Fe-Ni-Rich Serpentines in the Saprolite Horizon of Ni-Late... from Thermodynamic Calculations

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Abstract. The main Ni ores in hydrous silicate type Ni-laterites are Fe-Ni-bearing serpentines from the saprolite horizon, which are formed by weathering of partially serpentinitised ultramafic rocks under tropical conditions. This serpentine (namely serpentine I) is of hydrothermal origin and yields similar Ni and lower Fe than the primary olivine. It has an average structural formula of (Mg2.52Fe0.48Ni0.02Ca0.03Al0.01)Si2O5(OH)4. In contrast, Fe-Ni-bearing serpentines (serpentine II) shows significantly high and variable Fe and Ni contents, with an average structural formula of Mg2.08Fe0.25Ni1.06Si2O5(OH)4, suggesting that serpentines experiment an enrichment in Fe and Ni under supergene conditions. This study presents detailed mineralogical, textural and chemical information on this serpentine II. In order to check if at atmospheric pressure and temperature, this Fe-bearing serpentine can be formed by precipitation, thermodynamic calculations assuming ideal solution between Fe-, Ni- and Mg- pure serpentines have been carried out. Preliminary results indicate that this conceptual model is thermodynamically supported; being pH, Eh and precipitation reaction equilibrium constant the parameters that affect the results more significantly. More work is currently being performed to elucidate the uncertainties arisen from these preliminary calculations.

Keywords. Fe-Ni-serpentine, saprolite, Ni-laterite deposits, Caribbean, PHREEQC, MEDUSA

1 Introduction

Fe-Ni-serpentines represent one of the main Ni ore in hydrous silicate type Ni-laterite deposits worldwide (Freyssinet et al. 2005). Ni-laterite deposits account for about 40% of the world’s annual production of Ni, they host over 60% of the world land-based Ni resources (Gleeson et al. 2003; Kuck 2013) and the amount of Ni being mined from laterite ores is increasing steadily (Mudd 2010).

These deposits result from the tropical weathering of ultramafic rocks, which are usually partially serpentinitised harzburgites, lherzolites and dunites in ophiolite complexes. Ni-laterites are classified into three groups, according to the main Ni-bearing assemblages: a) oxide type, dominated by Fe oxyhydroxides; b) clay silicate type in which Ni is concentrated in smectite group minerals; and c) hydrous silicate type where the ore is mainly Mg-Ni phyllosilicates, including Fe-Ni-serpentines and garnierites, the later being the ones with higher grades, from 1.8 to 2.5 wt.% Ni (Brand et al. 1998, Freyssinet et al. 2005).

The hydrous silicate Ni-laterite deposits are characterised by a thick serpentine-dominated saprolite horizon covered by a Fe-oxyhydroxides-dominated layer, the limonite horizon (Fig. 1). The combination of high temperature, intense rainfall, low water table and continuous tectonic uplift leads to the dissolution of the primary ferromagnesian minerals of the ultramafic protolith and the precipitation of secondary Ni-bearing Mg phyllosilicates and Fe-oxyhydroxides. Mg is leached out of the profile, and Fe³⁺ is oxidised to immobile Fe⁴⁺ and is concentrated as goethite in the limonite horizon.

Previous mineralogical, textural and chemical studies on samples from Caribbean Ni-laterites allowed distinguishing three stages of serpentine formation:
- Serpentine I occurs as pseudomorphs after olivine grains and develops sheeted aggregates. It has a low Ni and Fe contents. Ni is comparable to that of the primary olivine (less than 0.5 wt.% NiO) but Fe is even lower (3 wt.% FeO in the serpentine and 6-7 wt.% FeO in the olivine). This serpentine is mainly found in the partially serpentinitised ultramafic protolith and is of hydrothermal origin, formed prior to the exhumation of the peridotite body.
- Serpentine II replaces serpentine I and other primary minerals. It is the main constituent of the saprolite horizon in hydrous silicate type Ni-laterite profiles, and therefore represents the main Ni ore in volume in these deposits. This serpentine is enriched in Ni (1-7 wt.% NiO) and in Fe (3-20 wt.% FeO) with respect to serpentine I.

