



Biogenesis and biocycling of Fe^{II}-Fe^{III} hydroxysalt green rusts

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The green-rusts (GR) are lamellar Fe^{II}-Fe^{III} hydroxysalts primary identified as transitory intermediate products during the wet corrosion of iron-based materials. They are now recognized as a mineral, called 'fougerite' (IMA 2003-057), and are found in anoxic area such as hydromorphic soils where they are supposed to play the role of a turntable in the biogeochemical cycle of iron¹. Firstly, they are precursors of most known ferric oxides or hydroxides. Secondly, their high solubility comparatively to their ferric oxides counterparts, designates them as serious candidates to control the activity of iron species in the soil solution. In addition, their great reactivity towards many organic and inorganic pollutants, make them a potential reagents for contaminated soils and water remediation processes. Therefore, the control and the understanding of GR production represents an interesting challenge from a fundamental and applied point of view.

Since GR occurrences has been shown to be associated with iron reducing bacteria, it appears obvious to determine if such bacteria were able to generate large amount of GR and to define the optimum culture conditions leading to the target mineral precipitation.

For this purpose, we have used *Shewanella* spp. (*S. putrefaciens* CIP 80.40 and CN32, *S. oneidensis* MR-4) as models of iron reducing bacteria. It is an ubiquitous genus found in several systems such as drinking water network, seawater, soils and sediments, intestinal tracts, fish spoilage, ...etc. We determined the conditions allowing the bio-transformation of different iron oxides into the two types of GR: a GR1, the carbonated GR, and a GR2, the sulfated GR. In each case the bio-formed GR was the

main secondary mineral and up to 85-90 % of the initial iron oxide were transformed. The GR production is controlled by several factors as the starting iron substrate, the electron donor (organic *versus* inorganic), or the ratio [bacterial cells] / [Fe^{III}]². The highest rate of Fe^{II} – Fe^{III} GR formation (~ 9 mM h⁻¹) was observed when the starting Fe^{III} substrate was a ferric GR (GR*). This GR* is obtained after air-drying of a stoichiometric GR (Fe^{III}/Fe_{total} = 0.33) and have the same structure than Fe^{II} – Fe^{III} GR except that is completely ferric³. It is interesting to note that the Fe^{II}- Fe^{III} GR bio-formed either from GR* or γ -FeOOH (lepidocrocite) leads to a Fe^{III}/Fe^{II} ratio within the range of natural fougérite sample.

These results showed that GR mineral formation can be controlled by biologically driven process from different types of ferric crystalline solids. They open new insight to an applied research coupling the GR and bacteria as reagents for abiotic decontamination and catalyst to GR formation / regeneration respectively. Therefore, the GR appear as a flexible mineral which can be alternatively serve as an electron donor for oxidized pollutants or electron acceptor for iron reducing bacteria.

¹Herbillon A.J. (2006) *C.R. Geoscience*, **338** :393.

²Zegeye A., Ruby C . and Jorand F. (2007) *Geomicrobiol. J.*, in press.

³Ruby C., C. Upadhyay, A. Géhin, G. Ona-Nguema, and J-M.R. Génin (2006) *Environ. Sci. Technol.* **40** :4696.