Incorporation of Ni into natural goethite: An investigation by X-ray absorption spectroscopy

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ABSTRACT

Goethite (α-FeOOH) is abundant at the Earth’s surface and has the unusual capacity to adsorb and fix ions from migrating solutions. Understanding the mechanisms by which foreign elements are incorporated into natural goethite has implications for environmental and mining problems. X-ray absorption spectroscopy (XAS) was used to obtain structural information on the local environment around Ni in natural Ni-containing goethite (1.8–4.1 mol% Ni) from Vermelho lateritic deposit of Serra dos Carajás (Brazil) and in synthetic analogues. The data were collected at the LNLS XAS beam line at the Ni and Fe K-edges, at room temperature, and at the Ni K-edge at 8 K. Nickel was found in essentially the same environment in all natural and synthetic samples, with negligible thermal disorder. The coordination polyhedron is a tetragonal dipyramid of oxygen atoms showing that Ni preserves its usual local symmetry. This finding is compatible with a model in which substitution of Ni for Fe is accompanied by a proton capture resulting in NiO₆(OH)₄ octahedra. The polyhedral linkages are similar to that of pure α-FeOOH, consisting of four shared edges at about the same metal-metal distances, as in the pure mineral. The third and longest metal-metal distance is about 6% larger than the expected corner-sharing distance in the α-FeOOH structure, showing that incorporation of Ni locally distorts and opens the structure.

INTRODUCTION

The special importance of goethite (α-FeOOH) in geochemistry results from the combination of its ubiquitous presence in soils and sediments and its exceptional chemical reactivity. Formed under Earth’s surface conditions as a result of hydrolysis reactions, goethite is a poorly and imperfectly crystallized material having a large surface area. These characteristics and its open channel structure result in an unusual capacity to incorporate, adsorb, and fix ions from migrating solutions. Understanding how metallic species are incorporated into goethite has many implications for environmental management, mineral exploration, and ore processing.

The association of goethite with several metals has been studied experimentally in synthetic analogues (Schwertmann et al. 1989; Gerth 1990; Wolska and Schwertmann 1993; Schwertmann and Pfab 1994), but the techniques used in those studies did not provide a structural characterization of how these metals are incorporated. The sensitivity of X-ray absorption spectroscopy (XAS) to the immediate environment of cations in solids can provide new insights about the structure of poorly crystallized materials like Fe-oxyhydroxides. Quantitative short-range structural results obtained in XAS investigations of some Me-containing goethites and adsorbed ionic species at the mineral/water interface allowed different incorporation mechanisms to be distinguished. Among them, isomorphous substitution (Bernstein and Waychunas 1987; Martin et al. 1997; Manceau et al. 2000), epitaxially inter or over-grown domains (Manceau and Combes 1988; Manceau et al. 1992a, 1992b; Hazemann et al. 1992; Manceau et al. 2000; Scheinost et al. 2001), and different sorption sites or complexes at the surface of the crystals (Charlet and Manceau 1992; Spadini et al. 1994; Bargar et al. 1997; Fendorf et al. 1997; Collins et al. 1998) have been observed.

Usually, the amount of “foreign” metals found in goethite in common soils is very low. Consequently, it is very difficult to obtain natural samples with high metal contents. It is even more difficult to isolate goethite from the bulk samples because they usually consist of several very fine-grained, intimately mixed phases. In a previous study (Carvalho-e-Silva and Oliveira 1995), goethite was separated from bulk samples collected in the oxidation zone of a lateritic Ni-ore. These Ni-enriched goethite samples provided a very rare opportunity to study an occurrence of this potentially toxic metal. Results of previous characterization by X-ray diffraction (XRD), transmission electron microscopy (TEM), differential thermal and thermal gravimetric analysis (DTA-TGA), Fourier Transform Infrared and Mössbauer spectroscopies showed weak to moderate correlation with the Ni content in goethite, suggesting in corporation of Ni (Carvalho e Silva et al. 2002). The results were inconclusive regarding substitution of Ni for Fe, because the low Ni uptake by goethite caused only small changes in the crystal structure that could not be detected clearly by those techniques.

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