Numerical modeling of oxide-type Ni-laterite deposits: preliminary results

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ABSTRACT: The eastern Cuba Ni-laterite deposits are classified as oxide-type. In these deposits, Ni and Co occur mainly in the limonite zone, composed of Fe oxyhydroxides as the dominant minerals in the upper part of the profile. The quantitative mineralogical composition along the laterite profile, together with a structural characterization of the main crystalline phases present, are obtained by X-ray diffraction full profile matching (Rietveld method). On the basis of these results and on chemical and hydrological data, we try to build a quantitative reactive transport model to explain the formation of the laterite profile. One important difficulty encountered in these initial attempts is the present lack of understanding of the stability field of lizardite.

KEYWORDS: Nickel, Ni-Laterite, Reactive transport, Cuba

1 INTRODUCTION

Ni laterite deposits are currently producing about the 40% of the world’s annual Ni (Dalvi et al. 2004). Three main types of deposits can be distinguished based on the mineralogy of the dominant mineral carrier of Ni (Brand et al. 1998, Gleeson et al. 2003). In the oxide-type deposits, the upper limonite is the main ore horizon, and the ore minerals are Fe oxyhydroxides (mainly goethite).

The studied profile (Fig. 1) come from the Punta Gorda Ni-Co laterite deposit, located in the Moa mining district (northeast of Cuba). This deposit can be classified as oxide-type (Oliveira et al. 2003) and, as many Cuban deposits, the typical section through the profile consists of four principal horizons, from bottom to top: (1) serpentinized peridotite, (2) saprolite, (3) limonite and (4) ferricrete (Lewis et al. 2006). Occasionally the profile may contain gabbro bodies altered to bauxite. The Ni and Co is contained mainly in the limonite zone but doubts about the detailed location of metals (adsorbed onto the surface or in solid solution) still remain.

This particular profile has been characterized mineralogically by qualitative and quantitative powder X-ray diffraction and by whole rock analyses (ICP-MS, 43 elements). In addition, ground waters from similar profiles in the Moa district were also sampled and analyzed.

In this work, we present the mineralogical
composition along the laterite profile obtained by quantitative diffraction and try to reproduce by reactive transport modeling this observed profile, on the basis of different hypotheses regarding parent rock, uplift rate, climate and other intrinsic parameters as porosity, hydraulic conductivity and others.

2 QUANTITATIVE XRD

Representative fractions of the samples were powdered below 30μm and back mounted in the holder to avoid preferential orientation. Quantitative analyses were achieved by full diffraction profile matching method (Rietveld method), using the TOPAS V2.1 software. Results are given in Fig. 2. The detailed crystallographic characterization of the phases may afford relevant information regarding the genesis of the profile.

Goethite, which contains most of the Ni, is the major phase. The refined parameters were: cell parameters, atomic occupation factors and crystal size. The cell volume is always smaller than the accepted value for goethite, indicating some substitution of Fe by Al, in agreement with the atomic occupation factors encountered. Crystallite domain size is rather small (11-23 nm), indicating a large specific surface estimated in 65-30 m²/g. Thus value suggests the importance of the goethite surface in the retention of metals, and plays an important role in the kinetics of dissolution-precipitation. In most samples, goethite coexists with maghemite and hematite. In only one sample, goethite coexists with lizardite (M8, 33m), and is absent in deeper samples (M9 and M10).

Maghemite, appears in all the profile beneath the first 5 m. The refined cell parameter is very similar to the accepted value of 8.3505 Å, indicating a composition near the ideal Fe₂O₃. Magnetite, which is considered a precursor of maghemite, has not been found.

Hematite, the second most important Fe-bearing mineral, has almost an ideal composition and structure. However it presents a rather low crystallite size (30 to 40 nm). In several samples enriched in Mn (M3 and M6), haematite is completely absent.

Gibbsite, is a less soluble alteration product of plagioclase from the gabbro bodies in the parent rock. The cell volume suggests some degree of substitution of Al by Fe. Gibbsite is more abundant in the top of the limonitic horizon and in ferricrete.

Serpentine minerals present are the lizardite polymorphs 1T and 2H₁, the former being dominant, and the latter minor, less crystalline, with many stacking faults. The cell volume is slightly bigger than that corresponding to the ideal end member Mg₃Si₂O₅(OH)₄, due to substitution of some Mg by Fe and minor Ni and Mn, as confirmed by chemical analyses. In the deeper sample M10, lizardite appears together with olivine, enstatite and maghemite as the only iron oxide. It is apparent that magnetite formed by the hydration of olivine is quickly transformed to maghemite in atmospheric conditions, and later on, in goethite.

The insufficient data available for a realistic evaluation of the stability field of serpentine polymorphs, as well as their equilibrium constants and dissolution rates, poses the main problem when trying to approximate the real observed profile by reactive transport modeling (Evans 2004).

Other minor phases encountered are asbolane, appears only in sample M3 corresponding to the altered gabbro body, pyrochlore (1.5 wt.% in M6), and quartz (1.6 wt.% in sample M8, coexisting with lizardite).

