Ferrous denitrification by biogenic hydroxycarbonate green-rust

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Nitrate is a common contaminant causing eutrophication, particularly in agricultural areas, such as in Brittany (France). In this region, natural green-rust phases (fougerite) significantly contribute to the bluish color of hydromorphic soils. These minerals are thought to form upon reduction of Fe(III)-minerals by bacterial activity under anoxic conditions [1,2]. Since synthetic green rusts phases are known to reduce NO_3^- to NH_4^+ [3], potential for *in situ* denitrification involving bacterial metabolism and abiotic reduction by biogenic green-rust has been raised.

In the present study, biogenic hydroxycarbonate green-rusts, $GR(CO_3)$, were produced in the laboratory from the reduction of either lepidocrocite or ferric oxyhydroxycarbonate [4] by *Shewanella putrefaciens* strain ATCC 12099. These biogenic Fe(II,III)-containing minerals were characterized by XRD, TEM and transmission Mössbauer spectroscopy, and their interactions with nitrite were studied. Results show that kinetics of reduction by biogenic $GR(CO_3)$ differ from those reported for synthetic analogues [5]. In addition, XRD and EXAFS analysis of time-series samples help to elucidate the chemical mechanisms involved when green rusts get oxidized.

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An integrated geochemical, hydrological and hydrodynamic approach to model arsenic at a fluvial confluence

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Fluvial confluences are natural reactors where geochemistry, hydrology and hydrodynamics can interact in complex ways to determine the fate of contaminants in a watershed. Seasonal and diurnal changes in flow, chemical composition and the non-uniform, impermanent, three dimensional field of velocities induce relevant deviations from simplified models. This is particularly relevant in watersheds receiving acid mine drainage (AMD), where confluences are primary producers of highly reactive solid phases like hydrous iron oxides (HFOs) and hydrous aluminum oxides (HAOs). We used geochemical-hydrodynamic modeling, field measurements, and laboratory experiments to study a model confluence. Our field scale model is the Azufre River (pH<2, E.C>10000μS/cm, $[Fe]_{Total}$~60mg/L, $[Al]_{Total}$~65mg/L, $[As]_{Total}$~2 mg/L)-Caracarani River (pH~8.6, E.C~1500μS/cm) confluence, located in the Chilean Altiplano. We performed geochemical simulations for the mixing ratio $C_{Azufre}=Q_{Azufre}/Q_{Total}$ (L/L) in a range of 0 to 0.5 and coupled them to 3D numerical simulations of flow. Heterogenous spatial/temporal profiles of pH-induced HFOs and HAOs and a downstream buffer is achieved at pH~2.8-3.2, where As concentration is not only diluted by mixing, but also sorbed onto the assemblage of the amorphous phases (up to 30%). Experimental mixtures of natural waters in the laboratory and field measurements were consistent with our simulations. Despite the assumptions and limitations of geochemical modeling, this integrative approach allows the study of critical scenarios and highlights the importance of evaluating kinetic and equilibrium assumptions. Our study improves the knowledge on the fate of As in surface waters, vital for the design of treatment systems or monitoring programs in extreme environments such as the Altiplano.