

# Mineralium Deposita

## Reactive transport model of the formation of oxide type Ni-laterite profiles (Punta Gorda, Moa Bay, Cuba) --Manuscript Draft--

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<b>Abstract:</b>	<p>Oxide type Ni-laterite deposits are characterized by a dominant limonite zone with goethite as the economically most important Ni ore mineral, and a thin zone of hydrous Mg silicate-rich saprolite beneath the magnesium discontinuity. Fe, less soluble, is mainly retained forming goethite, while Ni is redeposited at greater depth in a Fe(III) and Ni rich serpentine (serpentine II) or in goethite, where it adsorbs or substitutes for Fe in the mineral structure.</p> <p>Here, a 1D reactive transport model, using Crunchflow, of Punta Gorda oxide type Ni-laterite deposit (Moa Bay, Cuba) formation is presented. The model reproduces the formation of the different laterite horizons in the profile from an initial, partially serpentinized peridotite, in 106 years, validating the conceptual model of the formation of this kind of deposits in which a narrow saprolite horizon rich in Ni-bearing serpentine is formed above peridotite parent rock and a thick limonite horizon is formed over saprolite. Results also confirm that sorption of Ni onto goethite can explain the weight percent of Ni found in the Moa goethite.</p> <p>Sensitivity analyses accounting for the effect of key parameters (composition, dissolution rate, carbonate concentration, quartz precipitation) on the model results are also presented. It is found that aqueous carbonate concentration and quartz precipitation significantly affects the laterization process rate, while the effect of the composition of secondary serpentine or of mineral dissolution rates is minor. The results of this reactive transport modeling have proven useful to validate the conceptual models derived from field observations.</p>
<b>Response to Reviewers:</b>	Please see attachment.

# 1 Reactive transport model of the formation of oxide type 2 Ni-laterite profiles (Punta Gorda, Moa Bay, Cuba)

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12  
13 ABSTRACT

14 Oxide type Ni-laterite deposits are characterized by a dominant limonite zone with goethite as the  
15 economically most important Ni ore mineral, and a thin zone of hydrous Mg ~~silicate-silicate~~-rich saprolite  
16 beneath the magnesium discontinuity. Fe, less soluble, is mainly retained forming goethite, while Ni is  
17 redeposited at greater depth in a Fe(III) and Ni rich serpentine (serpentine II) or in goethite, where it  
18 adsorbs or substitutes for Fe in the mineral structure. ~~Nevertheless, these mechanisms are still not clear.~~  
19 ~~In this paper~~Here, a 1D reactive transport model, using -Crunchflow-, of Punta Gorda oxide type Ni -  
20 laterite deposit (Moa Bay-~~mining area~~, Cuba) formation is presented. ~~Simulations are done with~~  
21 ~~Crunchflow~~. The model reproduces the formation of the different laterite horizons ~~observed~~ in the profile  
22 from an initial, partially serpentinized peridotite, in 10<sup>6</sup> years, validating the conceptual model of the  
23 formation of this kind of deposits in which a narrow saprolite horizon rich in Ni-bearing serpentine is  
24 formed above peridotite parent rock and a thick limonite horizon is formed over saprolite. Results also  
25 confirm that sorption of Ni onto goethite ~~surface~~ can explain the ~~percentages-weight percent~~ of Ni found  
26 in the Moa goethite, ~~of Moa~~.  
27 Sensitivity ~~eases-analyses~~ accounting for the effect of ~~some~~ key parameters (composition, dissolution rate,  
28 carbonate concentration, quartz precipitation) on the model results are also presented. It is ~~observed-found~~  
29 that aqueous carbonate concentration and quartz precipitation significantly affects the laterization process

30 rate, while the effect of the composition of secondary serpentine ~~H-composition~~ or of mineral dissolution  
31 ~~mineral~~ rates is minor.

32 ~~Although still preliminary, The~~ results of this reactive transport modeling have ~~been proved to be~~ useful  
33 to validate the conceptual models derived from field observations.

34

35 KEYWORDS,

36 Oxide type Ni-laterites, Reactive Transport Modeling, Sorption, Goethite, Cuba

37

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42 ~~original manuscript.~~

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44

## 45 **1. Introduction**

46 Nickel laterite deposits are an important source of nickel and cobalt (Golightly 1981, 2010; Freyssinet et  
47 al. 2005, Lambiv Dzemua et al. 2013) and ~~have potential are considered worthy targets~~ for Sc and  
48 platinum group element ~~by-products exploration~~ (Aiglsperger et al. 2016 ~~and references therein~~).

49 Ni-laterite deposits formed from the chemical and mechanical weathering of ultramafic rocks exposed to  
50 the surface under favorable ~~topography and~~ climatic ~~and topographic~~ conditions. Laterite formation is  
51 controlled by ~~different factors, namely~~ intrinsic or extrinsic factors (Freyssinet et al. 2005, Moore et al.  
52 2012, Butt and Cluzel 2013). Intrinsic factors include, among others, the chemical and mineralogical  
53 composition of protolith (mainly peridotites), the dissolution rates of ~~their forming~~ minerals and their  
54 surface area. The geological context where laterites develop, the hydrological properties of the terrain  
55 (controlling ~~the~~ water flow), the climate (temperature and rainfall) and the duration of the weathering  
56 process are examples of extrinsic factors that may condition ~~the~~ laterite formation.

57 According to Golightly (1981, 2010) a typical Ni-laterite profile consists, from bottom to top of: a)  
58 partially or totally serpentinized ultramafic rock (protolith) characterized by unweathered minerals; b)  
59 saprolite horizon ~~formed by a regolith material~~ with textural features inherited from the protolith and  
60 dominated by secondary Si<sub>2</sub> and Mg<sub>2</sub> ~~bearing~~ minerals; and c) limonitic horizon composed mainly ~~by of~~  
61 goethite that evolves to hematite with time. The interaction of ~~slightly acidic~~ meteoric waters (~~slightly~~  
62 ~~acidic~~) with the ultramafic bed-rocks causes the release of Mg, Si and Ni<sub>2</sub> which are transported  
63 downwards. In particular, Ni, less soluble, is redeposited at depth producing ~~different~~ Ni<sub>2</sub>-enriched zones.

64 In the saprolite zone, Ni is mainly found in garnierite and/or secondary Ni-rich lizardite (serpentine II)  
65 and Ni-smectites (Pelletier 1996, Wells et al. 2009, Villanova-de-Benavent et al. 2014) ~~and references~~  
66 ~~therein~~. In the limonitic horizon, Ni is mainly retained by goethite, either adsorbed or substituting Fe in  
67 the mineral structure, and by minor Mn- oxyhydroxides (Roqué-Rosell et al. 2010; Dublet et al. 2015) ~~and references therein~~.

68 ~~and references therein~~.

69 Ni-laterites are usually classified according to their dominant Ni-bearing mineralogy in a) hydrous silicate  
70 type, b) clay type and c) oxide type (Brand et al. 1998; Freyssinet et al. 2005). Oxide type deposits,  
71 ~~objective of discussed in~~ this contribution, are characterized by a dominant limonite horizon with goethite  
72 as the economically most important Ni ore mineral. These deposits represent about 60% of the current  
73 total Ni laterite resources, with mean grades ranging from 1.0 to 1.6 wt% Ni (Butt and Cluzel 2013) ~~and~~  
74 ~~references therein~~.

75 Ni-laterites ~~have been formed~~, or are currently forming (Butt and Cluzel 2013), under humid tropical  
76 climates, where rainfall is higher than 1000 mm/y and temperatures range between 15-31 °C (Freyssinet  
77 et al. 2005; Thorne et al. 2012).

78 The mechanisms controlling the retention of Ni in goethite determine the mobility of the metal and the  
79 supergene enrichment of the Ni-bearing phases in the laterite horizons (Roqué-Rosell et al. 2010; Dublet  
80 et al. 2012). However, these mechanisms ~~are still not clear~~ controlling Ni mobility remain partly  
81 understood.