The aims of the present study are to shed light on the process of Fe enrichment in the Fe-Ni-serpentines in Ni-laterite deposits and to check if under the conditions of saprolite horizon, this serpentine can be thermodynamically stable.
2 Sampling and analytical techniques

Four samples from the saprolite horizon of two different Ni-laterite deposits were selected for the present study: two were sampled from Falcondo (Dominican Republic) and the other two from Moa Bay (Eastern Cuba). These samples were analysed by powder X-ray diffraction (XRD; PANalytical X’Pert PRO MPD Alpha1, Cu Kα1 radiation, 45 kV, 40 mA), and prepared as polished thin sections in order to be examined under optical microscopy (OM) and scanning electron microscopy coupled to an energy dispersive spectrometer (SEM-EDS; Quanta 200 FEI-INCA Energy 250 EDS, 20 kV and 5 nA). Finally, the chemical composition of the Fe-Ni-serpentines was determined by electron microprobe (EMPA; Cameca SX50, 20 kV, 10 nA). All the aforementioned instruments are from the Centres Científics i Tecnològics of the Universitat de Barcelona (CCiT-UB).

Thermodynamic calculations have been performed by using the PHREEQC v.3 code (Parkhurst and Appelo 2012). Solubility curves and Eh-pH diagrams have been calculated with the MEDUSA software package (Puigdomènech 2010).

3 Mineralogy and chemistry of Fe-Ni-serpentines in the saprolite horizon

The X-ray diffractograms confirm that the serpentine II samples are mostly composed by lizardite and minor Fe-oxyhydroxides. Observations under the optical microscope show that this lizardite forms pseudomorphs after olivine and serpentine, develops rims around other serpentines and fills micron-thick veinlets. As seen in Figure 2, SEM-EDS and EMPA results reveal a wide range of compositions with variable and remarkably high Ni and Fe contents.

For the present thermodynamic approach, the composition of a serpentine II from Falcondo (Dominican Republic), with 6.41 wt.% Fe₂O₃ (5.78 wt.% FeO) and 4.01 wt.% NiO, was chosen. The corresponding structural formula is Mg₂.30Fe₀.23Ni₀.16Si₂O₉(OH)₄. This Fe-Ni-serpentine structural formula contrasts with the average formula (Mg₂.72Fe₀.06Ni₀.02Ca₀.003Al₀.01)Si₂.08O₅(OH)₄ obtained in a serpentine of hydrothermal origin (serpentine I) from the unweathered serpentinisated ultramafic protolith. Therefore, there is a significant enrichment in Fe and Ni in serpentine II.

4 Thermodynamic calculations

A log K value of -30 for r.1 can be calculated assuming an ideal solution between Fe(III)-; Ni-; and Mg-pure serpentines and thermodynamic constants of Table 1.

\[
2.50 \text{Mg}^{2+} + 0.23 \text{Fe}^{3+} + 0.16 \text{Ni}^{2+} + 2 \text{H}_2\text{SiO}_4 + \text{H}_2\text{O} = \text{Mg}_{2.50}\text{Fe}_{0.23}\text{Ni}_{0.16}\text{Si}_2\text{O}_9(\text{OH})_4 \quad r.1
\]

Landauro-Sotelo (2008) provides porewater compositions of Falcondo laterite deposit. pH of these porewaters is in the range 8.3-9.3. Porewaters have high Mg and HCO₃- concentrations (10⁻³ mol/kgw), Ni concentrations between 10⁻⁷ and 10⁻⁶ mol/kgw and Fe aqueous concentrations below 10⁻⁶ mol/kgw. No information regarding redox value of these porewaters is provided.
Table 1. Dissolution reactions and log K values of different serpentines.

