Diel iron cycling in acidic rivers of southwestern Spain

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Background

In June 2006, diel sampling was conducted on the Tinto, Odiel, and Agrio Rivers of Huelva Province, Spain. These rivers are highly acidic due to acid rock drainage from massive sulfide deposits of the Iberian Pyrite Belt (Cánovas *et al*., 2007). Variables quantified included streamflow, temperature, pH, Eh, photo-synthetically active radiation, and concentrations of dissolved and total metals, anions, Fe(II)/Fe(III), and As(III)/As(V).

Results

Average 24-h pH values were 2.36, 2.30, and 3.04 at the Tinto, Agrio, and Odiel Rivers, respectively. Both pH and streamflow were essentially constant with time in each river. The only solute that showed a robust diel concentration cycle in all three rivers was dissolved Fe(II). Concentrations of Fe(II) at mid-day were 1.8 to 28 times higher than concentrations in the early morning (pre-dawn). The daytime $m_{Fe(II)}$ increases were most likely caused by photoreduction of dissolved or solid-phase Fe(III). The night-time $m_{Fe(II)}$ decreases were attributed to biologically catalyzed re-oxidation of Fe(II) to Fe(III). First-order rate constants of (2 to 7) x 10^{-5} sec^{-1} for the bacterial oxidation of Fe(II) were estimated from the observed decreases in $m_{Fe(II)}$ during the night. Maximum rates of bacterial Fe(II) oxidation (estimated to be > 3 µmol/L/h) occurred at mid-day. This amount of Fe(II) oxidation can support a growth rate of over 10^6 cells/L/h for *At. ferrooxidans*, the dominant procaryote in the Tinto River (López-Archilla *et al*., 2001).

Conclusions

Photoreduction plays a key role in biogeochemical cycling of Fe in the Tinto and neighboring rivers, and it has not been reported in previous geochemical and ecological studies of this extremely acidic and Fe-rich environment (e.g., Amils *et al*., 2007). Further work is needed to quantify the relative rates of Fe(II) production by photoreduction and by heterotrophic Fe(III)-reducing bacteria. The results of this study have implications for the primitive life that may have existed in acidic aqueous environments on early Earth or other planetary bodies such as Mars.

References

Cánovas C.R. and 4 others (2007) *Sci. Total Environ.* **373**, 363-38.

Amils R. and 10 others (2007) *Planetary Space Sci.* **55**, 370-381.

López-Archilla A.I., Marin I., and Amils R. (2001) *Microb. Ecol.* **41**, 20-35.

Interaction of the magma with the sedimentary wall rock and magnetite ore genesis in the Panzhihua mafic layered intrusion, SW China

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The Panzhihua intrusion is a gabbroic Fe-Ti-V oxide ore-bearing sill associated with the Emeishan flood basalts in SW China (Zhou *et al*. 2005). It is overlain by a syenitic body and it concordantly intrudes late-Proterozoic dolomitic limestones, remnants of which can be found as metamorphosed xenoliths in the gabbroic body. Compositions of metasediments from the contact aureole show evidence for a pronounced transfer of certain major and trace elements between magma and sediments, perhaps linked to hydrothermal circulation driven by magma emplacement.

Numerical modeling with PELE (Boudreau, 1999) shows that when magma with the average chemical composition of Emeishan basalt fractionally crystallizes under oxidising conditions (oxygen buffer > FMQ) and/or with high water contents, magnetite appears early in the crystallization sequence. This is a condition for an efficient segregation of magnetite and for the formation of the ore deposit.

Mineralogical and chemical studies of the contact aureole demonstrate that footwall dolomites were degassed during intrusion of the gabbro. We propose that CO_2-rich fluids released by this degassing increased the oxygen fugacity of the magma and caused early and massive crystallization of magnetite.

Because magnetite crystallized when the intrusion was largely molten, it migrated to the base of the gabbroic body. The increase of the viscosity in the magma and the decrease of its density during the late stages of crystallization promoted the segregation of evolved felsic liquids that solidified as syenite intrusions. The association of gabbroic and syenitic bodies in Panzhihua region results from fractional crystallization of common parental magmas.

References

Zhou M.-F., Robinson P.T., C. Lesher M., Keays R.R. , Zhang C.-J., Malpas J., 2005, *J. Petrology*, 2005, **46**, 2253-2280

Boudreau A.E., 1999, *Computers and Geosciences*, **25**, 201-203