{-3}) markedly reduced $\Delta x_{\text{S}}(t)$ and $\Delta x_{\text{Fe(II)}}(t)$, similar to the addition of 15 mmol dm^{-3} Cu(II) ions. The redox reaction involved in the adsorption of Cu(II) ions on pyrite suggests a stronger bonding of Cu species to the pyrite surfaces than simple physical adsorption. So far, we have no explanation why Cu(II) and Fe(II) ions are so highly adsorptive to the pyrite surface. Acid mine water often contains cations from sulfides, so that the present data would be useful when evaluating sulfide ore weathering, but more detailed experimental and theoretical studies are necessary.

5. Conclusion

Cation suppression of pyrite dissolution in the presence of Fe(III) ions around pH 2 may be summarized as follows :

(1) None of Na^+ , K^+ , Mg(II) , Ni(II) , Zn(II) , or Cd(II) ions affected the reactivity of pyrite with Fe(III) ions. This suggests that the effects of cations on pyrite dissolution, cannot always be explained by HSAB theory.

(2) Due to the formation of insoluble sulfates, the Ba(II) and Pb(II) ions apparently suppress dissolution of only S species in pyrite, while Ca(II) ions did not suppress dissolution of S species. The order of suppression of $\Delta x_s(t)$ was $\text{Ba(II)} > \text{Pb(II)} > \text{Ca(II)}$, parallel to the values of the solubility product, K_{sp} . These results indicate that sulfate minerals are formed in the aqueous phase, not on the surface of pyrite.

(3) The Cu(II) ions suppressed dissolution of both Fe and S species from pyrite, that is, inhibited the reactivity of pyrite with Fe(III) ions. These results were interpreted by a mechanism where Cu(II) ions were preferentially adsorbed on active sites of pyrite-S over Fe(III) ions, and reduced to Cu(I) ions stabilized on pyrite-S.

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pH 2 付近における Fe(III) イオンによる黄鉄鉱の酸化溶解に及ぼす陽イオンの影響

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pH 2 付近における Fe(III) イオンによる黄鉄鉱 (FeS_2) の酸化溶解に及ぼす、種々の陽イオン (アルカリ金属, アルカリ土類金属, 遷移金属イオン) の影響を、溶液分析および XPS により検討した。 Na^+ , K^+ , Mg(II) , Ca(II) , Ni(II) , Zn(II) および Cd(II) イオンはほとんど影響を及ぼさなかった。それに対し、 Pb(II) および Ba(II) イオンは黄鉄鉱から溶出した硫酸イオンと沈殿を生成した。また、 Cu(II) イオンを添加すると、黄鉄鉱からの硫黄および鉄化学種の溶出が抑制された。HSAB 理論によると黄鉄鉱はやわらかい塩基であるが、 Cd(II) , Ni(II) および Zn(II) のようなやわらかい酸あるいは中間の酸は黄鉄鉱にあまり吸着せず、その溶解を抑制することもなかった。このことは、上記の反応に及

ぼす陽イオンの影響は HSAB 理論によって説明できないことを示している。 Cu(II) イオン存在下では溶解後の黄鉄鉱表面に Cu(I) 化学種が生成しており、これは Cu_2Se 中の Cu(I) の状態に極めて類似していた。 Cu(II) イオンは、 Fe(III) イオンよりも優先的に黄鉄鉱の S サイトの反応活性部位に吸着し、黄鉄鉱表面で Cu(I) の状態に還元され安定化するものと推察され、このことが黄鉄鉱の溶解抑制をもたらしたのと考えられる。

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