82 The Ni-goethite association has been explained either by sorption of Ni onto the goethite surface (Cornell  
83 1991; Rose and Bianchi-Mosquera 1993; Bryce et al. 1994; Coughlin and Stone 1995; Beukes et al. 2000;  
84 Trivedi and Axe 2001; Trivedi et al. 2001; Buerge-Weirich et al. 2002; Fisher et al. 2007; Arai 2008;  
85 Marcussen et al. 2009) or by the incorporation of Ni into the goethite structure or ~~by~~ both (Manceau et al.  
86 2000; Singh et al. 2002; Carvalho-e-Silva et al. 2002, 2003; Fan and Gerson 2011; Dublet et al. 2012).

87 Sorption of Ni on goethite has been studied both in natural and synthetic goethite by means of sorption  
88 experiments and spectroscopic techniques. Ni sorbs onto goethite forming inner-sphere mononuclear  
89 bidentate complexes (Trivedi et al. 2001; Xu et al. 2007), and sorption increases from pH 5 to 8 (Rose  
90 and Bianchi-Mosquera 1993; Beukes et al. 2000; Buerge-Weirich et al. 2002; Arai 2008). Sorption of Ni  
91 onto goethite has been modelled by considering Langmuir isotherms (Trivedi et al. 2001), a Diffuse Layer  
92 Model (Bryce et al. 1994; Buerge-Weirich et al. 2002; Marcussen et al. 2009; Rajapaksha et al. 2012) or a  
93 Triple Layer Model (Coughlin and Stone 1995).

94 The incorporation of Ni in the goethite structure ~~could be~~ is facilitated by the similar ionic radii between  
95 Fe<sup>3+</sup> (0.64Å) and Ni<sup>2+</sup> (0.69Å). However, even this small difference ~~induces changes in~~ cell parameters,  
96 and together with the difference in charge between both cations, limits the maximum amount of Ni in  
97 goethite (Dublet et al. 2015). According to Cornell (1991), 15% of sites occupied by Fe in goethite can be  
98 substituted by other cations without destabilizing the goethite structure. Manceau et al. (2000) studied a  
99 natural goethite by extended X-ray Absorption Fine Structure (EXAFS) and ~~showed~~ observed that  
100 Ni was partially incorporated in the goethite structure ~~of goethite~~. Singh et al. (2002) demonstrated ~~an~~ up  
101 to 5 mol % isomorphic substitution of Ni<sup>2+</sup> in the FeOOH structure ~~up to 5 mol %~~, which was limited by  
102 ~~the~~ changes in the next-nearest-neighbour coordination environment. Differential thermal (DTA), thermal  
103 gravimetric (DTA/TGA, TGA) and EXAFS analyses of a natural lateritic goethite ~~of lateritic origin~~ (1.8-  
104 4.1 mol% Ni) ~~performed~~ by Carvalho-e-Silva et al. (2002, 2003) suggested that the charge imbalance

105 could be compensated by the incorporation of H<sup>+</sup> into the goethite structure. Fan and Gerson (2011)  
106 indicated that ~~the~~-Ni associated with goethite in Philippine laterites was substituting Fe within its  
107 structure. Dublet et al. (2012) and Cathelineau et al. (2016) studied the speciation of Ni ~~along their a~~ New  
108 Caledonian laterite profile and observed Ni-goethite as the predominant Ni-bearer.

109 Bryce et al. (1994) considered that although sorption ~~processes~~ should be reversible, ~~due to because of~~  
110 aging or hysteresis Ni might not be completely released from goethite surfaces. Dublet et al. (2015) stated  
111 that the incorporation of Ni in goethite may be affected by the sequence of dissolution-precipitation  
112 reactions forming goethite. Therefore, ~~and despite their spite of~~ evidences of both sorption of Ni on the  
113 goethite surface and its incorporation in the structure, there is still a lack of understanding of these  
114 processes, ~~that might occur simultaneously.~~

115 In order ~~to corroborate or discard hypotheses and~~ to test the validity of conceptual models derived from  
116 field and/or experimental observations, reactive transport ~~modeling~~ and geochemical modeling ~~codes~~  
117 ~~have been has~~ proved ~~as~~ successful ~~tools~~ (Soler and Lasaga 1998; Corbella et al. 2004). There are several  
118 ~~computer~~ codes available to perform reactive transport or geochemical calculations (Steeffel et al. 2015),  
119 although none of them can ~~cope consider with~~ all hydro-geochemical processes ~~occurring~~ simultaneously.  
120 ~~In recent years, some studies focused on modeling of weathering processes.~~ Soler and Lasaga (1996,  
121 1998) developed one dimensional models of bauxite (Al-laterite) formation, describing the alteration of a  
122 granitic protolith and the formation of the bauxite and saprolite horizons over long time scales (10<sup>6</sup> years)  
123 using mineral reaction kinetics ~~from the literature~~. Fletcher et al. (2006) performed a simple two-mineral  
124 model to study how ~~spheroidal~~ weathering can transform intact bedrock into saprolite. The model coupled  
125 physical processes (e.g. fracturing) to chemical processes (e.g. mineral dissolution) and the rate of  
126 displacement of the reaction front ~~resulted was shown~~ to depend on the composition of the reactant fluid  
127 ~~where (being~~ O<sub>2</sub> and CO<sub>2</sub> ~~are~~ the most critical components in the ~~studied~~ case of a Puerto Rico quartz  
128 diorite regolith). ~~Later on,~~ Lebedeva et al. (2007) incorporated saprolite-forming reactions and developed  
129 a four-mineral model to predict rates of formation of saprolite, ~~and whereas~~ Fletcher and Brantley (2010)  
130 developed a simplified one dimensional model to study ~~the a~~ weathering profile, including vertical fluid  
131 transport, kinetic ~~reactions~~ and erosion.

132 Navarre-Sitchler et al. (2011) used the reactive coupled transport ~~model code~~ CrunchFlow to simulate the  
133 chemical and physical transformations ~~occurring~~ during ~~the~~ weathering of a basaltic rock and compared  
134 their results with field observations of alluvial terraces ~~of in~~ Costa Rica, where erosion was not

135 significant. They used a 1D model of a total length of 100 mm and observed that for porosities higher  
136 than 9%, mineral reaction kinetics dominated over transport, and that the advance of the weathering front  
137 ~~rate~~ was controlled by the rate at which porosity was created.

138 Moore et al. (2012) modeled the dissolution of minerals in a granitic soil and in a granitic saprolite with  
139 the reactive transport model FLOTRAN. The modeled reaction front depth was highly dependent on the  
140 precipitation rate of secondary minerals and on ~~the~~ fluid flow. Moreover, they had to use reduced reaction  
141 rates, compared with rates from laboratory studies, reduce the laboratory rates by decreasing the surface  
142 reactive areas to fit the field observations. They concluded that reactive transport models can be used to  
143 understand the long-lived ( $10^6$  years) mineral weathering processes given that they consider the  
144 simultaneous non-linear processes, can cope with simultaneous processes that do not behave linearly.

145 In this study, a reactive transport model is used to simulate the formation of the oxide type Punta Gorda  
146 Ni-laterite deposit ~~of Punta Gorda~~ from an initial partially serpentinized peridotite at constant temperature  
147 (25°C). The Punta Gorda deposit is part of the Moa Bay mining area, one of the largest reserves of nickel  
148 and cobalt in the world (Linchenat and Shirakova 1964; Lavaut 1998; Lewis et al. 2006; Proenza et al.  
149 2007; Aiglsperger et al. 2016), and probably the best known example of Ni-laterite deposits of oxide type  
150 ~~in commercial production~~ (Gleeson et al. 2003).

151 The main objective of this contribution is to test a conceptual model for the formation of ~~this kind of oxide~~  
152 type Ni-laterite deposits and to identify and quantify, the key parameters affecting the development of the  
153 different laterite horizons. Moreover, ~~and~~ by considering that Ni is sorbed onto goethite, we aim ~~at~~  
154 checking to determine whether this process could account for the amount of Ni found in the goethite at  
155 Punta Gorda.

156 In this paper, we present a ~~first~~ modeling exercise that provides ~~new~~ valuable insights into the  
157 understanding of the formation of Ni-laterite deposits. ~~Theis~~ modeling ~~exercise~~ consists of a set of one  
158 dimensional models in which rain water infiltrates and flows vertically downwards simulating the  
159 infiltration through fractures and cracks. Formation of the goethite and saprolite horizons is achieved by  
160 ~~the~~ dissolution of primary minerals and ~~the~~ precipitation of secondary minerals. No solid solutions have  
161 been included for ~~a sake of~~ simplicity. Porosity changes reflecting different molar volumes of  
162 dissolving/precipitating minerals are taken into account.

