

# Pyrite (FeS<sub>2</sub>) oxidation as a function of pH: a multitechnique approach

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This work intends to identify the FeS<sub>2</sub> oxidation mechanism and to evaluate the effects of carbonates during its dissolution. Oxidative dissolution experiments are carried out at several pH associating solution speciation to surface solid analysis (XPS, FTIR, SEM and Nuclear Microprobe Analysis). The influence of carbonates is investigated at several contents in equilibrium with air.

We show that fast FeS<sub>2</sub> air oxidation explains the disparity of both results and oxidation mechanisms published.

Previous works indicate S at oxidation number 0 (FeSSO) and 2 (FeS<sub>2</sub>O<sub>3</sub>) on localized points of FeS<sub>2</sub> surface (Descostes *et al.*, 2001). SO<sub>4</sub><sup>2-</sup> and S<sub>2</sub>O<sub>3</sub><sup>2-</sup> are the main S aqueous species whatever the pH. Under acidic conditions (pH<3) a S deficit leads to ratios  $R=[S]_{tot}/[Fe]_{tot}<2$  (Descostes *et al.*, 2004). Given a kinetic model FeS<sub>2</sub> dissolution may be ruled by a localized first solid-state oxidation step followed by S<sub>2</sub>O<sub>3</sub><sup>2-</sup> dissolution. In acidic media S<sub>2</sub>O<sub>3</sub><sup>2-</sup> dismutation into S<sup>0</sup> and S<sub>4</sub>O<sub>6</sub><sup>2-</sup> explains the observed uncongruence with a predicted S/Fe ratio: R=1.6. This work offers a new sight of the well accepted iron preferential dissolution models.

In buffering conditions  $\Sigma\text{CO}_2 \geq 10^{-2}$  mol/L 90% of aqueous S is under S<sub>2</sub>O<sub>3</sub><sup>2-</sup> form. The dissolution rate raises with  $\Sigma\text{CO}_2$ . The observed FeS<sub>2</sub> → siderite FeCO<sub>3</sub> → goëthite  $\alpha$ -FeOOH → lepidocrocite  $\gamma$ -FeOOH → ferric sulfate transformation can't be predicted by an equilibrium thermodynamic model. The competition between Fe(II) oxidation and complexation - precipitation explains the raising of the dissolution rate vs  $\Sigma\text{CO}_2$ . Concurrently a component GR-SO<sub>3</sub> from the green rust compounds family incorporates SO<sub>3</sub><sup>2-</sup>.

## References

- Descostes M., Mercier F., Beaucaire C., Zuddas P. and Trocellier P. (2001), *Nucl. Instr. and Meth. B*, **181**, 603-609.
- Descostes M., Beaucaire C. and Vitorge P. (2004), *Geochimica et Cosmochimica Acta*, **68**, 4559-4569