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Monitoring green rust biomineralization with polymer addition

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Green-rusts (GR) are lamellar Fe^{II}-Fe^{III} hydroxysalts primarily 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 areas such as hydromorphic soils where they probably act as a turntable in the biogeochemical cycle of iron and are likely the product of iron reducing bacterial activity[1]. Our objective is to better understand the biological and / or chemical processes that determine the formation of GR and also of magnetite, since these two minerals have been identified as a final product of the iron oxide reduction by *Shewanella* spp. in laboratory experiments. The mechanisms and the factors controlling the two biomineralization pathways of magnetite and GR remained unclear. Among the several conditions tested to identify the relevant factor(s), it was concluded that neither the presence of electron shuttles, nor the bacterial growth phase, nor the kinetics of the iron reduction, control the nature of the mineral phases obtained. In addition, we previously showed that the (E_h/pH) Pourbaix diagram cannot be used to forecast unambiguously the nature of the mineral formed[2]. Recently we identified that the ratio [bacteria]/[lepidocrocite] controls the nature of the mineral obtained[2] independently of the iron reduction rate, even if dead cells were added in complement to active bacteria. Furthermore, the addition of an organic polymer at a concentration above 50 mg

/ L to the mixture of bacteria and lepidocrocite in the incubation medium prevents the formation of magnetite and favors the formation of the green rust phase. Our results demonstrate that the nature of the ferrous mineral obtained (magnetite vs GR) strongly depends on the presence of organic polymers but not on bacterial activity. Such organic polymers and cells (dead or alive) influence the aggregation state of the iron oxide particles as it was shown by confocal and granulometric analysis. Two different hypotheses are proposed concerning the mechanisms controlling the formation of GR and magnetite : (i) the architecture of the heterogeneous aggregates of iron oxide and cells particles influences the diffusion of reactants and favors GR formation, (ii) the cell surface or/and polymers hinder the sorption of Fe^{2+} onto lepidocrocite and consequently also the formation of magnetite by the topotactic transformation. Finally, the mechanisms of GR formation in heterogeneous environment like soils will be discussed.

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