

The partially deprotonated Fe^{II-III} hydroxycarbonate green rust fougérite mineral and biogeochemistry of the cycles of iron, carbon and nitrogen in hydric soils

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A green rust has been recognised as a new mineral (IMA 2003-057) and given the name fougérite. Its chemical counterpart is Fe^{II-III} hydroxycarbonate GR1(CO₃²⁻) compound, which is partially deprotonated since formed by reduction of ferric oxyhydroxides through the activity of dissimilatory iron-reducing bacteria (DIRB) in anaerobic gley soils. Preparation of GR1(CO₃²⁻) by co-precipitation of Fe^{II} and Fe^{III} cations in carbonated medium shows by using Mössbauer spectroscopy that the domain of existence of GR1(CO₃²⁻) for $x = \{[\text{Fe}^{\text{II}}] / [\text{Fe}_{\text{total}}]\}$ lies within $[\sim 0.25, 0.33]$ with ordered limit $[\text{Fe}^{\text{II}}_4 \text{Fe}^{\text{III}}_2 (\text{OH})_{12}]^{2+} \cdot [\text{CO}_3 \cdot \sim 3 \text{H}_2\text{O}]^{2-}$. GR1(CO₃²⁻) gets oxidised into ferrihydrite evolving to goethite by oxidation, or into ferric green rust GR1(CO₃²⁻)*, $[\text{Fe}^{\text{III}}_4 \text{Fe}^{\text{II}}_2 (\text{OH})_4 (\text{OOH})_4]^{2+} \cdot [\text{CO}_3 \cdot \sim 3 \text{H}_2\text{O}]^{2-}$ by OH⁻ deprotonation. A mass balance of iron ox(yhydro)xides is drawn accordingly in the carbonated medium. Mössbauer spectra measured at 12 K show quite different magnetic properties and the three quadrupole doublets, comprising 2 ferrous and 1 ferric in GR1(CO₃²⁻), becomes 3 magnetically split sextets in GR1(CO₃²⁻)*. Crystallographic structure of ordered GR1(CO₃²⁻) and GR1(CO₃²⁻)* are drawn from XRD, XAS and Mössbauer spectroscopy, whereas E_{SHE} -pH diagrams are presented. Extension to other hydrotalcite-like compounds is proposed whereas occurrences of fougérite mixed with clay minerals are displayed. *In situ* Mössbauer measurements using the Mars probe MIMOS in the field will be discussed according to weather and depth variations in gley soils. The coupling between the cycles of Fe, C and N in hydric soils and the nitrate reduction by fougérite through ferric oxyhydroxides bioreduction due to DIRB is forwarded. The partially deprotonated green rust fougérite mineral is Fe^{II}_{6(1-x)}(OH)_{12(1-x)}Fe^{III}_{6(x-1)}(OOH)_{6(x-1)}Fe^{III}₂(OH)₄CO₃ where $1/3 \leq x < 2/3$. The proposal advocating a ferrosic hydroxide Fe(OH)_(2+x) is outdated.

Distribution and speciation of metals and metalloids at microbe/mineral interfaces

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Sorption and precipitation reactions at microbial and mineral surfaces provide critical controls on the speciation of trace and toxic elements in natural aquatic and sedimentary systems. Changes in speciation are particularly dynamic at microbe-mineral interfaces, yet our ability to directly probe the localized distribution, redox activity and chemical form of metals and metalloids at these interfaces has been limited. We will discuss how the coupling of several spectroscopic and scattering techniques (e.g. Reflectivity, TR-XRF, XSW, grazing-angle XANES) has enabled us to quantitatively determine the partitioning of metal(loid)s (e.g. Pb and Se) between microbial biofilms and the underlying mineral (e.g. metal-oxide) surfaces, and to identify the local structure and oxidation state of sorbed vs. precipitated or biomineralized species. We will also discuss recent advances in the ability to quantitatively measure the transfer of metal ions into microbial biofilms (or aqueous solutions) *from* minerals and rocks colonized by microbial organisms, and to define localized oxidation fronts of metals (e.g. Fe and Mn) at the nanometer scale, using the oxidative dissolution of basaltic glasses as an example.