

## Formation and transformation of Fe(II-III) hydroxysalts (GRs) in marine environments

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The Fe(II-III) hydroxysulfate green rust  $\text{GR}(\text{SO}_4^{2-})$  is one of the main corrosion products of carbon steel in marine environments [1, 2]. It is typical of the abiotic (i.e. purely electrochemical) process as demonstrated by laboratory experiments [3] in aerated and anoxic conditions as well. Even though the  $\text{Cl}^-$  to  $\text{SO}_4^{2-}$  concentration ratio is equal to 19 in seawater,  $\text{GR}(\text{SO}_4^{2-})$  forms preferentially to the hydroxychloride  $\text{GR}(\text{Cl}^-)$  because divalent anions gave to the layered structure of GRs a greater stability than monovalent anions. However, variations of seawater parameters such as pH, carbonate concentration or organic matter content can induce the transformation of  $\text{GR}(\text{SO}_4^{2-})$  into other Fe(II-III) bearing minerals such as hydroxycarbonate  $\text{GR}(\text{CO}_3^{2-})$ , magnetite  $\text{Fe}_3\text{O}_4$  or even other GRs built on organic anions. For instance, an increase of pH, leading to an increase of the  $\text{CO}_3^{2-}$  to  $\text{HCO}_3^-$  concentration ratio, may lead to the transformation of  $\text{GR}(\text{SO}_4^{2-})$  into  $\text{GR}(\text{CO}_3^{2-})$  [4]. The respective proportions of  $\text{GR}(\text{SO}_4^{2-})$  and  $\text{GR}(\text{CO}_3^{2-})$  in marine environments are mainly governed by the  $\text{SO}_4^{2-}$  to  $\text{CO}_3^{2-}$  concentration ratio [3]. On the other hand, the accumulation of bacterial cells and their lysis can induce the formation of unexpected GRs, e.g.  $\text{GR}(\text{C}_2\text{O}_4^{2-})$ , as for instance observed on steel immersed in marine sediments.

It is suspected that a partial substitution of  $\text{Fe}^{2+}$  by  $\text{Mg}^{2+}$  occurs in the GR structure at low corrosion rates, i.e. for low dissolved Fe(II) species concentrations. This was also observed for the naturally occurring fougérite mineral GR [5]. The presence of Mg(II) in the hydroxide layer of GRs should enhance the redox flexibility of GR minerals, hence improving their well-known ability to reduce oxidized pollutants such as nitrite, selenate, chromate, etc..

[1] Pineau *et al.* (2008) *Corros. Sci.* 50, 1099-1111. [2] Refait *et al.* (2016) *Corros. Sci.* 111, 583-595. [3] Refait *et al.* (2011) *Electrochim. Acta* 56, 6481-6488. [4] Refait *et al.* (2013) *Corros. Sci.* 71, 32-36. [5] Refait *et al.* (2001) *Amer. Min.* 86, 731-739.