163 Due to fact that the model is ~~only~~ one dimensional~~ed~~, ~~it the model~~ does not account for the formation of  
164 typical saprolite corestones as lateral water flow and matrix diffusion processes are not considered. Water

165 is allowed to equilibrate with ~~atmospheric~~ air along the whole domain, simulating unsaturated conditions.  
166 Calculations have been carried out for a ~~total~~ time span of  $10^6$  years. Past climatic changes, (~~such as~~  
167 variations in precipitation regime), ~~erosion-erosion~~, or collapse due to a ~~severe~~ increase in porosity in of  
168 the upper part of laterite profile are not considered.

169 The 1D models ~~described here~~~~conforming this modeling exercise~~ differ in ~~the~~ values for assigned to  
170 several parameters that ~~in~~ preliminary work had ~~been~~ identified as having a significant role in the  
171 formation of laterite profiles, such as (~~solubility constants, dissolution rates, CO<sub>2</sub>(g), precipitation of~~  
172 quartz,...). ~~A One of these models (Reference case) model~~ is explained in detail whereas, ~~while~~ the  
173 results of the others models (~~Sensitivity cases~~) are compared to the results of the Reference case.

174

175 ~~This modeling exercise must be considered as a first step in the modeling of laterite profiles. The results~~  
176 ~~will be of great utility when designing future models with higher complexity in terms of dimension (2D,~~  
177 ~~3D), number and type of processes (matrix diffusion, more complete mineralogies, Ni coprecipitation in~~  
178 ~~goethite), formation of solid solutions or chemical components (Mn, Co, Al,...).~~

## 179 **2. The Punta Gorda Ni-laterite deposit**

180 The Punta Gorda Ni-Co laterite deposit is located in the Moa Bay mining area (northeast of Cuba, ~~)~~  
181 (~~Fig.1~~). The Moa Bay laterite deposits are part of a larger province of nickel laterites in northeast Cuba.  
182 The deposits ~~were~~ developed over serpentized harzburgite of Moa-Baracoa ophiolitic massif (Proenza  
183 et al. 1999; Marchesi et al. 2006) with weathering and laterization commencing during the Miocene  
184 (Lewis et al. 2006; Proenza et al. 2007) and references therein. The elevation ~~above sea level~~ of the  
185 peneplain surface of the deposits varies from 60 to 950 m above sea level, and the weathering mantle can  
186 reach a total thickness of more than 50 m in the laterite profile (Linchenat and Shirakova 1964; Golightly  
187 et al., 2008b).

188 This deposit can be classified as oxide type (Oliveira et al. 2001; Rojas-Purón et al. 2012; Aiglsperger et  
189 al. 2016), and As with as many northeastern Cuban deposits, the typical vertical section ~~of a profile~~  
190 consists of four principal horizons, from bottom to top: (1) parent rock serpentized peridotite, (2)  
191 saprolite, (3) lower and upper limonite and (4) ferricrete or duricrust (Lewis et al. 2006; Proenza et al.  
192 2007; Aiglsperger et al. 2016; ~~)~~ (Fig. 2a). Occasionally, within a the profile some gabbro bodies  
193 weathered to bauxite ~~appear~~. Ni and Co are mainly in the limonite zone but the siting of doubts about the  
194 detailed distribution of metals (adsorbed or in solid solution) ~~still~~ remains debated.

195 ~~The~~ Punta Gorda deposit has been extensively studied (Oliveira et al. 2001; Galí et al. 2007; Roqué-  
196 Rosell et al. 2010; Rojas-Purón et al. 2012; Aiglsperger et al. 2016). ~~The m~~Mineralogy was characterized  
197 by qualitative and quantitative X-~~R~~ray ~~powder~~ diffraction, optical and scanning electron microscopy  
198 (SEM-~~EDS~~) and electron ~~micro~~probe microanalysis (EMPMA; ~~)(Galí et al. 2007)~~). Concentrations of  
199 ~~relevant~~ major and minor elements (~~in wt.%)~~ as well as trace elements (~~in ppm or ppb)~~ in parent rocks  
200 and weathering products of Ni-~~laterite~~ profiles were measured analyzed by Aiglsperger et al. (2016).  
201 ~~Analytical conditions for the SEM and EMPA are summarized in Roqué Rosell et al. (2010) and~~  
202 ~~Villanova de Benavent et al. (2014).~~

203 ~~The M~~mineralogical composition of the studied profile in Punta Gorda is shown in Fig. 2b. ~~As seen,~~  
204 ~~mineral composition changes from bottom to top.~~ ~~The M~~main minerals of the parent ~~rock~~ serpentinized  
205 peridotite are forsterite, enstatite, serpentine and maghemite (Sample M10). ~~The S~~saprolite horizon is  
206 dominated by serpentine and goethite (Sample M9), whereas ~~and~~ in limonite and ferricrete horizons,  
207 goethite and hematite are the main minerals, although other minor phases such as pyrochroite, gibbsite,  
208 quartz, Mn-oxyhydroxide aggregate (lithiophorite, “lithiophorite–asbolane intermediates”) and asbolane  
209 (Roqué-Rosell et al. 2010) are also found (samples M8 to M1).

210 ~~Olivine and enstatite represent T~~he parent rock from which the Ni-laterite profile in the Moa district  
211 originated consists of. ~~This is a~~ partially serpentinized ophiolitic harzburgite (70%  $Mg_9Fe_{0.95}Ni_{0.05}Si_5O_{20}$ ,  
212 16%  $Mg_9FeSi_{10}O_{30}$ ) including plagioclase-rich bodies, impregnated by plagioclase, which was exposed to  
213 the surface during the late Miocene ( $\approx 10^7$  years; ~~)(Lewis et al. 2006)~~).

214 Serpentine minerals are ~~present as~~ polytype 1T and 2H1 lizardite. Lizardite 1T is the dominant polytype  
215 and whereas lizardite 2H1 is less crystalline and presents many stacking faults in its structure. The cell  
216 volume is slightly biglargger than that corresponding to the ideal end member  $Mg_3Si_2O_5(OH)_4$ , due to  
217 substitution of ~~some~~ Mg by Fe and minor Ni and Mn, as confirmed by chemical analyses. Two different  
218 types of serpentine have been identified. Serpentine I ~~represents the serpentine~~ formed by due to the  
219 alteration of forsterite and enstatite during ~~athe~~ hydrothermal stage, whereas ~~and~~ serpentine II ~~the~~  
220 ~~serpentine~~ formed after weathering of serpentine I. Serpentine II can be formed as a thermodynamically  
221 stable secondary phase in meteoric conditions, as shown in Villanova-de-Benavent et al. (2016a).

222 Serpentine I composition, has been calculated from ~~results obtained by EPMMPA data and considered~~  
223 equal to is  $Mg_{2.85}Fe_{0.14}Ni_{0.01}Si_2O_5(OH)_4$ . In serpentine II, Mg in octahedral coordination position is  
224 partially substituted by  $Fe^{3+}$  and  $Ni^{2+}$ . Serpentine II structural formulae calculated from EMPMA are