<table>
<thead>
<tr>
<th>Mineral name</th>
<th>Reaction</th>
<th>Log K</th>
</tr>
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<tbody>
<tr>
<td>Fe$_2$(SiO$_4$)(OH)$_4$</td>
<td>$2 \text{Fe}^{3+} + 2 \text{H}_2\text{SiO}_4 + \text{H}_2\text{O} = \text{Fe}_2\text{SiO}_3(\text{OH})_2 + 6 \text{H}^+$</td>
<td>4.0$^a$</td>
</tr>
<tr>
<td>Lizardite</td>
<td>$3 \text{Mg}^{2+} + 2 \text{H}_2\text{SiO}_4 + \text{H}_2\text{O} = \text{Mg}_2\text{SiO}_3(\text{OH})_2 + 6 \text{H}^+$</td>
<td>-33.1$^a$</td>
</tr>
<tr>
<td>Népouite</td>
<td>$3 \text{Ni}^{2+} + 2 \text{H}_2\text{SiO}_4 + \text{H}_2\text{O} = \text{Ni}_2\text{SiO}_3(\text{OH})_2 + 6 \text{H}^+$</td>
<td>-21.4$^a$</td>
</tr>
</tbody>
</table>

$^a$ThermoChimie database (Giffaut et al. 2014) $^b$Galí et al. (2012), $^c$derived from $\Delta G$ values calculated by the method proposed by Nriagu (1975).

Figure 3 shows the predominance diagram pH-Eh(V) (25ºC, 1 atm) of the Fe system drawn for water compositions of Falcondo laterite deposit. It can be seen that at pH around 9 (within the range of pH measured in Falcondo porewaters, dotted lines in Figure 3) and Eh close to -0.3 V, this Fe-bearing serpentine can be in equilibrium with goethite and Fe(II) aqueous complexes.

Solubility curves for both Fe-bearing serpentine and goethite are shown in Figure 4. Given to the Eh sensitivity of goethite solubility, three solubility curves have been drawn for goethite covering the range -0.25 to -0.35 V. In the case of Fe-bearing serpentine solubility has been calculated for the log K (r.1) reported above and for two more values differing one order of magnitude.

Figure 4. Solubility curves of Fe-bearing serpentine (serpentine II) (calculated for different log K (r.1) values) and of goethite (calculated for different Eh values) as a function of pH. Dotted line indicate the maximum value $(10^{-6} \text{ mol/kgw})$ that $[\text{Fe(aq)}]_{tot}$ can have in Falcondo laterite deposit porewater according to the analyses.

Nevertheless, sensitivity analyses of the system indicate that the pH value, log K(r.1) and Eh(V) are the most important parameters contributing to the composition of porewater composition. As can be seen in Fig. 4, solubility curves of Fe-bearing serpentine abruptly decrease above pH 8. Small changes in pH in the range pH 8.5 - 9.5 cause important changes in Fe-bearing serpentine solubility.

Premiminary results (not shown) also indicate that the stability field of both goethite and Fe-bearing serpentine are highly dependent on carbonate concentration. A high carbonate concentration increases the stability of Fe in solution through the formation of carbonate-Fe(II) aqueous complexes increasing mineral solubility. Further work is being carried out to elucidate this effect.

Therefore, and according to these preliminary results, the formation of a Fe-bearing serpentine in the saprolite horizon of a Ni-laterite deposit may be consistent with a process in which this Fe-bearing serpentine is formed by precipitation at atmospheric pressure and temperature.

Concluding remarks

The Fe-Ni-bearing serpentine (serpentine II) from the saprolite horizon of the hydrous silicate type Ni-laterite deposits presents significantly high Fe and Ni contents when compared to the earlier hydrothermal serpentine I from the unweathered protolith. Furthermore, the analyses show a wide variety of compositions in terms of Fe and Ni.

Preliminary thermodynamic calculations presented in this contribution indicate that the formation of Fe-bearing.

Concentration processes in sub-surface environments
serpentine (serpentine II) in the saprolite horizon of a Ni-laterite deposit seems to be thermodynamically consistent with a model in which serpentine II forms by precipitation and is in equilibrium with goethite at 25°C and atmospheric pressure.

More work is currently being carried out in order to elucidate some of the uncertainties arisen from these preliminary calculations. Published literature is being revised to widen the range of porewater compositions representative of Ni-laterite deposits and to reduce the uncertainties concerning the effect of other processes such as CO₂(g) degasification in the porewater compositions.

As seen in Fig. 4, log K value has been identified as one of the parameters which affect more the results of the model. Further work will consider the wide range of Fe and Ni contents analysed in the samples. In this way, the resulting model would cover the heterogeneity of serpentine II in the saprolite horizon.

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