



The formation of green rust induced by tropical river biofilm components

F. Jorand ^{a,*}, A. Zegeye ^a, J. Ghanbaja ^b, M. Abdelmoula ^a

^a Laboratoire de Chimie Physique et Microbiologie pour l'Environnement (LCPME) UMR 7564, CNRS-Nancy-Université, Institut Jean Barriol, 405 rue de Vandœuvre, F-54600 Villers-lès-Nancy, France

^b Service Commun de Microscopies Electroniques et Microanalyses X (SCMEM), Nancy-Université, Bvd des Aiguillettes, BP 239, 54506, Vandœuvre-lès-Nancy, France

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ABSTRACT

In the Sinnamary Estuary (French Guiana), a dense red biofilm grows on flooded surfaces. In order to characterize the iron oxides in this biofilm and to establish the nature of secondary minerals formed after anaerobic incubation, we conducted solid analysis and performed batch incubations. Elemental analysis indicated a major amount of iron as inorganic compartment along with organic matter. Solid analysis showed the presence of two ferric oxides ferrihydrite and lepidocrocite. Bacteria were abundant and represented more than 10^{11} cells g^{-1} of dry weight among which iron reducers were revealed. Optical and electronic microscopy analysis revealed that the bacteria were in close vicinity of the iron oxides. After anaerobic incubations with exogenous electron donors, the biofilm's ferric material was reduced into green rust, a Fe^{II} - Fe^{III} layered double hydroxide. This green rust remained stable for several years. From this study and previous reports, we suggest that ferruginous biofilms should be considered as a favorable location for GR biomineralization when redox conditions and electron donors availability are gathered.

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1. Introduction

The green rust (GR) compounds are mixed Fe^{II} - Fe^{III} layered double hydroxide unstable under oxic conditions, and identified in several sub-oxic environments like corroded surface of Fe-based materials (Refait et al., 2006), hydromorphic soils (Trolard et al., 1997) or ground water (Christiansen et al., 2009). The GR structure is related to that of the mineral fougérite (IMA 2003-057) (Génin et al., 2005; Trolard et al., 2007). The GRs are considered to be key components in biogeochemical cycle of iron (Herbillon, 2006) or in the applied research for polluted soil and water remediation processes due to their high reactivity towards oxidized organic (nitroaromatics, chloride derived,...) or inorganic compounds (Hg^{II} , Se^{VI} , Cr^{VI} ,...) (Myneni et al., 1997; Erbs et al., 1999; Loyaux-Lawniczak et al., 2000; Refait et al., 2000; O'Loughlin et al., 2003). However, the mechanisms implied in their formation and whether or not bacteria are a major actor for their precipitation in natural environments, remain under investigation (Zegeye et al., 2005; Zegeye et al., 2007a; Ahmed et al., 2010; Salas et al., 2010; Zegeye et al., 2010).

The dissimilatory iron-reducing bacteria (DIRB) are well recognized to be involved in the formation of secondary iron-II minerals. By coupling the reduction of Fe^{III} to the oxidation of hydrogen or organic matter they gain energy for growth and the resulting Fe^{II} mainly precipitates in several mineral phases such as magnetite (Fe_3O_4), siderite ($FeCO_3$),

chukanovite ($Fe_2OH_2(CO_3)$), vivianite ($Fe_3(PO_4)_2 \cdot 8H_2O$), the hydroxycarbonate green rust 1 ($Fe^{II}_4Fe^{III}_2(OH)_{12}CO_3 \cdot 3H_2O$) and the hydroxysulfate green rust 2 ($Fe^{II}_4Fe^{III}_2(OH)_{12}SO_4 \cdot 8H_2O$) (Lovley et al., 1987; Jorand et al., 2000; Glasauer et al., 2002; Ona-Nguema et al., 2002; Kukkadapu et al., 2005; Zegeye et al., 2005). The nature of the secondary iron mineral is partly controlled by the presence of its chemical constituents. For instance, phosphate or sulfate are needed to form vivianite or GR2(SO_4^{2-}), respectively. But lower phosphate, concentration (i.e. undersaturated for vivianite precipitation) plays additional role, as organic polymers, bacterial cells or silicate, which is to promote the formation of GR over the magnetite without being constituent of this mineral. Thus, the supplementation of the incubation medium by microbial or synthetic polymers (polyacrylate) or autoclaved cells (Zegeye et al., 2007a; Jorand et al., 2008; O'Loughlin et al., 2010; Zegeye et al., 2010), phosphate (Kukkadapu et al., 2004), quartz particles (SiO_2), silicic acid (H_4SiO_4) or a panel of oxyanions (O'Loughlin et al., 2010; Sergent et al., 2010) significantly promote the formation of GR1 over magnetite from lepidocrocite or ferrihydrite bioreduction.