225 shown in [Online resource 1 Table 1](#). ~~As can be seen, s~~Serpentine II contains more Ni than serpentine I.  
 226 These Ni-bearing serpentines (Srp-II), in addition to “garnierites”, ~~is are~~ the main Ni ores in saprolite  
 227 horizon of Ni-laterite deposits (~~e.g.~~ Golightly and Arancibia 1979; Pelletier 1996; Villanova-de-Benavent  
 228 et al. 2014, 2016b). ~~In and in t~~In the case of Punta Gorda deposit, this second generation of serpentines is the  
 229 major Ni-bearing silicate phase in the saprolite horizon. Nickel content in Ni-rich serpentine ranges from  
 230 1 to 7 wt.% NiO, in contrast with ~~primary-serpentine I~~, which has the same Ni content is no more  
 231 enriched in Ni than the olivine (~ 0.4 wt.%).  
 232 Iron oxides are ~~present as~~ maghemite, goethite and hematite. The refined cell parameter of maghemite,  
 233 very similar to the accepted value of 8.3505 Å, indicates a composition near the ideal Fe<sub>2</sub>O<sub>3</sub> (Galí et al.  
 234 2007). In near surface conditions, maghemite can form by from the oxidation of magnetite (Gehring et al.  
 235 2009, Lilova et al. 2012) that in turn, results from the hydration of primary olivine and pyroxene. Under  
 236 atmospheric conditions, maghemite is transformed into goethite. Hematite (Fe<sub>2</sub>O<sub>3</sub>) has almost an ideal  
 237 composition and structure, although it has a presents a rather low crystallite size (30 to 40 nm; ~~;) (Galí et al~~  
 238 2007). Goethite (FeOOH), the major phase containing most of the Ni in this profile (from 0.8 to 4 wt.%  
 239 with an average value of 1.23 wt.%), coexists with maghemite and hematite in limonite samples and with  
 240 lizardite in samples M8 and M9 (Galí et al. 2007). Crystallographic studies indicate that there is some  
 241 substitution (2-17%) of Fe by Al as the cell volume is always smaller than the accepted value for goethite.  
 242 ~~Recently, an additional characterization of this goethite based on t~~The analyses of different diffraction  
 243 peaks of goethite using through the Scherrer’s relation (~~eq. 1~~) (Klug and Alexander 1962; Langford 1978;  
 244 De Keijser et al. 1982; Louër et al. 1983) ~~has been done.~~

$$245 \quad D_{hkl} = \frac{\lambda}{FWHM_{hkl} \times \cos \theta} \quad (1)$$

246 ~~The Scherrer’s relation allows the obtention of the mean shape and dimensions of crystallites (D<sub>hkl</sub>, in nm)~~  
 247 ~~from the length of the radiation used (λ, in nm), the width of the hkl diffraction peak (FWHM<sub>hkl</sub>, in radian~~  
 248 ~~units) and the diffraction angle (θ). and U~~Using values for the 110, 020, 120 and 130 ~~selected~~ peaks in  
 249 the space group P<sub>bnm</sub> (a=4.605 Å, b=9.96 Å and c=3.02 Å; ~~;) (Fig. 3), and a value of λ[Kα1,Cu] of 1.5406~~  
 250 Å, yields an the most approximate surface to the ideal mean ~~particle is an~~ elongated prism in the c  
 251 direction, with 8.7 nm in the **a** direction and 18.1 nm in **b** direction. The length in **c** could not be  
 252 determined, but ~~morphological~~ observations have shown that the ~~morphological c/b~~ aspect ratio e/b is not  
 253 less than 4.5 (Strauss et al. 1997). With these data, the calculated specific surface for goethite is 84.8  
 254 m<sup>2</sup>/g. If, instead of adjusting a prismatic shape, an elliptical cylinder elongated in the **c** direction is fitted

255 ~~to the obtained directional dimensions~~, a specific surface of 87.2 m<sup>2</sup>/g is obtained, which is ~~very~~ similar to  
256 the previous value.

257 The specific surface obtained by the BET (Brunauer-Emmet-Teller) method (Brunauer et al. 1938) for the  
258 same material is 65.2 m<sup>2</sup>/g. As expected, the BET value is lower than the value calculated through X-ray  
259 ~~Ray powder~~ diffraction which reflects the dimension of the coherent diffracting domains, rather than the  
260 dimension of the material particle that ~~consists of an usually is formed by~~ aggregate ~~ion~~ of several  
261 ~~d~~domains.

262

### 263 ~~3.~~ Materials and methods

264 The reactive transport model presented in this work is based on the direct formation conceptual model  
265 described in Butt and Cluzel (2013). According to this model, oxide type Ni-laterite deposits form as a  
266 result of ~~a~~ continuous weathering of ~~a~~ partially serpentinized peridotite under tropical climate. During  
267 weathering, the water table is high and fluctuating, and erosion rates are low. The system is ~~well drained~~  
268 ~~and~~ fully saturated. Meteoric water, in equilibrium with atmospheric O<sub>2</sub> and CO<sub>2</sub>, flows through the  
269 profile at a constant rate. Therefore, Ni is expected to be released from olivine or serpentine I and retained  
270 by the formation of a Fe(III)-rich serpentine II and by sorption onto goethite, while Mg and Si are  
271 expected to be leached out of the system (Ulrich et al. 2014, Villanova-de-Benavent et al. 2016a) because  
272 of serpentine and silicate dissolution. ~~This might~~ Dissolution can cause an increase in porosity that may  
273 accelerate the ~~occurring~~ processes due to the ~~corresponding~~ decrease ~~in the~~ solid/water ratio.  
274 According to ~~the conceptual model described in~~ Butt and Cluzel (2013), Ni may be ~~further~~ leached from  
275 goethite ~~and form~~ to garnierite deeper in the profile, ~~and~~ goethite may transform to hematite, ~~in~~  
276 ~~special~~ particularly in the upper most limonite horizon. Neither the formation of garnierite, nor the  
277 formation of hematite, is considered in this ~~first model~~ presented here.  
278 Temperature is considered constant ~~and equal to~~ at 25 °C. According to Thorne et al. (2012), ~~the formation~~  
279 ~~of Ni--laterite forms s-occurs~~ in tropical areas where monthly temperatures are in the range of 22-31 °C  
280 in the summer and between 15-27 °C in the winter.

281 The partially serpentinized unweathered peridotite is composed of Ni-bearing forsterite, enstatite and  
282 serpentine I, ~~as representative mineral phases of the unweathered peridotite~~. In our ~~this~~ model, ~~the~~  
283 ~~inclusion of~~ maghemite is not considered ~~has been discarded~~ given its low stability. Its precursor,  
284 magnetite is ~~has been~~ considered instead (Gehring et al. 2009). Serpentine I and magnetite ~~are supposed~~

285 ~~to formed~~ during a previous hydrothermal serpentinization ~~eventperiod~~ (pre-weathering), ~~whose~~  
286 ~~formationthat~~ is ~~outside of~~ the scope of this study.

287

288 ~~3.1~~ Chemistry solver, modeled domain and hydrodynamic system

289 The ~~code~~ computer code used for the simulations is Crunchflow, a software package for simulating  
290 reactive transport ~~modeling~~ developed by Steefel and co-workers (Steeff and Lasaga 1994; Steff  
291 2009). This code can take into account ~~handle~~ aqueous speciation, surface complexation, ion exchange,  
292 mineral dissolution/precipitation and transport processes under fully saturated flow conditions and  
293 ~~different temperatures~~ variable temperature (Steeff et al. 2015). ~~AIn the code,~~ all mineral transformations  
294 are ~~always~~ treated as dissolution and precipitation reactions. Kinetic reaction rates, depending on reactive  
295 surface area, are used to describe these reactions. Transformations in the solid state (without  
296 dissolution/precipitation) are not considered. However, if reaction rates are fast compared to solute  
297 transport ~~by~~ {advection, dispersion ~~or~~, diffusion}, when the dissolution of a mineral ~~can~~ causes  
298 supersaturation of the solution with respect to another phase, this new phase will precipitate at the same  
299 location as that of the dissolving mineral, causing an effect similar to a potential solid-state  
300 transformation. The code uses an integrated finite difference discretization to solve the advection-  
301 dispersion-reaction differential equations that link flow, solute transport and geochemical processes.  
302 Total porosity ( $\phi_T$ ) ~~is~~ ~~may be~~ updated after each time step according to eq. 21, where  $N_m$  is the number of  
303 minerals in the model (Navarre-Sitchler et al. 2011) and  $\phi_m$  the volume fractions of minerals.