![Figure 2. Quantification of mineral species.](image)

3 HYDROGEOCHEMICAL MODEL

The geochemical calculations were performed with the simulator RETRASO (Saathuk et al. 2004), in two steps. In the first simulation, the equilibrium between the minerals forming the parent rock and pore water is attained as a function of the equilibrium constants, dissolution-precipitation rates and time. This simulation allows to find the approximate composition of the initial water pore solution. In the second step, this pore water will mix with percolating water from rain, and a column of downwards reactive transport is numerically simulated in isothermal conditions. Along the column, poss-
sible reactions include aqueous complexation, gas dissolution and dissolution/precipitation of minerals (Figs. 3 and 4).

The modeled parent rock consists of an harzburgite impregnated by plagioclase according to the following modal proportions and compositions: olivine 70% (Feg95Fe3); pyroxene 16% (En90Fs5); anortite 14%. A fraction of serpentine, could also be included. However, given the great instability of olivine and pyroxene in presence of water, serpentine appears immediately, and its introduction as mineral forming the parent rock would not change significantly the final results. Nickel is still not included in the model, which considers only major components. Nevertheless, in oxide laterite profiles, Ni concentrates mainly in goethite.

The new precipitating minerals resulting from alteration are lizardite, goethite and gibbsite. The reason for excluding magnetite and haematite as iron bearing minerals is the very small Gibbs free energy of the reactions relating these minerals with goethite, that makes their presence rather contingent, depending on small climatic variations. As a rule, magnetite changes its structure to haematite, and is absent in the top of the profile, which samples the most ancient altered parent rock not eliminated by erosion. In addition, haematite may result from dehydration of goethite produced in drier levels, located in the top of the profile as well.

**Table 1. Conditions used for the reactive transport simulations.**

<table>
<thead>
<tr>
<th>Geometry and length of the initial rocks</th>
<th>A column of 200 m</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>25°C</td>
</tr>
<tr>
<td>Porosity</td>
<td>0.05</td>
</tr>
<tr>
<td>Permeability</td>
<td>10^{-12} m²</td>
</tr>
<tr>
<td>Molecular diffusion</td>
<td>10⁻²³ m² s⁻¹</td>
</tr>
<tr>
<td>Dispensivity</td>
<td>0.5 m</td>
</tr>
<tr>
<td>Flux</td>
<td>3.10^-12 m² m² s⁻¹, which corresponds to one tenth of the annual precipitation in tropical to subtropical climate</td>
</tr>
<tr>
<td>Saturated zone</td>
<td>the whole column</td>
</tr>
<tr>
<td>Initial pore water</td>
<td>in equilibrium with lizardite, goethite and gibbsite, and a partial pressure of oxygen of 0.05</td>
</tr>
<tr>
<td>Rain water</td>
<td>distilled water in equilibrium with atmospheric oxygen (pH = 5.65)</td>
</tr>
<tr>
<td>Duration of the simulated process</td>
<td>10 Ma</td>
</tr>
</tbody>
</table>

In these preliminary attempts, the reactive transport simulations have been performed in simplified conditions (Table 1); these will become more complete in future work, that will include a better evaluation of equilibrium and kinetic constants for the phases involved, the possible influence of minor, but important elements like Ni, (adsorption effects), and flow velocities.

### 4 RESULTS AND DISCUSSION

In Fig. 3 the calculated volume fractions of minerals as a function of depth, at time 10 Ma are shown. The same results recalculated on the basis of the exclusion of lizardite, given in Fig. 4, would be a better approximation to real existing laterite profile. It is noteworthy that, once all hydrated magnesium silicates is eliminated, there is a big volume contraction: oxide laterites represent only 7% volume of the parent rock.
The main trends of the mass balance for iron and aluminium, and the corresponding simulated chemical profiles are coincident with real observations. In particular, it is shown that all iron contained in olivine and pyroxene would remain in the laterite profile. However, in the conditions of the present simulation, a great deal of magnesium and silicon forming lizardite, that is considered to precipitate in equilibrium, is not leached, and remain in the altered rock. The pre-emption of lizardite and other hydrated magnesium silicates (talc, chlorites) makes the difference between two main typologies of lateritic profiles, and poses the main problem to be solved by numerical simulation. We envisage several hypotheses to be proven in future work: a) lizardite does not precipitate in the higher horizons, due to kinetic factors (i.e. high supersaturation needed); b) equilibrium constant used for lizardite is not correct; c) pH of rain water is lower than the values introduced (i.e. due to organic matter influence and/or atmospheric CO2); d) more than one rock zone has to be taken into account (i.e. saturated versus not saturated zone). In summary, the model is still too simplistic and future attempts should include a revision of the chemical and kinetic constants for lizardite, the inclusion of nickel as a component, a more realistic geometrical model formed by two or more rock zones, the possible influence of the uplift and erosion rates, and a complete characterization of the percolating water.

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