Supergene Co-Ni-Mn mineralization in Ni-laterite deposits from northeast Cuba

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ABSTRACT: The Mn-Co-Ni oxide minerals in northeast Cuba Ni-laterite deposits occur particularly at the transition zone between saprolite and limonite horizons, as surface coatings on minerals and in fractures. The mineralogical composition is dominated by lithiophorite (up to 8.7 wt. % Ni and up to 12.8 wt. % Co) and asbolane and phases with compositions between those of lithiophorite and asbolane "lithiophorite-asbolane intermediates" (up to 21.7 wt. % Ni and up to 10 wt. % Co). Microprobe analyses suggest the existence of continuous series between lithiophorite and asbolane.

KEYWORDS: Nickel. Cobalt. Manganese. Mineralization. Supergene. Ni-Laterite. Cuba

1 INTRODUCTION

In Ni-laterite deposits, Ni and Co may be incorporated in Mn oxides and hydroxides where they have been precipitated by redox reactions (Elias *et al*. 1981). In addition to asbolane (Ni- and Co-rich), there are other Co minerals as heterogenite and lithiophorite (Chukhrov *et al*. 1983, Manceau *et al*. 1987, Llorca and Monchoux 1991). Generally, in these laterite deposits all black Mn- and Co-rich products, essentially amorphous or with a low degree of crystallinity, have been named "asbolane". These black products constitute an excellent guide for mineralization.

Here, we report the mineralogical results of the study of a Co-Ni-Mn mineralization in northeast Cuba Ni-laterite deposits (Fig. 1), no detailed studies have been previously published on such mineralization. Mineralogy was investigated using X-ray Diffraction (XRD), Optical Microscopy (OM), Scanning Electron Microscopy (SEM), Electron Microprobe (EMPA), Transmission Electron Microscopy (TEM), Selected Area Electron Diffraction (SAED) and Electron Energy Loss Spectrometry (EELS).

2 GEOLOGICAL OCCURRENCE AND SAMPLING

The nickel laterite deposits of northeast Cuba were developed on serpentinised harzburgite. The following lateritic zone can be defined (Fig. 1), from bottom to top these are: (1) serpentinized peridotite, (2) saprolite, (3) limonite and (4) ferricrete. The boundary between the saprolitic zone and the peridotitic substrate (transition zone) is extremely irregular (Lewis *et al*. 2005). The average thickness of the lateritic crust formed over the peridotite bedrock is 10 meters although it can reach 50 meters (Lavaut, 1998).

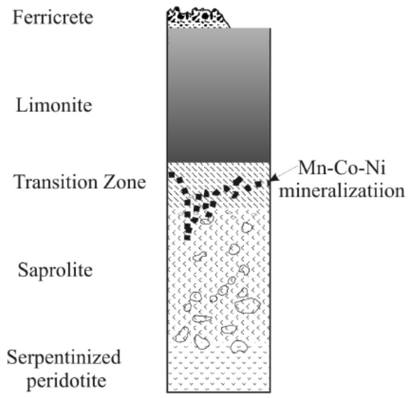

Figure 1. Schematic representation of the Ni-laterite profile from eastern Cuba, showing the location of Mn-Ni-Co mineralization.