$$304 \phi_T = 1 - \sum_{k=1}^{N_m} \phi_m \quad (21)$$

305 The  $\phi_m$  values are updated after each time step according to eq. 32, where  $t-1$  indicates the parameter  
306 value of the previous time-step,  $\Delta t$  is the time step length (s),  $V_m$  the molar volume of the mineral  
307 ( $\text{m}^3/\text{mol}$ ) and  $R_m$  the mineral reaction rate ( $\text{mol}/\text{m}^3/\text{s}$ ). Rate equations follow the Transition State Theory  
308 (Lasaga 1998) and are calculated according to eq. 4-3 where  $A_m$  is the mineral surface area ( $\text{m}^2/\text{m}^3_{\text{rock}}$ ),  
309  $k_{25}$ , the reaction rate constant ( $\text{mol}/\text{m}^2/\text{s}$ ) at 25°C,  $R$  is the gas constant (8.3144 J/mol/K),  $E_a$  is the  
310 activation energy (J/mol),  $T$  is temperature (K),  $a_i^{n_i}$  is the term describing the effect of species  $i$  on the  
311 rate, and  $f_m(\Delta G)$  is the function describing the dependence of the rate on the solution saturation state  
312 (Soler 2013). This function is calculated with eq. 5-4 where IAP is the ionic activity product of the  
313 solution with respect to the mineral,  $K_{eq}$  is the equilibrium constant of that mineral, and  $m_1$ ,  $m_2$  and  $m_3$  are

314 empirical parameters defining the shape of this function (assumed to be equal to 1 if no experimental data  
 315 are available).

$$316 \quad \phi_m = \phi_{m,t-1} + V_m (R_m \Delta t) \quad (32)$$

$$317 \quad R_m = A_m \sum_{\text{terms}} k_{25} e^{\frac{-E_a}{R} \left( \frac{1}{T_{25}} - \frac{1}{T} \right)} \left( \prod_i a_i^{n_i} \right) f_m(\Delta G) \quad (34)$$

$$318 \quad f_m(\Delta G) = \left[ 1 - e^{\left( m_2 \left( \ln \frac{IAP}{K_{eq}} \right)^{m_3} \right)} \right]^{m_1} \quad (54)$$

319 The mineral surface area ( $A_m$ ) is calculated according to eq. ~~6-5~~ where,  $A_{\text{specific}}$  is the mineral specific  
 320 surface area ( $\text{m}^2/\text{g}$ ) and  $MW_m$ , the mineral molecular weight ( $\text{g}/\text{mol}$ ). - A threshold mineral volume  
 321 fraction value must be provided for secondary minerals not initially present in the system to calculate the  
 322 bulk surface area until the computed time-evolving volume fraction exceeds the threshold value.

$$323 \quad A_m = \frac{\phi_m A_{\text{specific}} MW_m}{V_m} \quad (65)$$

324 Activity coefficients for aqueous species are calculated according to the extended Debye-Hückel equation  
 325 (Steefel 2009). ~~For more detailed information on CrunchFlow, the reader is referred to the user's manual~~  
 326 ~~that can be found in [www.esteeffel.com](http://www.esteeffel.com).~~

327 The physical system chosen to conduct the reactive transport model is a 1D column of 88 m length  
 328 representing the laterite profile. In the model, rainwater flows from top to bottom. -The column is  
 329 discretized into a mesh of 250 elements of 0.35 m length each. Models are run for  $10^6$  years, with a  
 330 maximum time step of 1 year.

331 Meteoric water has a constant composition (Table [12](#)), ~~from a typical of~~ rainwater ~~from of~~ tropical areas  
 332 (Veneklaas 1990; Williams et al. 1997; Bertolo et al. 2006). It has an ionic strength of  $1.4 \times 10^{-4}$  mol/L. pH  
 333 has been set ~~equal~~ to 4.5, accounting for both the acidic pH of rainwater and the acidity generated in soils  
 334 due to the formation of organic acids ~~as a consequence of fer-organic~~ as a consequence of organic matter decomposition (Soler and  
 335 Lasaga, 1996). Rainwater is flowing along the column at a constant rate during ~~the modeling time~~. The  
 336 average annual rainfall at Moa ~~(Cuba)~~ in the period 1900-2009 is 1360 mm, of which 990 mm fall during  
 337 the two wet seasons (data from ~~Climate Change climatic portal~~,  
 338 <http://sdwebx.worldbank.org/climateportal>).

339 This value agrees with the values between 900 and 1800 mm/y reported by Butt and Cluzel (2013) as  
 340 summer rainfall for laterite deposit in Caribbean areas. Assuming ~~a~~ retention by the soil of 15% (~~between~~  
 341 ~~12 and 18% as proposed by~~ Veneklaas, (1990)) the infiltration flow rate is 1156 mm/y ( $4.0 \times 10^{-8} \text{ m}^3/\text{m}^2/\text{s}$ ).

342 Neither dry periods nor changes in the infiltration rate are considered during the modeling. Transport is  
343 mainly advective. A water diffusion coefficient for solutes of  $1.0 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$  is considered and  
344 dispersivity is assumed to be equal to 1 m based on the length of the domain (~~83-88~~ m). Diffusivity and  
345 dispersive transport are is not significant. ~~There is no lateral flow of water.~~

346

### 347 ~~3.2~~ Geochemical system

348 Initially, the system has a homogeneous mineralogical composition, representing the partially  
349 serpentinized peridotite (Table ~~32~~). Initial mineral volume fractions are based on ~~the~~ field observations  
350 ~~done in the~~ Punta Gorda laterite deposit (M10 sample in Fig. 2b). An initial porosity of 12 % is used ~~has~~  
351 ~~been considered~~ to account for the fracture porosity. ~~associated to fractures trough which water flows.~~  
352  $\text{En}_{90}$  and  $\text{Fo}_{90}$  are chosen as representative of the pyroxene and olivine ~~minerals~~ from the unaltered  
353 peridotite ~~samples studied~~, respectively.  
354 Initial porewater composition is calculated to be in equilibrium with this set of minerals (Table ~~21~~). It has  
355 an ionic strength of  $1.1 \times 10^{-4} \text{ mol/L}$ . K and Na are found as free ions, Si is forming ~~the~~ aqueous species  
356  $\text{H}_4\text{SiO}_4$  (68%) and  $\text{H}_3\text{SiO}_4^-$  (32%). The most abundant aqueous species of carbonate at pH 9.5 is  $\text{HCO}_3^-$   
357 (86%) although  $\text{CO}_3^{2-}$  is also significant (13%), together with minor amounts of  $\text{MgCO}_3(\text{aq})$  and  
358  $\text{FeCO}_3(\text{aq})$  (<1%). All iron is found as Fe(II), and is present as  $\text{Fe}^{2+}$  (50%),  $\text{FeOH}^+$  (48%) and  
359  $\text{Fe}(\text{OH})_2(\text{aq})$  (2%). Mg aqueous speciation is dominated by  $\text{Mg}^{2+}$  (99%) although a small amount of  
360  $\text{MgOH}^+$  (1%) is ~~also observed~~ computed. Finally, the main Ni aqueous species are  $\text{Ni}(\text{OH})_2$  (83%),  $\text{Ni}^{2+}$   
361 (9%) and  $\text{NiOH}^+$  (8%).

362 Besides the primary minerals considered in the initial composition, serpentine II and goethite are included  
363 in the calculations and are allowed to precipitate in the case where that porewater is saturated ~~s~~ with  
364 respect to those minerals. Although several compositions for serpentine II are available (Online resource  
365 1 Table 1), only one composition ~~has been considered~~ was used in the model for ~~the~~ sake of simplicity. In  
366 the Reference case, the ~~selected~~ composition is set to ~~has been~~  $\text{Mg}_{2.798}\text{Fe}_{0.102}\text{Ni}_{0.049}\text{Si}_2\text{O}_5(\text{OH})_4$  but the  
367 effect of different compositions has been studied in ~~additional~~ sensitivity analyses ~~cases~~.

368 In many oxide deposits ~~the presence of~~ abundant secondary silica has been observed in the form of  
369 chalcedony or quartz (Butt and Cluzel 2013). In the model presented here, the saturation index of quartz  
370 is monitored and the formation of quartz is ~~further~~ considered in a sensitivity analysis ~~case~~.

