

# Preliminary Studies on Ni in Laterite Deposits from Moa Bay (Cuba) by Means of $\mu$ XRF and $\mu$ XAS using Synchrotron Radiation

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## INTRODUCTION.

The Caribbean holds about 10% of the global Ni-laterites resources. Cuba has most of these, which are located at NE of the island, and they developed from serpentinized peridotites enclosed in Faja Ofiolítica Mayari-Baracoa (FOMB) (Proenza et al., 2007). These deposits are mainly classified as oxide-type. In this case, the upper part (limonite zone) is the main ore horizon. Laterite profiles are generally constituted by essentially fine-grained minerals, and this problem has distorted the knowledge of the crystallochemistry of the laterite-forming minerals.

In Ni lateritic mineral deposits all the materials rich in Mn, Co and Ni are amorphous or of very low crystallinity, but the ore is also constituted by goethite, maghemite, and lithiophorite and intermediate products. A detailed study to determine the mineral phases rich in Mn-Co-Ni have not been made for most lateritic deposits, nor is the oxidation state of Ni and the structural relationship of Ni with their bearing minerals fully characterized.

## OBJECTIVES.

These experiments aim to fill a number of gaps in the current knowledge of Mn-Co-Ni lateritic ores:

- First there is a lack of understanding between the relationship between goethite and Ni (is Ni structural substituting Fe(III), adsorbed or forming interstratified hydroxides?).
- Secondly, there is little information on the nature of the Mn species in the deposits.
- Finally, an intermediate hydrated phase between asbolane and lithiophorite bearing Mn-Ni-Co is believed to exist.

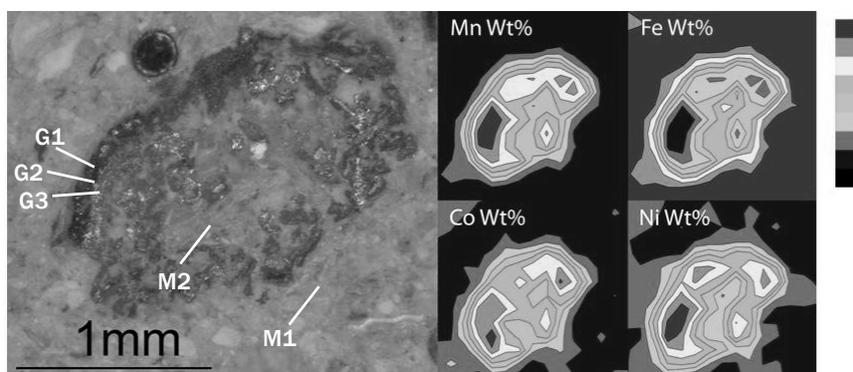


fig 1. Left: optical micrograph of analyzed limonite sample showing micronodules of Mn enriched in Ni and Co within a Fe-rich matrix (mainly goethite). Right: qualitative mappings obtained with an ED-XRF Fisher X-ray XDAL. The points studied by means of  $\mu$ XAS are labeled within the OM picture.

The present work is focused on looking at the distribution of Ni, its chemical state and local environment within the laterites on a micron scale.

## METHODOLOGY.

The sample was collected from limonite horizon of the Yagrumaje laterite Ni deposit. It shows a high degree of heterogeneity with micronodules of Mn embedded in a Fe rich matrix (fig. 1), and Ni is present in a multiplicity of sites. Ni is correlated with the presence of Fe in the matrix, but it is much more strongly associated with the Mn micronodules (fig. 1). This distribution suggests two Ni species and two different Ni structures exist, however the structural specificities of lateritic soils, such as low crystallinity, mean that is difficult to apply crystallographic tools to solve the problem. To fully understand this system we used micro X-ray fluorescence ( $\mu$ XRF) and micro X-ray absorption spectroscopy ( $\mu$ XAS) at the Ni K edge. All these techniques have been performed on the sample at the Microfocus Spectroscopy (I18) Beamline at Diamond Light Source.

## $\mu$ XRF.

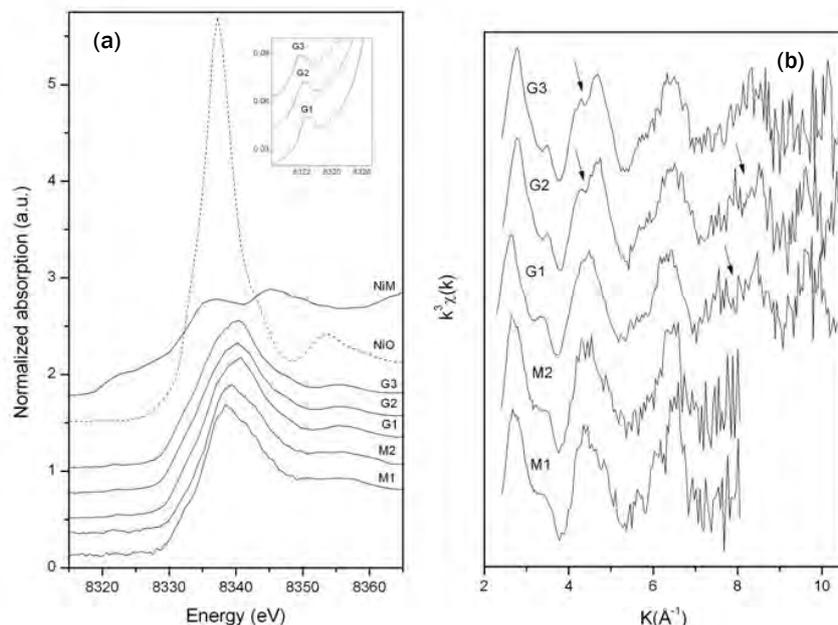
For this study we used a microfocused beam with a 5 micron spot size (c.f. the mineral grain size of 50-1000 microns) to map the sample for Mn, Fe and Ni. This allowed us to define a region of interest and hot spots of Ni to be studied by means of  $\mu$ XANES/EXAFS (maps not shown).

