



Role of electron donor upon the formation of hydroxysulphate green rust 2 in *Shewanella putrefaciens* cultures

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Fe(II)-Fe(III) layered double hydroxysalts are very reactive compounds commonly named green rusts, which tend to occur during the aqueous corrosion of iron (1) and in reductomorphic soils (1). Hydroxycarbonate green rust 1, GR1(CO₃²⁻), can be observed in the rust covering urban pipes in drinking water networks, while hydroxysulphate green rust 2, GR2(SO₄²⁻), was clearly demonstrated to be a major product of corrosion of steel sheet piles in a harbour (2, 3). Such minerals play a key role in corrosion and soil science since they are intermediate products of aqueous corrosion during the oxidation of the initial metal Fe(0) and steels and in addition control by equilibrium iron in soil solution in hydromorphic soils. Here we report the formation of hydroxysulphate green rust 2 by a dissimilatory iron-respiring bacterium, *Shewanella putrefaciens* under non-growth conditions. Reduction experiments were performed under anoxic conditions using a ferric oxyhydroxide, lepidocrocite gamma-FeOOH, as electron acceptor, and an organic (methanoate HCO₂⁻) or inorganic (H₂) compound as electron donor. Different experimental conditions were carried out to investigate the formation of biogenic GR2(SO₄²⁻), for example: (i) various sulphate concentrations (25-175 mM) in the presence of 80 mM of gamma-FeOOH with methanoate as the electron source; and (ii) various gamma-FeOOH concentrations (30-100 mM) in the presence of 25 mM of sulphate with H₂ as the electron source. The resulting biogenic solids, after iron-respiring activity, were characterized by X-ray diffraction (XRD), transmission Mössbauer spectroscopy (TMS) and electron microscopy (SEM and TEM). The

sulphate has been identified as the intercalated anions by diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). When an organic compound was used as the electron source, lepidocrocite bioreduction leads to bicarbonate production in the medium. The results show the competitive formation of GR1(CO₃²⁻) and GR2(SO₄²⁻) that depends upon the relative ratio (R) of bicarbonate and sulphate concentrations. When $R \geq 0.17$, GR1(CO₃²⁻) only was formed, whereas a mixture of GR2(SO₄²⁻) and GR1(CO₃²⁻) was obtained when $R < 0.17$. These results demonstrate that the hydroxysulphate GR2 can originate from the microbial reduction of gamma-FeOOH and confirmed the preference for carbonate over sulphate during green rust precipitation (4). When the electron donor was H₂, the results demonstrate that the biogenic solid was a GR2(SO₄²⁻), as the sole iron(II-III) bearing mineral, regardless of the initial lepidocrocite concentration. The crystals of the biotically formed GR2(SO₄²⁻) are significantly larger than those observed for synthetic GR2(SO₄²⁻), >15 micrometers diameter as against 0.5-4 micrometers, respectively (5).

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