Reactive Transport Modelling: the Formation of Ni-laterite Profiles (Punta Gorda, Moa Bay, Cuba)

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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). The Punta Gorda Ni laterite deposit is part of a larger province of nickel laterites in northeast Cuba (Moa Bay district) (Lavaut, 1998) developed from serpentinized peridotites.

This laterite profile is composed of four principal horizons, from bottom to top: (1) serpentinized peridotite, (2) saprolite, (3) limonite and (4) ferricrete (Proenza et al. 2007). Based on the mineralogy of the principal ore-bearing phases, the Punta Gorda deposit is classified as oxide-type. In this case, the upper part (limonite zone) is the main ore horizon and is mainly composed of goethite (>50 wt%), and minor hematite, maghemite, gibbsite and Mn-Ni-Co oxyhydroxides (lithiophorite and "asbolane-lithiophorite intermediates"). The nickel content in goethite varies from 0.3 to 4.5 wt.% (average value = 1.4 wt.%) (Proenza et al., 2007).

Nevertheless, the exact location of nickel in goethite is still unclear. Several authors (Arai, 2008 and references therein) suggest that nickel is sorbed onto goethite surface, while others defend that Ni is incorporated into goethite structure (Singh et al. 2002, Landers et al. 2009). Both processes are thought to occur, simultaneously.

In this study a 1D reactive transport model is applied to simulate the formation of this deposit aiming at improving the understanding of the different factors governing the process of lateritization of ultrabasic serpentinized rocks. Specifically, in this model, the sorption of Ni onto goethite surface has been tested as the main process governing Ni accumulation in the goethite of this profile.
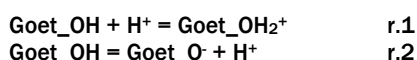
CONCEPTUAL AND NUMERICAL MODEL

The formation of the Punta Gorda Ni laterite deposit is simulated by assuming the weathering of a column of partially serpentinized peridotite due to the meteoric water flow. This peridotite parent rock is assumed to be composed of Ni-bearing forsterite (~0.4%wt Ni), enstatite, oceanic (primary) serpentine (~0.4%wt Ni) and magnetite (Table 1). The dissolution of the forsterite and enstatite is assumed to be kinetically controlled (Palandri & Karakha 2004) whereas that of primary serpentine and magnetite is considered to occur according to local equilibrium. As a consequence of the dissolution of these minerals, goethite (chosen as representative of Fe-bearing oxides) and a secondary Ni-rich serpentine (>1 wt% Ni) are allowed to precipitate if oversaturated, following local equilibrium (Table 1).

Once released from primary minerals Ni is considered to sorb onto the goethite surface and/or to precipitate with the secondary serpentine.

Information concerning the sorption of Ni onto goethite is scarce (Marcussen et al. 2009, Rajapaksha et al. 2012). In the model presented here, sorption of Ni onto goethite surface is modelled according to the one-site DLM proposed in Marcussen et al. (2009), where Ni sorbs onto goethite surface following reaction r.3. The authors used for r.1 and r.2 the values of the equilibrium constant (K) proposed by Richter et al. (2005) but an update of these values (Richter & Brendler, 2008) is used in this model.

$$Goet\_OH + H^+ = Goet\_OH_2^+ \qquad r.1$$
$$Goet\_OH = Goet\_O^- + H^+ \qquad r.2$$

$$Goet\_OH + Ni^{2+} = Goet\_ONi^+ + H^+ \qquad r.3$$

Assuming elongated prisms in the **c** direction, a surface area of 84.8 m²/g is calculated from XRD analyses. The BET specific surface is 65.2 m²/g. The Ni sorption capacity of goethite has been calculated from the maximum % of Ni content in goethite and the surface area of goethite, resulting in a value of 5 sites/nm² if surface area is 84.8 m²/g and of 6.5 sites/nm² if surface area is 65.2 m²/g. This last pair of values has been chosen for the numerical calculations.

As logK values were all provided for a site density of 2.31 sites/nm², constants are recalculated to be consistent with the site densities of Moa goethite (Table 1).

Site/nm²	LogK		
	2.31[a]	5[b]	6.5[b]
r.1	7.00	6.7	6.6
r.2	-9.39	-9.7	-9.8
r.3	-0.35	-0.69	-0.80

Table 1. LogK (equilibrium constant) values for reactions r.1, r.2 and r.3. [a]Values from literature (see text). [b]Values recalculated in this study to account for the site density found for Moa goethite.

Calculations are done at 25ºC with the code PHREEQC v. 3.0 (Parkhurst & Appelo, 2013). Lo K values for minerals listed in Table 2 have been recalculated from end-member minerals to account for their chemical composition.