The mechanisms involved in such secondary iron biomineralization remains under investigation. Recently, the organization of mixed aggregates constituted by iron oxide and bacterial cells was proposed to influence the GR vs magnetite mineralization routes (Zegeye et al., 2010). It was suspected that an aggregate constituted by densely packed particles promotes areas at a micro-scale level. These micro-area would exhibit high concentrations of both bicarbonate and Fe^{II} , resulted from the bacterial metabolism, which would explain the formation of GR. Competitive binding site of oxyanions and Fe^{II} onto ferric oxide surface was also suggested as a factor controlling the nature of the bioreduction product (O'Loughlin et al., 2010) as well as

* Corresponding author at: LCPME UMR 7564 CNRS-Nancy-University, 405 rue de Vandœuvre, F-54600 Villers-lès Nancy, France. Tel.: +33 3 83 68 52 48; fax: +33 3 83 27 54 44.

E-mail address: jorand@pharma.uhp-nancy.fr (F. Jorand).

the iron reduction rate (Ona-Nguema et al., 2003). In addition, since the carbonated GR1 is relatively unstable as regards to magnetite (Tronc et al., 1992), it has been suggested that the components cited above (phosphate, polymers or silicate), could also promote the formation of GR by playing a protective role on the GR crystals. The sorption of anionic components onto the crystals, especially on the lateral faces, would impair their dissolution and thus their subsequent transformation into magnetite (Benali et al., 2001; Bocher et al., 2004; Sergent et al., 2010).

In natural environments, bacteria are usually present in association with complex organic matter, heterogeneous and diverse minerals and inorganic particles. For instance, biofilms, which are a widespread form of life for bacteria, are mainly constituted by an arrangement of bacteria embedded in exo-cellular polymeric substances (EPS) (De Beer and Stoodley, 2006). Thus, since the presence of EPS and large cell densities were identified to be favorable factors for the (bio) mineralization of GR, as afore mentioned, one could expect that biofilms, especially those rich in iron, display a suitable environment for the GR's formation. However, to our knowledge, the formation of GR in a more complex environmental media or from a biofilm material remains poorly studied. Recently, one study has reported the formation of a GR1 by anaerobic incubation of a ferric material collected from a groundwater seep (Blöthe and Roden, 2009).

The purpose of this study was therefore to evaluate the potentiality of a biofilm material to promote the formation of GR and other Fe^{II} phases. To that end, we used ferruginous biofilms present in the Sinnamary Estuary (Atlantic Ocean, French Guiana), a well-described mercury contaminated area, due to past and present anthropic activity (Dominique et al., 2007; Muresan et al., 2008). We evaluated the capability of the biofilm components to display an iron

reducing activity and to promote the formation of GR especially because of its high reactivity towards pollutants such as cationic mercury.

2. Materials and methods

2.1. Sites and biofilm sampling

The biofilm samples were collected in the Sinnamary Estuary in French Guiana (Fig. 1) where a hydroelectric dam was built in 1994. The resulting reservoir has flooded more than 350 km² of tropical rainforest inducing a major disturbance of biogeochemical cycles in both the reservoir and the Sinnamary Estuary downstream the dam (Richard et al., 1997; De Mérona et al., 2005). For example the biodegradation of the huge immersed biomass has led to a significant decrease of the E_h in the water column, decreasing the O₂ level from 7.2 mg l⁻¹ in 1992 to 0.4 mg l⁻¹ just after the dam from 1995 to present (Richard et al., 1997; Dominique, 2006). As a result, the dam effluent water is significantly concentrated in reduced species such as soluble Fe^{II} species (up to 15–20 μmol l⁻¹) (Muresan et al., 2008) and increased by a factor 10 (from 2 μmol l⁻¹ to 23 μmol l⁻¹) after the dam construction (Dominique, 2006). These Fe^{II} species are probably the precursor of the red flocs transported by the estuary river and of the thick red-brown slimes recovering any surface in contact with the water up to ~30 km after the dam (Fig. 2a and b). In addition, the anaerobic conditions occurring in the reservoir contribute to the formation of the methyl mercury in the Sinnamary Estuary (Dominique et al., 2007; Muresan et al., 2008).