371 Moore et al. (2012) highlighted the role of ~~the~~ weathering of silicate mineral as a sink for atmospheric  
 372 CO<sub>2</sub>(g). ~~Min fact,~~ magnesite deposits associated to serpentine bodies have been reported (Foster and  
 373 Eggleton 2002; Ulrich et al. 2014; Quesnel et al. 2016). However, magnesite precipitation, although  
 374 thermodynamically stable, is inhibited in near surface environments given the strong hydration shells that  
 375 form around Mg<sup>2+</sup> ions (Power et al. 2013; Morgan et al. 2015). In these conditions, Königsberger et al.  
 376 (1999) suggested that hydrated magnesium carbonate minerals, such as nesquehonite (MgCO<sub>3</sub>·3H<sub>2</sub>O)  
 377 form instead. Power et al. (2013) reported that CO<sub>2</sub>(g), in turn, may affect the weathering rate of silicate  
 378 mineral. In order to elucidate the effect of CO<sub>2</sub> in the formation of this type of deposits, the saturation  
 379 index of nesquehonite is monitored and the effect of different CO<sub>2</sub>(g) concentrations is considered in  
 380 sensitivity ~~analysis~~ analyses.

381

### 382 ~~3.3~~ Thermodynamic and kinetic data

383 Thermodynamic data used in the calculations for aqueous species and for the dissolution/precipitation of  
 384 quartz and goethite ~~come from~~ are from ThermoChimie v.9 database (Giffaut et al. 2014);  
 385 [www.thermochimie-tdb.com](http://www.thermochimie-tdb.com).

386 The total list of solute species included in the simulations is shown in Online resource 2. ~~H<sup>+</sup>, CO<sub>3</sub><sup>2-</sup>,  
 387 O<sub>2</sub>(aq), Cl<sup>-</sup>, Fe<sup>2+</sup>, H<sub>4</sub>(SiO<sub>4</sub>)(aq), K<sup>+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup>, Ni<sup>2+</sup>, OH<sup>-</sup>, CO<sub>2</sub>(aq), HCO<sub>3</sub><sup>-</sup>, MgHCO<sub>3</sub><sup>+</sup>, NaHCO<sub>3</sub>(aq),  
 388 FeCO<sub>3</sub>OH(aq), MgCO<sub>3</sub>(aq), NaCO<sub>3</sub><sup>-</sup>, NiCO<sub>3</sub>(aq), NiHCO<sub>3</sub><sup>+</sup>, Fe(CO<sub>3</sub>)<sub>3</sub><sup>3-</sup>, FeHCO<sub>3</sub><sup>+</sup>, FeCO<sub>3</sub>(aq), FeCO<sub>3</sub>OH<sup>-</sup>  
 389 , Ni(CO<sub>3</sub>)<sub>2</sub><sup>2-</sup>, Fe(CO<sub>3</sub>)<sub>2</sub><sup>2-</sup>, FeOH<sup>+</sup>, Fe(OH)<sub>2</sub>(aq), Fe(OH)<sub>3</sub><sup>-</sup>, Fe(OH)<sub>4</sub><sup>2-</sup>, Fe<sup>3+</sup>, FeOH<sup>2+</sup>, Fe(OH)<sub>2</sub><sup>+</sup>,  
 390 Fe(OH)<sub>3</sub>(aq), Fe(OH)<sub>4</sub><sup>-</sup>, FeH<sub>3</sub>SiO<sub>4</sub><sup>2+</sup>, Fe<sub>2</sub>(OH)<sub>2</sub><sup>4+</sup>, Fe<sub>3</sub>(OH)<sub>4</sub><sup>5+</sup>, H<sub>2</sub>(aq), MgOH<sup>+</sup>, Mg<sub>4</sub>(OH)<sub>4</sub><sup>4+</sup>, MgH<sub>3</sub>SiO<sub>4</sub><sup>+</sup>,  
 391 Ni(OH)<sub>2</sub>(aq), NiOH<sup>+</sup>, Ni(OH)<sub>3</sub><sup>-</sup>, Ni<sub>2</sub>(OH)<sub>3</sub><sup>3+</sup>, Ni<sub>4</sub>(OH)<sub>4</sub><sup>4+</sup>, H<sub>2</sub>SiO<sub>4</sub><sup>2-</sup> and H<sub>3</sub>SiO<sub>4</sub><sup>-</sup>.~~

392 Solubility constants for En<sub>90</sub>, Fo<sub>90</sub>, serpentine I and serpentine II have been modified given that they are  
 393 not pure magnesium end member minerals. ~~In these cases and for the sake of simplicity,~~ an ideal solid  
 394 solution between pure end members has been considered for each mineral. For an ideal solid solution  
 395 A<sub>χ</sub>B<sub>(1-χ)</sub>C, where the pure end members are AC and BC, the solubility constant of a given discrete  
 396 composition can be calculated using eq. 76, where K<sub>AC</sub> is the solubility constant of pure AC, K<sub>BC</sub> is the  
 397 solubility constant of pure BC and χ the molar fraction of A in the solid solution.

$$398 \quad K = (K_{AC}\chi)^{\chi} (K_{BC}(1-\chi))^{1-\chi} \quad (76)$$

399 The pure end members considered for Fo<sub>90</sub> are fayalite (Fe<sub>2</sub>SiO<sub>4</sub>), forsterite (Mg<sub>2</sub>SiO<sub>4</sub>) and the phase  
 400 Ni<sub>2</sub>SiO<sub>4</sub>; for En<sub>90</sub>, the pure end members are enstatite (MgSiO<sub>3</sub>) and ferrosilite (FeSiO<sub>3</sub>). In the case of

401 serpentine I the pure end members are lizardite ( $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$ ), népouite ( $\text{Ni}_3\text{Si}_2\text{O}_5(\text{OH})_4$ ) and  
 402 greenalite ( $\text{Fe}_3\text{Si}_2\text{O}_5(\text{OH})_4$ ) while in the case of serpentine II, Fe(III)-lizardite ( $\text{Fe}_2\text{Si}_2\text{O}_5(\text{OH})_4$ ) is  
 403 considered instead of greenalite to account for the difference of the valence state of Fe in the octahedral  
 404 site. ~~between these two serpentines.~~ The log K values of these pure end members are taken from  
 405 ThermoChimie v.9 when available. ~~However, as this database does not provide data for all of them,~~  
 406 ~~Additional log K values data are selected from other databases (e.g. forsterite), are~~ calculated in this  
 407 study from published  $\Delta G_r^\circ$  (e.g.  $\text{Ni}_2\text{SiO}_4$ ) or estimated  $\Delta G_f$  values (e.g. Fe(III)-lizardite, Villanova de  
 408 Benavent et al. 2016a) from literature (Villanova-de-Benavent et al. 2016a). Selected log K values for  
 409 pure end-members are ~~shown listed~~ in Table 43, whereas log K values calculated for the solid solutions  
 410 are ~~listed~~ in Table 54.  
 411 In CrunchFlow, dissolution/precipitation of minerals is ~~always~~ kinetically controlled. As dissolution  
 412 and/or precipitation of serpentine I, serpentine II, goethite and magnetite is considered to occur under  
 413 local equilibrium, the rates for these minerals have been modified in order to rapidly achieve equilibrium  
 414 (large surface areas and/or large rate constants). The threshold volume fraction considered is  $10^{-8}$  and  $10^{-4}$   
 415 for goethite and serpentine II, respectively.