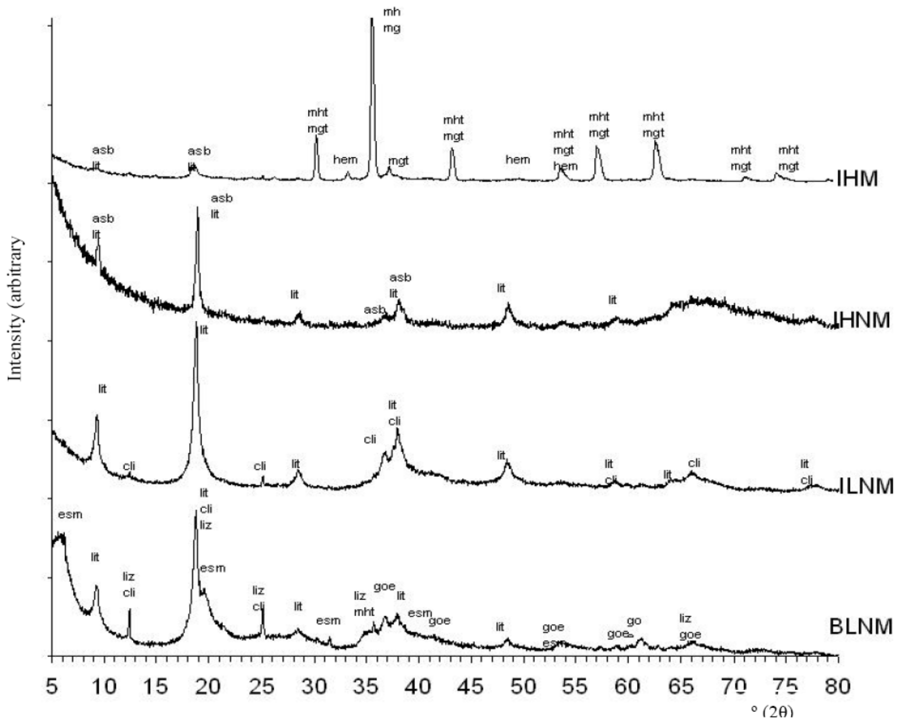

Figure 2. XRD patterns for IHM, IHNM, ILNM and BLNM fractions. Identified phases: asbolane (asb); lithiophorite (lit); magnetite (mgt); maghemite (mht); haematite (hem); goethite (goe); Ni-smectite (esm); chlorite (cli) and lizardite (liz).

Ni-Co-Mn mineralization occurs as veins and surface coatings on minerals and in fractures as those described by Llorca and Monchoux (1991) in New Caledonia. The samples were obtained from a lateritic profile located 5 km far from the city of Moa, where the black Co-rich horizon occurs (Fig. 1).

3 RESULTS

3.1 *XRD*

Figure 2 shows the powder X-ray patterns obtained from the different analyzed fractions.

Previously to the XRD analysis the samples were submitted to a magnetic and density separation using both diiodomethane and bromoform as dense liquids. As a result four fractions were obtained, three of them from diiodomethane (1) heavy magnetic fraction (IHM); (2) heavy non magnetic fraction (IHNM); (3) light non magnetic fraction (ILNM) and one from bromoform: (4) lighter non-magnetic fraction (BLNM). X-ray powder diffraction measurements were performed in a Bragg-Brentano $\theta/2\theta$ Siemens D-500 diffractometer (radius = 215.5 mm) with Cu Kα radiation, selected by means of a secondary graphite monochromator. The divergence and receiving slits were of 1° and 0.15° respectively. The starting and the final 2θ angles were 4° and 80° respectively. The step size was 0.03° 2θ and the measuring time of 18 seconds per step. Mineral identification was made with the Diffract (Bruker) software.

Magnetite and maghemite are the dominant phases in the heavy magnetic fraction; furthermore some signs for haematite, asbolane and lithiophorite are presents.

For the rest of samples, lithiophorite is the main phase and it is the only mineral, together with some indications for asbolane, in the heavy non-magnetic fraction.

For lighter fractions also lizardite, Mg-Ni-chlorite, Ni-smectite and goethite have been identified.

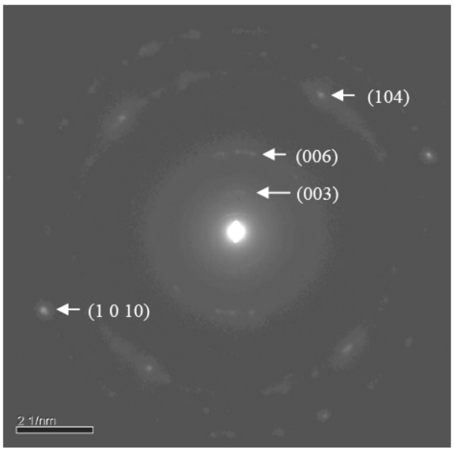

Figure 3. SAED image for a lithiophorite particle.

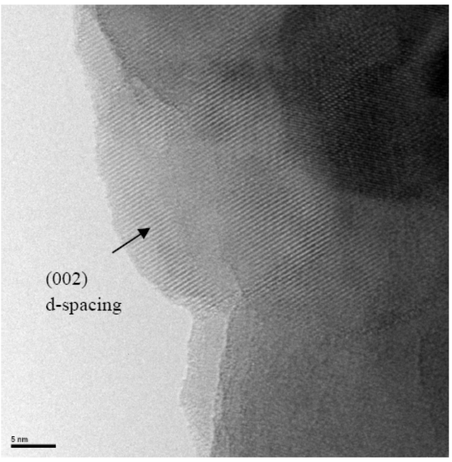

Figure 4. HRTEM image showing the d-spacing for (002) reflection for an asbolane particle

3.2 *TEM*

TEM studies were performed for ILNM fraction. It has been used a Philips CM30 electron microscope working at an accelerating voltage of 300 kV and a field emission JEOL JEM 2010F electron microscope at an accelerating voltage of 200 kV equipped with an EELS device. Both lithiophorite and asbolane have been observed (Fig. 3, 4). EELS analyses of the asbolane reveal higher contents of Ni and Co than in lithiophorite.