The samples were collected between March 2005 and March 2008 at three sampling stations: i) the *Passerelle* station (N5°03'54", W53°03'

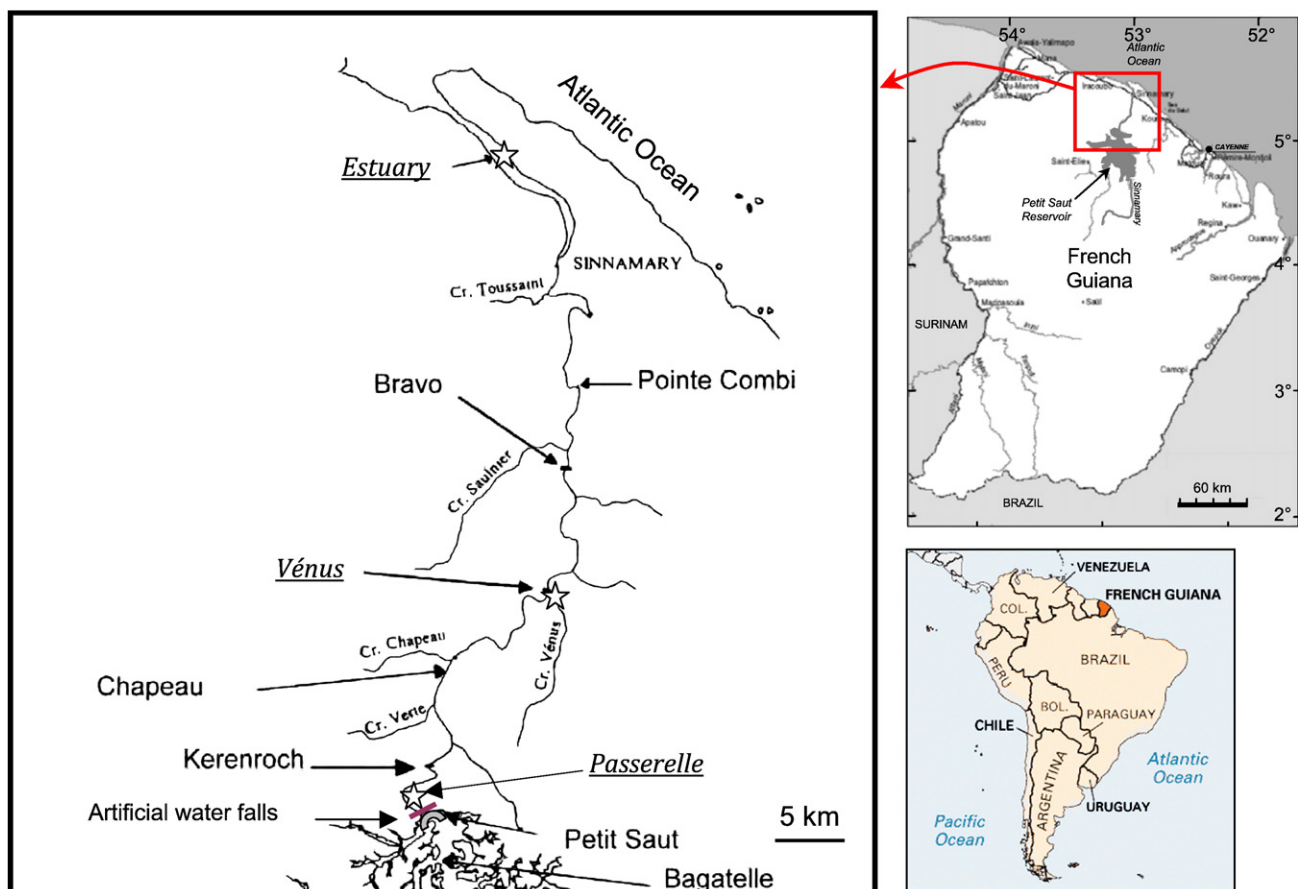


Fig. 1. Map showing the location of the Petit-Saut dam and the stations *Passerelle*, *Vénus* and *Estuary* (indicated as a white star) along the Sinnamary Estuary in French Guiana. The semi-circle indicates the location of the dam.

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