

Distribution and Speciation of Ni in Sepiolite-falcondoite-type “Garnierite” by EXAFS

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INTRODUCTION.

Ni-laterites represent one of the main Ni sources worldwide, with about 40% of the annual production (Gleeson et al., 2003). A problem in laterites is to find a reliable system to control the exact partitioning of Ni among the different minerals in the lateritic profile, because laterite profiles are generally constituted by fine-grained minerals. The determination of Ni-sorption mechanisms during the process of lateritization arises as a very important target from both the mining and environmental point of view (e.g. Roqué-Rosell et al., 2010).

“Garnierites” are significant Ni ore minerals in the lower horizons of many hydrous silicate-type Ni-laterite deposits in the world (Freyssinet et al., 2005). They occur as a fine-grained aggregate including two or more Ni-bearing magnesium phyllosilicates, such as serpentine, talc, smectite, chlorite and sepiolite (e.g. Springer, 1974; Gleeson et al., 2003).

Sepiolite [$Mg_4Si_6O_{15}(OH)_2 \cdot 6H_2O$] is a common constituent of “garnierite” mineralizations (e.g. Freyssinet et al., 2005), whereas its nickel analogue, falcondoite [$(Ni,Mg)_4Si_6O_{15}(OH)_2 \cdot 6H_2O$], is a rare mineral species reported only in the Falcondo Ni-laterite deposit (Tauler et al., 2008). Several authors suggest the existence of an isomorphous series between these end-members (e.g. Springer, 1974; Brindley, 1978). The similarity in ionic radii and charge of Mg^{2+} and Ni^{2+} allows the formation of a solution series between Mg and Ni end-members. However, data about Mg-Ni substitution is scarce. The analyses of Ni-phyllosilicates provided by Extended X-ray Absorption Fine Structure (Manceau & Calas, 1985) indicate a heterogeneous distribution of Ni in the

octahedral sheet and suggest segregation (or clustering) of the Ni atoms into discrete domains. Spectroscopic studies have shown that many solid solutions, which were considered to be random, have a heterogeneous structure on a scale of several ångströms (Manceau, 1990). Actually, Ni clustering has been described in all natural Ni-bearing phyllosilicates studied, including Ni-sepiolite (Manceau & Calas, 1985; Manceau, 1990).

The present work investigates the coordination of Ni in sepiolite-falcondoite samples from Falcondo Ni-laterite deposit (Dominican Republic) through XANES/EXAFS. These samples were previously studied by SEM-EDS, TEM, EMPA, XRD, XRF, ICP-MS (Tauler et al., 2009).

PRELIMINARY WORK.

According to petrographic observations, at least three generations of Ni-sepiolite-falcondoite with different composition are present in individual samples. Chemical analyses obtained by EMPA cover a wide range of values within the Ni-sepiolite-falcondoite solid solution series: from Fal_3 to Fal_{77} (Tauler et al., 2009).

METHODS AND DISCUSSION.

A polished sample was prepared and mapped using XRF with a resolution of 5 microns, illuminating with incident energy of 9.2 keV. The optical microscope image is shown in Fig. 1. In this sample, the higher concentration of the Ni is associated with the green regions. We then collected μ EXAFS at the Ni-K edge (8.333 keV) in fluorescence mode at different points on the sample corresponding to both the green and white regions identified by

means of OM to identify the chemical state and local environment of Ni.

Metal foils were measured as standards in transmission mode. Since the extent of radiation damage during μ EXAFS scans will depend on the number of photons absorbed — and the specific chemical changes induced can change the structure from the mineralogically relevant form leading to wrong conclusions — the amount of photon flux reaching the sample during the experiments has been reduced by placing aluminum foil between the sample and the source. Data for this sample was collected up to 12 \AA^{-1} .

To optimize the signal to noise ratio as many as 5 spectra were acquired at each point in order to achieve sufficient data quality. The EXAFS analyses were performed using the EXCURV98 program (Tomic et al., 2004) and the refinement included multiple scattering, which can be significant in these phases. It was assumed that the sepiolite - falcondoite phases are quite large and thus the parameters chosen to be refined corresponded to the atomic potentials, the interatomic distances and the Debye-Waller factor. However, the shell occupancy numbers were set at their normal values and were not refined in an idealized sepiolite site.

The length of the EXAFS signal is important to determine the number of parameters to be fitted. In the present EXAFS experiments, for a data length Δk of 8.5 \AA^{-1} and a filtering window in real space about 3.1 \AA , the number of independent parameters N_{ind} that can be refined is 18. This is sufficient to fit structural Ni, and also to elucidate between a random solid solution with Ni surrounded by a second shell of Mg and a heterogeneous solid solution with a clustering corresponding to Ni sites

palabras clave: Sepiolite-falcondoite, EXAFS, República Dominicana.

key words: Sepiolite-falcondoite, EXAFS, Dominican Republic.

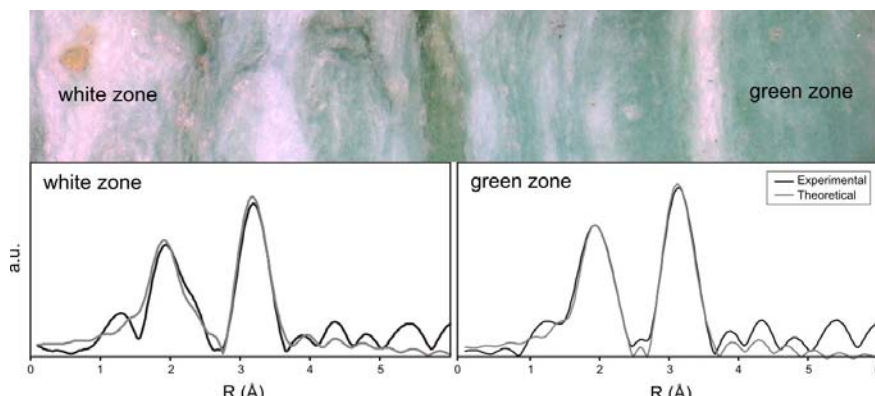


fig 1. Fourier transform corresponding to the EXAFS signal from the white and green zones on a sepiolite - falcondoite type garnierite. Green zones correspond to the areas richer in Ni. The fitting appears to be better in the green zone than in the white zone when applying the model of Manceau & Calas, 1985, Manceau, 1990 for a heterogeneous solid solution with a clustering effect.