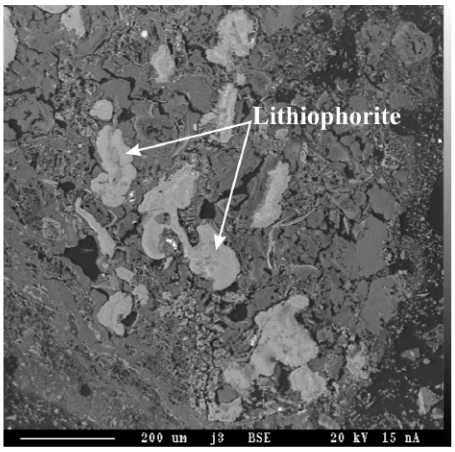

Figure 5. Back-scattered electron image of lithiophorite.

3.3 *SEM-EMPA*

SEM observations were made by a JEOL JSM-840 Microscope while EMPA analyses were performed with a CAMECA SX-50 microprobe. Lithiophorite (Fig. 5) shows high Co content (between 5.32 and 12.82 wt. %), and Ni (4.77 and 8.68 wt. %). MnO_2 content varies between 37.15 and 52.58 wt. % and Al_2O_3 between 14.86 and 20.95 wt. % (Fig. 6).

These compositions point out that lithiophorite from laterite deposits of Moa is Co- and Ni-richer than those from New Caledonia (Llorca & Monchoux 1991).

The other predominant Mn-Ni-Co phases analyzed show chemical compositions which are intermediate between lithiophorite and true asbolane (Fig. 6). These phases have high Ni contents (up to 21.65 wt. %) and Co (up to 9.60 wt. %), MnO_2 between 39.32 and 46.29 wt. %, and low contents of Al_2O_3 (<7 wt. %).

Finally a Mn-rich phase has been analyzed showing MnO_2 contents about 80 wt. % and a very low Co content (< 2 wt. %) and Ni (1< wt. %).

4 CONCLUSIONS

The main Mn phases containing Ni and Co in the studied samples are lithiophorite, asbolane and intermediate products between lithiphorite and asbolane (Al-rich asbolane). These results suggest the existence of continuous series between lithiophorite and asbolane. Other-

wise, heterogenite [(Co, Ni), OOH]), a characteristic mineral from laterites of New Caledonia (Llorca *et al.* 1991) has not been detected. These results confirm that ones obtained by Chukhrov *et al.* (1983). The presence of lithiophorite implies the availability of Al in the environment which is consistent with the presence of impregnate peridotites (with plagioclase and clinopyroxene) and sills of gabbro in the peridotitic substrate from which the lateritic crust were developed (Proenza *et al.* 2003). On the other hand the lithiophorite crystal structure does not allow having a great Co and Ni content (Chukhrov *et al.*1983). This implies that the main Ni and Co in Mn-phases from the meteoric crust developed on ultramaphic rocks is the asbolane. On the contrary to Ni, Co does not form secondary silicate therefore asbolane and lithiophorite are the main Co phases in the laterites from northeast Cuba.

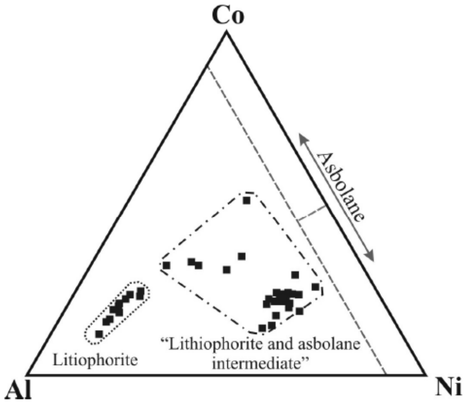

Figure 6. Cationic composition in terms of Mn-Al-Co of analyzed lithiophorite from eastern Cuba laterite.

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