Mössbauer and XAS study of a green rust mineral; the partial substitution of Fe\(^{2+}\) by Mg\(^{2+}\)


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ABSTRACT

Layered double hydroxysalt green rusts, GRs, are very reactive compounds and their general formula, \([\text{Fe}_{2x},\text{Fe}_y(\text{OH})_z\text{m}_n\text{H}_2\text{O}]^{+}\) \(\times/\text{n} A^-m \text{H}_2\text{O}^{-}\), 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 \(A^-\) 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 GR(CO\(_3\))\(^{2-}\) and pyroaurite, that is between the Fe\(^{2+}\)-Fe\(^{3+}\) and Mg\(^{2+}\)-Fe\(^{3+}\) hydroxycarbonates. Consequently, a partial substitution of Fe\(^{2+}\) by Mg\(^{2+}\) occurs, leading to the general formula of \([\text{Fe}_{2x},\text{Mg}_y\text{Fe}_n(\text{OH})_{z-2}\text{m}_n\text{H}_2\text{O}]^{+}\) where \(A^-\) 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\(^{2+}\) \(\delta \equiv 1.26 \text{ mm/s and } \Delta E_q \equiv 2.5\) and \(2.9 \text{ mm/s, respectively}\) and \(D_3\) and \(D_4\) due to Fe\(^{3+}\) \(\delta \equiv 0.46 \text{ mm/s and } \Delta E_q \equiv 0.5 \text{ and } 1.0 \text{ mm/s, respectively}\). Finally, synthetic Mg\(^{2+}\)-Fe\(^{2+}\)-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 \(D_1\).

INTRODUCTION

The mobility of Fe is of utmost importance in soil- and ore-forming, biogeochemical and environmental processes because of its abundance and its variety of oxidation states. In oxidizing conditions, Fe oxides present are goethite and hematite. The relative stability of these latter minerals is affected first by water activity, secondly by particle size (Ferrier 1966), and thirdly by Al\(^{3+}\) substitutions in the lattice (Trolard and Tardy 1987). In moderately reducing conditions, Fe is reduced and siderite occurs in sediments, whereas in strongly reducing conditions, Fe oxides present are goethite and hematite. In moderately reducing conditions, Fe oxides present are goethite and hematite. In strongly reducing conditions, sulfate is reduced, too, and pyrite forms. The relative stabilities of hematite, siderite, and pyrite have been discussed using Eh-pH diagrams by Krumbein and Garrels (1952), Huber et al. (1979). These phases were designated as "the theoretical compound hydromagnetite, Fe\(^{2+}\)(OH)\(^{4-}\)" and considered as metastable phases with no explicit link being made between this compound and GRs (Taylor 1981). It was only recently that such a mineral, for which the name fougerite was proposed, was characterised by Mössbauer and Raman spectroscopies in hydromorphic soils (Trolard et al. 1996, 1997). It was assumed to be one of the various forms of GRs. By analogy with pyroaurite, it consists of positively charged brucite-like layers characterised by moderately reducing conditions were recognized very early (Vysotskii 1905) as showing a distinct greenish-blue chroma that upon exposure to the air turned yellowish, and ascribed to the fact that some Fe was undoubtedly present as FeO. This green-blue color was much later suggested by Taylor (1981) to come from Fe\(^{2+}\)-Fe\(^{3+}\) double layered hydroxides, commonly named green rusts (GRs) i.e., Fe\(^{2+}\)-Fe\(^{3+}\) hydroxy-chlorides and -sulfates or -carbonates. The solid phases that control iron in soil solution have long been searched for, but no equilibrium between Fe\(^{4+}\) oxides and solution was observed in moderately reducing conditions and instead evidence for the equilibrium with a mixed Fe\(^{2+}\)-Fe\(^{3+}\) hydroxide was derived from laboratory experiments (Arden 1950) or field soil solution studies (Ponnampерuma et al. 1967; Ponnamperuma 1972; Lindsay 1979). These phases were designated as "the theoretical compound hydromagnetite, Fe\(^{2+}\)(OH)\(^{4-}\)" and considered as metastable phases with no explicit link being made between this compound and GRs (Taylor 1981). It was only recently that such a mineral, for which the name fougerite was proposed, was characterised by Mössbauer and Raman spectroscopies in hydromorphic soils (Trolard et al. 1996, 1997). It was assumed to be one of the various forms of GRs. By analogy with pyroaurite, it consists of positively charged brucite-like layers...