The *N* corresponds to the number of pairs of atoms, *DWF* to the Debye-Waller factor and *R* to the fit index of the proposed model.

<i>N</i> Clus	<i>sigma</i>	Shell	<i>N</i>	<i>R</i> (Å)	<i>sigma</i>	<i>DWF</i>	<i>sigma</i>
1	0	Ni1	1	0	0	0.01	0
		O2	2	2.00969	0.07522	0.01379	0.01582
		O3	2	2.07593	0.13823	0.02259	0.05834
		O4	2	2.23532	0.08673	0.0202	0.02995
		Ni5	1	3.04612	1.07366	0.01905	0.25995
		Ni6	1	3.09154	0.72043	0.00831	0.07687
		Ni7	2	2.95047	0.2583	0.02274	0.06135
		Ni8	2	3.10601	0.76133	0.01256	0.12723
<i>R</i>	40.51						
<i>Chi</i> ²	6.054						

Table 1. Fitting values for idealized sepiolite site from collected μ EXAFS on the white region with a lower concentration of Ni. The fit index has a high value suggesting that the model of an octahedron of Ni surrounded with a second shell of Ni is inaccurate. The fitting in the white zone gives the idea that Ni clustering could not be the only explanation of Ni distribution within sepiolite - falcondoite series in garnierites.

The *N* corresponds to the number of pairs of atoms, *DWF* to the Debye-Waller factor and *R* to the fit index of the proposed model.

<i>N</i> Clus	<i>sigma</i>	Shell	<i>N</i>	<i>R</i> (Å)	<i>sigma</i>	<i>DWF</i>	<i>sigma</i>
1	0	Ni1	1	0	0	0.01	0
		O2	2	2.37489	0.04928	0.05129	0.0391
		O3	2	2.13314	0.05347	0.0234	0.01525
		O4	2	2.05195	0.01998	0.01284	0.00615
		Ni5	1	3.32564	0.26166	0.02823	0.11752
		Ni6	1	3.10284	0.06316	0.00233	0.00614
		Ni7	2	3.1114	0.04539	0.03307	0.255
		Ni8	2	3.0444	0.21153	0.02226	0.08737
<i>R</i>	30.5041						

surrounded by a second shell of Ni as described by Manceau & Calas (1985), Manceau (1990).

In the white zone shown in Fig. 1, the model of heterogeneous solid solution seems to show a poor fit (table 1), suggesting that Ni at low concentrations could not be arranged into clusters inside the sepiolite - falcondoite. On the contrary, in the green zone (table 2) the model fits with the model proposed by Manceau & Calas (1985), Manceau (1990).

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REFERENCES.

- Brindley, G. W. (1978): The structure and chemistry of hydrous nickel containing silicate and aluminate minerals. *Bull. BRGM, section II*, **3**, 233-245.
- Decarreau, A., Colin, F., Herbillon, A., Manceau, A., Nahon, D., Paquet, H., Trauth-Badaud, D., Trescases, J.J. (1987): Domain segregation in Ni-Fe-Mg smectites. *Clay. Clay Miner.*, **35**, 1-10.
- Freyssinet, Ph., Butt, C.R.M., Morris, R.C. (2005): Ore-forming processes related to lateritic weathering. *Econ. Geol. 100th Anniversary Volume*, 681-722.
- Gleeson, S.A., Butt, C.R., Elias, M. (2003): Nickel laterites: A review: *SEG Newsletter*, **54**, 11-18.
- Manceau, A. (1990): Distribution of cations among the octahedral of phyllosilicates: insight from EXAFS. *Can. Mineral.*, **28**, 321-328.
- , Calas, G. (1985): Heterogeneous distribution of nickel in hydrous silicates from New Caledonia ore deposits. *Am. Mineral.*, **70**, 549-558.
- Roqué-Rosell, J., Mosselmans, F., Proenza, J.A., Labrador, M., Galí, S., Atkinson, K.D., Quinn, P.D. (2010): Sorption of Ni by "lithiophorite-asbolane" intermediates in Moa Bay lateritic deposits, eastern Cuba. *Chem. Geol.*, **275**, 9-18.
- Springer, G. (1974): Compositional and structural variations in garnierites. *Can. Mineral.*, **12**, 381-388.
- Tauler, E., Proenza, J.A., Galí, S., Lewis, J.F., Labrador, M., García-Romero, E., Suarez, M., Longo, F., Bloise, G. (2009): Ni-sepiolite-falcondoite in garnierite mineralization from Falcondo Ni-laterite deposit, Dominican Republic. *Clay Miner.*, **44**, 435-454.
- Tomic, S., Searle, B.G., Wander, A., Harrison, N.M., Dent, A.J., Mosselmans, J.F.W., Inglesfield, J.E. (2004): New Tools for the Analysis of EXAFS: The DL EXCURV Package. CCLRC Technical Report DL-TR-2005-001: 1-10.