XAS evidence for Ni sequestration by siderite in a lateritic Ni-deposit from New Caledonia

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ABSTRACT

Mineralogical and spectroscopic analyses were conducted on a lateritic Ni-deposit from Southern New Caledonia. Results show that Ni is incorporated in siderite (FeCO₃) found between 37 and 40 m depth in the laterite and saprolite units of the regolith. SEM-EDXS and XEDS analyses of siderite-rich samples indicate that a significant amount of nickel can be hosted by this crystalline phase (~0.8 wt% NiO). Ni and Fe K-edge extended X-ray absorption fine structure (EXAFS) spectroscopic analyses of the siderite-rich samples from the regolith as well as comparison with synthetic Ni-bearing and Ni-free siderites demonstrate isomorphous substitution of Ni²⁺ for Fe²⁺ in the siderite structure. Linear combination fitting (LCF) of the Ni K-edge EXAFS data reveals that this Ni-bearing siderite species accounts for more than 90% of the total Ni pool (1 wt% NiO) in the siderite-rich horizons of the regolith. In addition, LCF analysis of the EXAFS spectra indicates that goethite and serpentine are the major Ni hosts in the upper horizons (laterite) and lower horizons (saprolite) of the regolith, respectively. Formation of siderite, an uncommon mineral species in such oxidized environments, is attributed to the development of swampy conditions in organic-rich lateritic materials that accumulated at the bottom of dolines. These results thus show the importance of siderite as a host for nickel in lateritic Ni deposits that have been affected by late hydromorphic and reducing conditions.

Keywords: Siderite, XAS, nickel, laterite, speciation

INTRODUCTION

Siderite (FeCO₃) is a common carbonate mineral in sedimentary environments where it is considered as a diagenetic product (Postma 1981, 1982; Pye et al. 1990; Mozley 1989; Mozley and Wersin 1992; Ohmoto et al. 2004). Siderite is also classically found in wetland soils where it usually occurs as millimeter-scale spherulites known as sphaerosiderite (Ludvigson et al. 1998; Ufnar et al. 2001, 2004; White et al. 2001, 2005; Sheldon and Tabor 2009). Occurrences of pedogenic siderite with non-spherulitic morphologies have also been reported for poorly drained and swampy peat soils (McMillan and Schwertmann 1998; Driese et al. 2010). In most of these soil environments, siderite is considered to result from in situ reaction between dissolved carbon and ferrous iron after microbially mediated oxidation of organic matter and coupled reduction of Fe-oxides under reducing conditions (Ellwood et al. 1988; Mortimer et al. 1997; Mortimer and Coleman 1997; Frederickson et al. 1998). In addition to this classical route of formation, direct precipitation of siderite from the water column has also been proposed for evaporitic systems like in the Plio-Pleistocene section of the Black Sea (Rajan et al. 1996). Finally, in contrast with these ambient or low-temperature reactions, a few occurrences of siderite have also been found associated with high-temperature metasomatic processes as in the Huttenberg siderite deposit (Carinthia, Austria; Bau and Moller 1992) and in the alteration halo of actinolite-bearing metabasic rocks in the Kalgoorlie area (Western Australia; White et al. 2003). In addition, non-biologically driven transformations of goethite or hematite to siderite have been studied at elevated temperatures or hematite to siderite have been studied at elevated temperatures with supercritical CO₂ and aqueous sulfide (Lammers et al. 2011; Murphy et al. 2011).

The routes of siderite formation thus generally involve reducing conditions, which suggests that precipitation of siderite in oxidizing lateritic environments should not be common. However, several occurrences of siderite in lateritic regoliths have been reported. For instance, this mineral species was found in a lignitic horizon in a buried laterite from the Late Cretaceous (Cenomanian) in southwestern Minnesota (Fritz and Toth 1997; Toth and Fritz 1997; Feng and Yapp 2009). Siderite has also been found in association with rhodocrosite (MnCO₃) in the Ni-rich laterites from the swampy area of the Plaine des Lacs in the southern part of New Caledonia (Podwojewski and Bourdon 1996; Chen et al. 2004), and siderite occurrences have been reported in the Katjeli lateritic Ni-deposit in Albania and Greece associated with karstified Triassic limestones (Economou-Eliopoulos et al. 2003).

To our knowledge, isomorphous Ni²⁺ for Fe²⁺ substitution in siderite has not yet been directly reported for natural systems, although these two divalent ions have close effective ionic radii [Ni²⁺Fe²⁺ = 0.78 Å and Ni²⁺Fe²⁺ = 0.69 Å; Shannon 1976; Rimstidt et al. 1998]. Several Ni-rich carbonate-hydroxide