Direct *vs.* indirect quantification of pyrite oxidation rates

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Experimental mineral dissolution studies typically measure bulk solution changes normalized to surface area, and thus indirectly evaluate reaction kinetics and mechanisms. Although direct mineral volume loss evaluations are still in their infancy, novel approaches (i.e., Vertical Scanning Interferometry, VSI) can now provide direct and quantitative measures for dissolution rates based on actual solid mineral volume loss [1, 2]. So far, no direct evaluations of pyrite (Py) dissolution rates are available, and all published Py dissolution rates (e.g., [3, 4]) have been determined using batch experimental approaches.

In this study the first direct and quantitative 3D dissolution rate data for the inorganic and anaerobic oxidation of pyrite in low pH solutions (mimicking hydrothermal vent fluid conditions) are presented. From time resolved direct volume loss evaluations (via VSI) a reaction rate of $\sim 2 \times 10^{-10}$ mol/m^2/min was derived, but this rate was 2-4 orders of magnitude slower than previous indirect batch rates ($\sim 10^{-6}$ to 10^{-8} mol/m^2/min; [3, 4]). In order to assess the reasons for this discrepancy two types of batch experiments (indirect via solution chemistry) were conducted: (a) VSI type (single ~ 1 mm^3 Py grain) and (b) batch (same as [3, 4], 3 g of Py, 125-250µm size fraction). The rate for (a) was $\sim 4 \times 10^{-10}$ mol/m^2/min and equivalent to the direct VSI derived rate, while the rate for (b) was $\sim 5 \times 10^{-7}$ mol/m^2/min which is within the range of the literature data. Although equilibrium in term of chemical compounds in the indirect batch experiments was reached quickly (similar to [3, 4]) the disparity in measured rates was primarily a consequence of differences in water to rock ratios, vigorous *vs.* gentle stir rates, and grain size effects. However, the VSI derived rates are more representative of Py oxidation in natural environments (e.g., seafloor or AMD conditions) where high solution to solid conditions and more static conditions usually prevail. The large discrepancy in rates indicates that dissolution rates for many minerals used in geochemical models may be vastly overestimated and may need revisiting.

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Gibbs free energy of formation for sulphate green rust

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Layered Fe^{II}-Fe^{III} hydroxide salts (green rusts, GR) form in anoxic soils and sediments and when iron corrodes, and they are important as scavengers of heavy metals [1], as powerful reductants of environmental pollutants [2, 3] and due to their influence on iron oxide dynamics and properties [4].

We have determined the Gibbs free energy of formation of the sulphate form of GR (GR$_{SO4}$) by slow acid titration of synthetic GR$_{SO4}$ under strict exclusion of oxygen. During titration crystalline magnetite is formed:

$$Fe_4^{II}Fe_2^{III}(OH)_{12}SO_4 + 4H^+ \rightleftarrows Fe_3O_4 + 3Fe^{2+} + 8H_2O + SO_4^{2-}$$
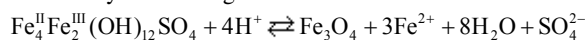
The ratio of H$^+$ consumed versus Fe^{2+} produced was close to the ideal ratio of 0.75, the lowest ratio of 0.71 indicating that the magnetite was not fully stoichiometric which was further corroborated by Mössbauer spectroscopy. No other solid phases than GR$_{SO4}$ and magnetite could be observed. Measurements of the activities of Fe^{2+}, SO$_4^{2-}$ and H$^+$ allow the calculation of the Gibbs free energy of the dissolution reaction:

$$\Delta G_r^o = -RT \ln\left[\frac{(Fe^{2+})^3(SO_4^{2-})}{(H^+)^4}\right]$$

Based on the ΔG_r^o determined and the ΔG_f^o values of products and reactants we obtained ΔG_f^o (GR$_{SO4}$) = -3820.6 ± 8.0 kJ mol^{-1} corresponding to a solubility product for GR$_{SO4}$ of -139.4 ± 5.2 kJ mol^{-1}. The ΔG_f^o (GR$_{SO4}$) value is about 30 kJ mol^{-1} more negative than the value published by Refait *et al.* [5]. Both values refer to the anhydrous form of GR$_{SO4}$. A recent study indicates that the ΔG_f^o (GR$_{SO4}$) is rather insensitive to variations in the Fe^{II}:Fe^{III} of the GR$_{SO4}$ [6]. Using our value for ΔG_f^o (GR$_{SO4}$) the standard redox potential for the Fe$_3O_4$-GR$_{SO4}$ couple is 0.53 V; at pH 7 the redox potential of the couple is -0.29 V demonstrating the strong reducing power of green rusts.

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[3] Erbs *et al.* (1999) *Environ. Sci. Technol.* **33**, 307-311.
[4] Cornell & Schwertmann (2000) *The Iron Oxides*, Wiley-VCH. [5] Refait *et al.* (1999) *Clay Miner.* **34**, 499-510.
[6] Mazeina *et al.* (2008) *GCA* **72**, 1143-1153.