416 Dissolution rates for Fo<sub>90</sub> and En<sub>90</sub> are assumed equal to those for pure forsterite and enstatite reported in  
 417 Palandri and Kharaka (2004), ~~and shown in eq.8 and eq.9 respectively, where R is the gas constant (in kJ~~  
 418 ~~K<sup>-1</sup> mol<sup>-1</sup>), T the temperature (in K) and  $\Omega$  the mineral saturation ( $\Omega = \text{IAP}/K_{eq}$ ),  $m_1$ ,  $m_2$  and  $m_3$  of eq. 5 are~~  
 419 ~~considered equal to 1.~~

$$420 \text{rate} \left( \text{mols}_{\text{Mg}_{10}\text{Si}_5\text{O}_{20}} \text{m}^{-2} \text{s}^{-1} \right) = \frac{1}{s} \left( 10^{-6.85} \times e^{\frac{-67.2 \text{kJ/mol} \left( \frac{1}{T} - \frac{1}{298.15 \text{K}} \right)}{R}} \times a_{\text{H}^+}^{0.47} + 10^{-10.64} \times e^{\frac{-79 \text{kJ/mol} \left( \frac{1}{T} - \frac{1}{298.15 \text{K}} \right)}{R}} \right) \times (1 - \Omega) \quad (8)$$

$$421 \text{rate} \left( \text{mols}_{\text{Mg}_{10}\text{Si}_{10}\text{O}_{30}} \text{m}^{-2} \text{s}^{-1} \right) = \frac{1}{s} \left( 10^{-9.02} \times e^{\frac{-80 \text{kJ/mol} \left( \frac{1}{T} - \frac{1}{298.15 \text{K}} \right)}{R}} \times a_{\text{H}^+}^{0.60} + 10^{-12.72} \times e^{\frac{-80 \text{kJ/mol} \left( \frac{1}{T} - \frac{1}{298.15 \text{K}} \right)}{R}} \right) \times (1 - \Omega) \quad (9)$$

422 The assignment of a value for the reactive area of forsterite and enstatite is not straightforward.  
 423 Dissolution rates measured in the laboratory are ~~from~~ 2 to 5 orders of magnitude faster than in field due to  
 424 a variety of factors such as the presence/absence of inhibitors or catalyzers ~~such as (e.g. organic acids),~~  
 425 hydrologic regimes, armoring of natural surfaces or the affinity of secondary minerals (Navarre-Sitchler  
 426 et al. 2011) ~~and the way how the specific surface for calculating the rates of dissolution of different~~  
 427 ~~minerals in a model has yet to be solved (Sokolova 2013).~~ After preliminary calculations, a reactive area  
 428 of 0.0005 m<sup>2</sup>/g for Fo<sub>90</sub> and of 0.005 m<sup>2</sup>/g for En<sub>90</sub> is considered in the model. These values ~~give~~ results

429 comparable to field observations. Nevertheless, the effect of higher surface areas (~~and thus, higher~~  
430 ~~dissolution rates~~), is studied in ~~additional~~ sensitivity ~~analyses~~ ~~cases~~. - Mn- oxyhydroxides have not been  
431 considered.

432 The Ni content in the goethite ~~from of~~ Punta Gorda ranges from 0.8 to 4.0 wt.% Ni. In the model  
433 presented here, this Ni is sorbed onto the goethite surface. Assuming that when the Ni content is 4.0 wt.%  
434 all surface sites are occupied by Ni, the maximum sorption capacity of goethite can be calculated, being  
435 6.5 sites/nm<sup>2</sup> for a surface area of 65.2 m<sup>2</sup>/g. This value is consistent with the values proposed by Davis  
436 and Kent (1990) (2.6-16.8 sites/nm<sup>2</sup> for Fe oxyhydroxides), or Hayes and Leckie (3-11 sites/nm<sup>2</sup>).  
437 Information concerning the sorption of Ni onto goethite is scarce (Marcussen et al. 2009; Rajapaksha et  
438 al. 2012). Sorption of Ni onto the goethite surface is modeled following a one-site non electrostatic  
439 sorption model based ~~on in the model proposed in~~ Marcussen et al. (2009) (Table ~~65~~), where Ni sorbs onto  
440 goethite surface forming the surface complex >Fe\_ONi<sup>+</sup>. These authors used a log K for goethite surface  
441 protonation/deprotonation from Richter et al. (2005) but an update of these values (Richter and Brendler  
442 2008) is used in ~~this model~~ our study. The original log K values were provided for a density site of 2.31  
443 sites/nm<sup>2</sup> and they have been recalculated to account for the site density of Punta Gorda goethite  
444 according to eq. ~~740~~ (Richter et al. 2005), where K are the sorption equilibrium constants, Γ the site  
445 density (sites/nm<sup>2</sup>), and the subscript *o* stands for the new values calculated for 6.5 sites/nm<sup>2</sup>. Total  
446 sorption capacity of goethite is 0.0625 moles sites/moles goethite.

$$447 \log K_o = \log K + \frac{\Gamma}{\Gamma_o} \quad (740)$$

448

#### 449 **4-Results and discussion**

450 The modeling ~~result~~ ~~exercise~~ presented in this paper consists of a Reference case whose initial and  
451 boundary conditions have been detailed above and a set of Sensitivity ~~cas~~ analyses in which some  
452 parameters have been modified with respect to those of the Reference case, ~~in order to evaluate the effect~~  
453 ~~of their uncertainty in the results.~~

454

##### 455 **4.1-Reference case**

456 The residence time of water in the profile is 2.7 years. This residence time is very short compared to the  
457 total time of modeling (10<sup>6</sup> years) and indicates, as expected, that the influence of the initial porewater  
458 composition on the final results can be neglected.

459 Fig. 4 shows the evolution of the mineral composition (% wt), sorbed Ni concentration, and porosity as a  
460 function of depth at different elapsed times. When looking at Fig. 4 the reader must take into  
461 consideration ~~remember~~ that the weight percentage of a given mineral can increase either because of its  
462 precipitation or because of the dissolution of other minerals without precipitation.

463 ~~As explained previously and if~~ In order to simulate the effect of unsaturated flow, once the model run  
464 starts, porewater is equilibrated with atmospheric O<sub>2</sub>(g) and CO<sub>2</sub>(g) all along the profile. Due to ~~the~~  
465 ~~availability of O<sub>2</sub>(g)~~ equilibrium, ~~some immediate changes are observed in the initial mineral composition~~  
466 ~~of the profile.~~ Magnetite becomes unstable and is transformed into goethite, ~~some~~ serpentine II  
467 precipitates, and porosity decreases before 1000 years of elapsed time to values down to 5% (Fig. 4).  
468 Although this is realistic ~~to occur here~~, changes at the bottom of the weathering profile are clearly an  
469 artifact caused by the assumption of equilibrium with atmospheric O<sub>2</sub>(g) and CO<sub>2</sub>(g). Given the  
470 impossibility of fixing a realistic depth in which the system changes from unsaturated to saturated  
471 conditions, we have carried out the *Less\_carb* sensitivity case in which only the infiltrating rainwater (not  
472 along the profile) is in equilibrium with atmospheric O<sub>2</sub>(g) and CO<sub>2</sub>(g).

473 During the first 1000 years, two different reactions are observed to occur in the profile. Dissolution of En  
474 and Fo occurs ~~in~~ all along the profile, while precipitation of Srp I and Srp II occurs ~~in all~~ along the profile,  
475 except at the top. ~~As Srp I and Srp II react at equilibrium,~~ pH is buffered to 8.6 (Fig. 5) and Ni aqueous  
476 concentration is ~~very~~ low (<10<sup>-15</sup> mol/L). The main species occupying the goethite surface is >FeOH  
477 (>95%).

478 However, at the top of the profile, where rainwater is acidifying the system, Srp I dissolves together with  
479 Fo<sub>90</sub> and En<sub>90</sub> and the saprolite horizon begins to develop. Srp II and goethite precipitate removing Ni and  
480 Fe from solution. In fact, the amount of Srp II precipitating depends on the amount of Ni released from  
481 the dissolution of Fo<sub>90</sub> and Srp I. Fe released by En<sub>90</sub>, Fo<sub>90</sub> and Srp I that has not been incorporated into  
482 Srp II, precipitates as goethite. The presence of both Srp I and Srp II ~~still~~ buffers pH at a value of 8.6 and  
483 ~~causes~~ keeps Ni aqueous concentration remain at ~~to~~ very low values. Goethite surface speciation is  
484 dominated by >FeOH.

485 ~~Formation of Srp II occurs while either Srp I or Fo<sub>90</sub> dissolve as they are the primary minerals providing~~  
486 ~~Ni to the system.~~ Between 1000 and 10000 years of elapsed time, no significant changes are observed,  
487 except that, at the top of the profile, Srp I has been exhausted. As a consequence, porosity has  
488 significantly increased. However, as Fo<sub>90</sub> and En<sub>90</sub> are still in the system, they dissolve and Srp II and

489 goethite precipitate. Although in the model Fo<sub>90</sub> is the first silicate mineral to dissolve followed by En<sub>90</sub>,  
490 as observed by Freyssinet et al. (2005), Golightly (2010) and Hewawasam et al. (2013), their coexistence  
491 with Srp II and Gth without Srp I is not in agreement with the paragenesis observed in the field in which  
492 neither enstatite nor forsterite are in contact with Srp II. ~~As will be discussed later in the Rate sensitivity~~  
493 ~~case (in which En<sub>90</sub> and Fo<sub>90</sub> dissolve faster), one~~ One of the most uncertain parameters in reaction  
494 kinetics is the choice of reactive area, ~~which suggests. The results observed here let us think~~ that the  
495 reactive areas used in ~~this~~ Reference case could be too low. In any case, ~~it is worth to say that~~ this is a  
496 transitory effect that is not observed after 10<sup>6</sup> years of elapsed time.

