

Mössbauer and XAS study of a green rust mineral; the partial substitution of Fe²⁺ by Mg²⁺

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ABSTRACT

Layered double hydroxysalt green rusts, GRs, are very reactive compounds and their general formula, $[\text{Fe}_{(1-x)}^{2+}\text{Fe}_x^{3+}(\text{OH})_2]^{x+} [x/n \text{A}^{n-} \cdot m \text{H}_2\text{O}]^{x-}$, where x is the ratio $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$, reflects the structure in which brucite-like layers alternate with interlayers of anions A^{n-} and water molecules. A GR mineral was extracted from hydromorphic soils in Fougères (France) and studied by X-ray absorption spectroscopy (XAS) and transmission Mössbauer spectroscopy (TMS). The XAS spectrum at the Fe K absorption edge of this mineral proved to be very similar to that of synthetic GRs. However, the radial distribution function obtained for the GR mineral proved to be intermediate between those of $\text{GR}(\text{CO}_3^{2-})$ and pyroaurite, that is between the $\text{Fe}^{2+}\text{-Fe}^{3+}$ and $\text{Mg}^{2+}\text{-Fe}^{3+}$ hydroxycarbonates. Consequently, a partial substitution of Fe^{2+} by Mg^{2+} occurs, leading to the general formula of $[\text{Fe}_{(1-x)}^{2+}\text{Mg}_x^{2+}\text{Fe}_x^{3+}(\text{OH})_{(2+2y)}]^{x+} [x/n \text{A}^{n-} \cdot m \text{H}_2\text{O}]^{x-}$ where A^{n-} is the interlayer anion. Unfortunately, the XAS spectra of various GR proved to be independent of the interlayer anion, and the nature of the anions present in the mineral GR could not be determined. The Mössbauer spectrum of the mineral, measured at 77 K, is composed of four quadrupole doublets: D_1 and D_2 due to Fe^{2+} [$\delta \cong 1.26$ mm/s and $\Delta E_Q \cong 2.5$ and 2.9 mm/s, respectively] and D_3 and D_4 due to Fe^{3+} [$\delta \cong 0.46$ mm/s and $\Delta E_Q \cong 0.5$ and 1.0 mm/s, respectively]. Finally, synthetic $\text{Mg}^{2+}\text{-Fe}^{2+}\text{-Fe}^{3+}$ hydroxycarbonates could be prepared by coprecipitation from Mg and Fe salts and lead to Mössbauer spectra similar to that of the mineral. In particular, the partial substitution of Fe^{2+} by Mg^{2+} proved to be consistent with the existence of the unusual doublet D_4 .