The system consists of a column of 35 m discretized in 100 cells of 0.35 m each. The total computing time is 10 My. Boundary water is a tropical rainwater with a constant infiltration rate of about 2000 mm/y. The system is considered fully water-saturated. The porosity is equal to 0.2. Due to code limitations, this porosity is constant throughout the calculations. However, as porosity is a key factor in the system evolution and is

	Reaction	Log K	End members
Forsterite	$Mg_9Fe_{0.95}Ni_{0.05}Si_5O_{20} + 20\ H^+ = 9\ Mg^{2+} + 0.95\ Fe^{2+} + 0.05\ Ni^{2+} + 5\ H_4SiO_4$	134.9	Forsterite, Fayalite, $Ni_2Si_2O_4$
Enstatite	$Mg_9FeSi_{10}O_{30} + 20\ H^+ + 10\ H_2O = 9\ Mg^{2+} + Fe^{2+} + 10\ H_4SiO_4$	109.4	Enstatite, Ferrosilite
1a Serpentine	$Mg_{2.85}Fe_{0.14}Ni_{0.01}Si_2O_5(OH)_4 + 6\ H^+ = 2.85\ Mg^{2+} + 0.14\ Fe^{2+} + 0.01\ Ni^{2+} + 2\ H_4SiO_4 + H_2O$	33.1	Serpentine, Nepouite, Greenalite
2a Serpentine	$Mg_{2.78}Fe_{0.16}Ni_{0.06}Si_2O_5(OH)_4 + 6\ H^+ = 2.78\ Mg^{2+} + 0.16\ Fe^{2+} + 0.06\ Ni^{2+} + 2\ H_4SiO_4 + H_2O$	32.7	

Table 2. *Mineral reactions and corresponding log K used in the calculations.*

known to increase as laterite deposit forms, several sensitivity cases have been done to study the influence of this parameter.

RESULTS AND CONCLUSIONS

Modelling results reproduce the mineral succession observed in the field. After 10 My, serpentinized peridotite has been partially weathered. Due to the infiltration of an oxidizing rainwater, enstatite, magnetite and forsterite dissolve. Porewater pH and Eh evolve from values of 9.5 and -463 mV in the peridotite domain to values of 4.5 and 400 mV close to the surface. A goethite rich layer develops at the top of the column, where conditions are more acidic and oxidizing, and a layer rich in secondary serpentine is formed at the contact with the initial peridotite. Small amounts of goethite are also present in contact with the secondary serpentine layer (fig.1). The thickness of the goethite rich layer is close to 7 m, although it increases up to 12 m if porosity is 0.4.

Once released from primary serpentine, Ni is sorbed onto goethite surface with values up to 2% wt Ni, especially in the goethite precipitated with the secondary serpentine. Close to this layer, pH is higher, enhancing sorption of Ni (fig.1). At lower pH, as the one prevailing in the upper goethite layer, Ni sorption is not favored and Ni is released to the porewater. In the field, however, it is thought that the flocculation of goethite particles with sorbed Ni onto their surface would prevent Ni desorption from goethite due to pH changes. However, this process as described here has not been implemented in the model.

After 10 My and for a porosity of 0.2, near 16% of Si and Mg are released from the column, while near all Ni and Fe are still there. For higher porosities, the amount of Si and Mg released from the system may reach values up to 35 % but Fe and Ni still remain in the system.

The obtained results show that both the mineral succession and the Ni content in

goethite observed in the field can be reproduced by considering the conceptual model described in this work. They also show that sorption of Ni onto goethite surface can account for the concentration of Ni measured in this horizon.

Nevertheless, there are some points that should be improved in the future. Discrepancies between the observed and the calculated thicknesses of the different layers might be due to a combination of different factors such as porosity changes, uplift, changes in soil water saturation that have not been considered in the present model. This kind of studies is thus to be considered as a useful tool to improve the understanding of the different factors governing the process of lateritization of ultrabasic serpentinized rocks.

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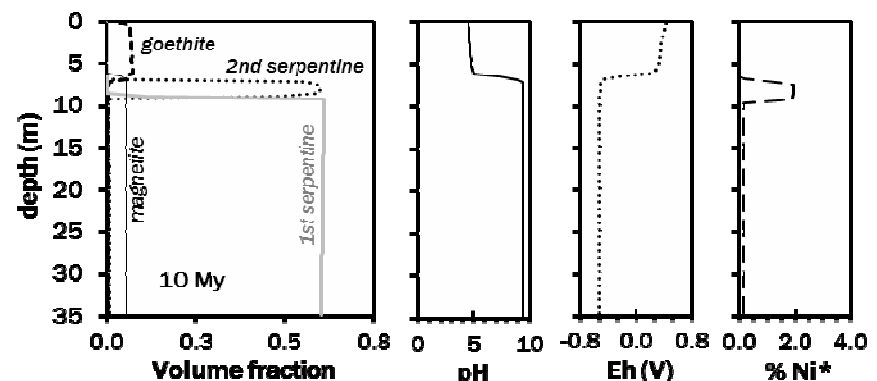
fig 1. *Laterite profile obtained after 10 My with a porosity of 0.2. *%wt Ni sorbed onto goethite.*