Kinetics of pyrite oxidation and denitrification

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Torrentó *et al*. (2007) showed that nitrate attenuation, denitrification, mediated by pyrite oxidation is enhanced by bacterial activity. However, this process (or part of it) may be controlled abiologically. The overall reactions describing the process of denitrification-pyrite-oxidation are

$$14\ NO_3^- + 5\ FeS_2 + 4\ H^+ \rightarrow 7\ N_2 + 10\ SO_4^{2-} + 5\ Fe^{2+} + 2H_2O$$

$$NO_3^- + 5\ Fe^{2+} + 6\ H^+ \rightarrow \tfrac{1}{2}\ N_2 + 5\ Fe^{3+} + 3\ H_2O$$

where denitrification occurs via oxidation of pyrite and Fe(II) and pyrite oxidation is enhanced by the presence of Fe(III).

The present contribution aims at studying the kinetics of pyrite oxidation and nitrate reduction under anoxic conditions. The process is investigated at different pH and nitrate content by means of long-term flow-through experiments at O_2 partial pressure of 0.003 atm, pH range of 4.5 to 7.5, and NO_3^- concentration from 0.1 to 1.7 mmol L^{-1}.

Results show that as pyrite oxidizes nitrate reduces. At low NO_3^- concentration (0.1 or 0.4 mmol L^{-1}) nitrate reduction is more effective, lasting longer than at high nitrate concentration (1.3 or 1.7 mmol L^{-1}). In the experiments in which nitrate reduction clearly takes place, two stages can be distinguished. First, nitrate is reduced to a mixture between nitrite and nitrogen gas, and secondly, nitrate is reduced only to nitrite. Thereafter, nitrate reduction halts (Fig. 1).

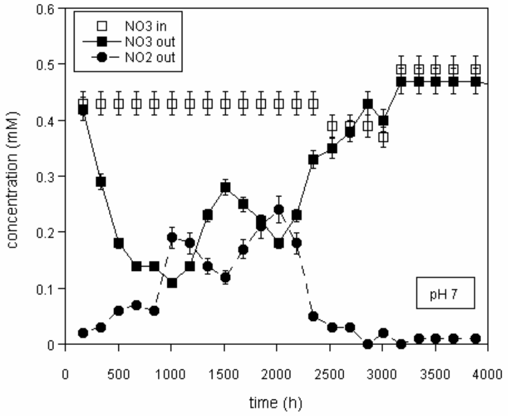

Figure 1: Variation of input and output nitrate concentration and output nitrite concentration with time.

It is observed that nitrate reduction is pH independent and the nitrate-reduction rate is $10^{-10.62\ (\pm 0.31)}$ mol s^{-1}. The pyrite dissolution rate at the studied conditions equals $10^{-12.54\ (\pm 0.14)}$ mol m^{-2} s^{-1}.

[1] Torrentó *et al*. (2007) *Goldschmidt Confer. GCA* **71**, A1032.

An experimental approach to clay mineral formation on Mars

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In this study, a laboratory-based approach is taken to delineate the chemical boundaries of clay formation on Mars. Ageing/co-precipitation experiments are conducted with synthetic basaltic weathering solutions at oxic and anoxic conditions and at varying pH (3-9).

Under oxic conditions, there is a sharp pH boundary between Fe-sulfate/oxide precipitation and clay mineral (saponite/nontronite) formation which is controlled by the solubility of a Fe^{2+}-bearing "clay precursor" phase. Under anoxic conditions, this pH boundary is removed and a spectrum of X-ray amorphous Fe-bearing silicate phases is formed from pH 4-9. The co-precipitation of Fe^{2+} with other cations in the anoxic system is initiated by Al hydrolysis, with pH controlling the crystallization kinetics of saponite/nontronite clay minerals from X-ray amorphous Fe^{2+}-bearing precursor phases. Our results indicate that the formation of Fe^{2+}- or Fe^{3+}-bearing smectites at the Martian surface through basaltic weathering may only have occurred under initially reducing conditions.

In all experiments, X-ray amorphous phases are initially produced, either as Fe^{2+}/SiO_2 (clay precursors) or Fe^{3+}/SiO_2-bearing phases. The latter do not transform into clays. These phases represent an important sink for SiO_2(aq) in Martian geochemical systems and provide a link between acid-sulfate and clay mineral precipitation regimes. In addition, despite thermodynamic supersaturation, carbonate mineral formation in these experiments appears to be inhibited by the formation of X-ray amorphous SiO_2-bearing phases, which control both cation concentrations and solution pH. The visible-near infrared and thermal infrared spectroscopic properties of these materials are being examined in detail and will enable such phases to be identified if they exist at the Martian surface.

To infer paleo-environmental conditions needed to produce specific clay assemblages observed on Mars, the experiments described above are compared to new basalt alteration experiments focusing on oxic and anoxic conditions as well as additional factors that control solution neutralization time.