## $\mu$ XAS.

Ni speciation was investigated using  $\mu$ XANES, comparing the absorption edges obtained from the sample to metallic Ni and NiO standards. The local structure of Ni is determined by  $\mu$ EXAFS providing information on the distances and nature of the nearest neighboring atoms. The use of both  $\mu$ XRF and  $\mu$ XAS techniques helps gain some insights of Ni crystallochemistry in laterite minerals from Moa Bay.

## RESULTS.

The measurements performed in the laboratory with the ED-XRF equipment demonstrate the presence of Mn micronodules in a matrix enriched with Fe oxides (fig 1). It is well known that



**fig 2.**  $\mu$ XAS spectra acquired on the Mn enriched grain and the surrounding matrix across Ni absorption edge. On (a) a shift on the  $\mu$ XANES can be seen from more oxidized Ni on M1 to more reduced on G1, the data can be compared to the metallic Ni and Ni(II) absorption edges. The inset graph shows the pre-peak of Ni compounds on the micronodule. On (b) the  $\mu$ EXAFS spectrum shows the oscillations due to the coordination spheres of atoms around Ni.

these micronodules show a great affinity with valuable transition elements such as Ni (Manceau et al., 2003). The close affinity between Mn and Ni suggests a chemical and structural relationship between Ni and Mn compounds.

We chose different locations on the sample that are representative data points to give reliable information with respect to the multiplicity of Ni oxidation states and structural environments within the Fe-rich matrix and the Mn micronodule.

The variation in the oxidation states of Ni has been determined by means of  $\mu$ XANES in fig. 2a. Ni appeared to be more oxidized within the Fe matrix than in the micronodule. Its absorption edge shows a chemical shift from higher energies in points M1 8351.43 eV and M2 8351.94 eV to lower energies across the points G1 8350.92 eV, G2 and G3

both 8350.41 eV. This shift could be linked to variation in the crystallochemistry of Ni within the Fe matrix and the micronodule itself. The  $\mu$ XRF maps obtained on the I18 - Microfocus Spectroscopy Beamline at Diamond (mapping not shown here) demonstrate that Ni is more reduced when associated with Mn, and variations can be determined. In general Ni K edge is at higher E in the outermost part of the granule at G1, where Ni is thought to be in Ni(II) form, and goes slightly to lower energies when measuring towards the center on G2 and G3. This shift between the Fe and Mn-associated Ni can be seen in fig. 2a. The pre-edge structure shown in the inset graph of fig. 2a displays the 1s to 3d transition in this nickel compound. This structure may provide reliable information regarding the oxidation state and coordination of the Ni sites.

Attempts to determine the local structure of Ni within the laterite have been made using  $\mu$ EXAFS. The Ni spectra acquired on the Mn micronodule have strong similarities as seen in fig. 2b. These spectra though show some small differences highlighted by the arrow. This is an extra oscillation that may be indicative of another Ni site or another coordination shell for Ni. On G1 the fitting (Table 1) is very similar to the local structure of Ni in a Ni-Al layered double hydroxide (LDH) where Ni and Al are in Oh sites sharing corners and stacked forming a layered structure (Scheinost et al., 1999). For G2 and G3 this model does not appear to be the whole picture, and thus higher Rf values are obtained (Table 1). For the Fe rich matrix, the spectra do not correspond to Ni inside the structure of goethite, and further attempts are being made to determine its local environment.

## CONCLUSIONS.

Ni is mainly associated with Mn and a Ni-Al LDH type of structure contains the highest concentration of Ni. Further research is being done to determine the local structure inside the Fe matrix.

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	1 <sup>st</sup> Shell						2 <sup>nd</sup> Shell									
	Ni-O			Ni-Ni			Ni-Al			Ni-Mn			Ni-Fe			Rf
	R(Å)	N	$\Delta\sigma^2(\text{Å}^2)$	R(Å)	N	$\Delta\sigma^2(\text{Å}^2)$	R(Å)	N	$\Delta\sigma^2(\text{Å}^2)$	R(Å)	N	$\Delta\sigma^2(\text{Å}^2)$	R(Å)	N	$\Delta\sigma^2(\text{Å}^2)$	
G3	2.01	5.9	0.017	3.02	2.64	0.013	3.02	1.76	0.013	3.02	4.4	0.013	-	-	-	53.89
G2	2.01	5.8	0.017	3.43	2.24	0.08	3.43	1.28	0.08	3.43	2.24	0.08	-	-	-	56.18
G1	2.05	6	0.019	3.06	4.88	0.014	3.06	1.22	0.014	-	-	-	-	-	-	48.19
M2	2	5.5	0.010	-	-	-	3.02	2.34	0.039	-	-	-	3.02	4.88	0.039	52.99
M1	2.01	5.4	0.012	-	-	-	3.03	2.4	0.037	-	-	-	3.03	5.6	0.037	53.23

**Table 1.** Fitting results for the first two shells for Ni K edge in the laterite sample. R corresponds to the interatomic distances, N is the shell occupancy number,  $\Delta\sigma^2$  the Debye Waller factor and Rf the fit index.