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

MARIA LUIZA CARVALHO-E-SILVA,¹ ALINE YVETTE RAMOS,³ HELIO CESAR NOGUEIRA TOLENTINO,² JACINTA ENZWEILER,^{1,*} SILVANIA MARIA NETTO,¹ AND MARIA DO CARMO MARTINS ALVES²

¹Instituto de Geociências, UNICAMP, CP 6152, CEP 13083-970 Campinas, Brazil ²LNLS CP6192 CEP13083-970 Campinas, Brazil ³LMCP UMR7590 Paris, France

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 NiO₂(OH)₄ octahedra. The polyhedral linkages are similar to that of pure a-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.