497 ~~B~~Moreover, also between 1000 and 10000 years of elapsed time, a new horizon starts to develop in the  
498 model first node, in contact with the infiltrating rainwater. The precipitation of goethite has increased its  
499 sorption capacity and causes the dissolution of Srp II because Ni is preferentially sorbed onto the goethite  
500 surface (>FeONi<sup>+</sup>). pH decreases from 8.6 to a buffered value of 8.3, ~~where it remains buffered~~. Ni  
501 aqueous concentration is close to 10<sup>-8</sup> mol/L.

502 During the period 10<sup>4</sup> – 10<sup>5</sup> years, two significant observations can be made. On one hand, Fo<sub>90</sub> is  
503 exhausted ~~out the system~~, which means that the only processes controlling Ni concentration in solution  
504 are the formation of ~~Srp I or~~ Srp II and the sorption of Ni onto goethite surface. On the other hand, a new  
505 ~~horizon (oxide horizon)~~ is starting to form at the top of the profile because Srp II has been dissolve  
506 exhausted. pH is no longer buffered at 8.3. Enstatite is dissolving ~~and provides~~ yielding Fe that  
507 precipitates as goethite. As a consequence, the porosity increases up to 75%. The formation of >FeONi<sup>+</sup>  
508 displaces H<sup>+</sup> from the goethite surface (Table 65) and contributes to the decrease of pH together with the  
509 input of acidic water. Ni aqueous concentration is about 3×10<sup>-7</sup> mol/L.

510 At 10<sup>5</sup> years of elapsed time, the three main horizons of a typical laterite profile ~~can already be~~  
511 identified have formed (Fig. 4). At the top of the column, there is the goethite-dominated horizon; below  
512 10 m depth, Srp I is in equilibrium with Srp II and Gth at pH 8.6 in a partially weathered peridotite  
513 horizon, ~~and~~ and between both layers, there is a narrow horizon in which serpentine II is in equilibrium with  
514 a goethite with Ni sorbed, the ~~(saprolite horizon)~~ (Fig. 4).

515 From 10<sup>5</sup> years on, slight changes are ~~observ~~ predicted. The oxide and saprolite horizons develop and  
516 ~~displace~~ the interfaces are displaced towards greater depths. ~~It is worth to say that~~ at the top of the  
517 profile, ~~as~~ there is no more forsterite providing Ni to the system and the pH is acid, such that desorption  
518 of Ni ~~is promoted~~, increasing Ni aqueous concentration. At 4×10<sup>5</sup> years of elapsed time, enstatite is

519 exhausted and goethite becomes the only phase in this horizon. pH is 4.5 and porosity is ~~very~~ high, about  
520 91% (Fig. 4). Ni released from the goethite surface is sorbed downflow on the goethite in the saprolite  
521 horizon until its surface ~~is saturated~~s (at  $8 \times 10^5$  years of elapsed time). From this moment, saprolite  
522 horizon develops faster given that no more Ni can sorb onto goethite and it is available for serpentine  
523 precipitation.  
524 The model results obtained ~~in the model~~ agree with the laterite formation rates reported in literature. In  
525  $10^6$  y, the thickness of weathered laterite might be 10-20 m (Freyssinet et al. 2005), 29-58 m (Golightly  
526 2010) or 2-75 m (Hewawasam et al. 2013). Hewawasam et al. (2013) observed that in Sri Lanka laterites,  
527 weathering processes are occurring at the reaction front, and are displaced towards greater depths as  
528 minerals become ~~totally~~ weathered. According to Goodfellow et al. (2011) this is because weathering  
529 reactions are inhibited in those areas where porewater is saturated with respect to weathering products  
530 that is, far from the water table, and ~~by contin~~ contrastrary, weathering ~~processes are~~ is enhanced in the  
531 vadose zone. In agreement with those authors, in the model presented here, the reaction front starts at the  
532 top of the profile and is moving downward with time as weathering reactions ~~occur~~ progress.  
533 The model satisfactorily explains the formation of the three different horizons observed in the field in a  
534 period of time around  $10^6$  y. The first one, with a ~~thickness~~ width of 61 m, is ~~located~~ at the top of the  
535 profile and is composed of goethite. In this horizon, the porosity is ~~very~~ high (Fig. 4), porewater  
536 composition is ~~very~~ poor in Mg, Si, Fe and Ni, pH is around 4.5 and the goethite surface is saturated with  
537  $H^+$  (Fig. 6).  
538 The second horizon is formed by goethite and serpentine II. It has a thickness of 11 m with an average  
539 porosity of 40%, although it increases at the bottom. pH increases up to 8.3 and goethite contains up to 4  
540 wt.% Ni sorbed onto its surface. ~~>Fe-ONi<sup>+</sup> is the~~ The main surface species is >Fe-ONi<sup>+</sup>. (Fig. 6). In this  
541 saprolite horizon, the ratios between Mg/Si and  $CO_3/Mg$  in solution are 1.4 and 2.0 respectively, in  
542 agreement with the observations of Golightly (1981). pH values also agree with those reported for  
543 saprolite horizons (Golightly 1981, 2010; Pelletier 1996).  
544 Another similitude with field observations is the difference between the development of the limonitic and  
545 saprolite horizons. ~~The~~ is larger thickness of the limonitic horizon in relation to that of saprolite has been  
546 observed in areas with maximum lixiviation (Butt and Cluzel 2013~~)-~~), and unsaturated conditios, i.e.  
547 porewater in equilibrium with atmospheric as the one considered in the model, where despite assuming  
548 saturated conditions,  $O_2(g)$  and  $CO_2(g)$  are available throughout the column. Nevertheless, the goethite

549 horizon is significantly thicker (61 m) than the saprolite horizon (11 m), ~~but this is~~ due to the fact that  
550 ~~code capabilities as~~ the model does not take into account ~~for~~ the collapse of this horizon. In case of  
551 collapsing, the thickness of the goethite horizon will be smaller and similar to that observed in the Punta  
552 Gorda deposit ~~at Moa Bay area~~ (30m, Fig. 1).

553 The third and deepest horizon, with a depth limited by model dimensions, represents a partially weathered  
554 serpentinized peridotite, with serpentine I in equilibrium with serpentine II and goethite. pH is 8.6 and Ni  
555 is not sorbed onto goethite (Fig. 6). Porosity is ~~very~~ low, close to 5%.

556 After 10<sup>6</sup> y, 76% of Mg and 80% of Si have been leached from the profile, in agreement with  
557 observations reported in Golightly (1981) and Butt and Cluzel (2013) (RC in Fig. 7). A significant  
558 increase of Mg aqueous concentration is observed between the goethite and saprolite horizons. Fe and Ni  
559 are scarcely leached out of the system.

560 The model results suggest ~~obtained confirm~~ that sorption of Ni onto the goethite surface can explain the  
561 amount of Ni found in the goethite at Moa. In the model, however, sorption of Ni occurs only in the on  
562 goethite in contact with serpentine II. This distribution, in accordance with the observations of Dublet et  
563 al. (2015) of a regular decrease in bulk Ni content upwards in the profile and of Soler et al. (2008) in the  
564 goethite horizon of Loma de Hierro deposit, is directly linked to the evolution of pH. Sorption of Ni onto  
565 goethite depends on pH, and as can be seen in Fig. 6, when pH decreases below 7, sorption of Ni  
566 significantly decreases achieving values around 10% or less at pH 5 (Dublet et al. 2015). In natural  
567 conditions, however, goethite particles with Ni sorbed onto their surface might flocculate or form  
568 aggregates. For goethite, the point of zero charge (PZC) is between pH = 6.5 to 9.5 (Strauss et al. 1997;  
569 Gaboriaud and Ehrhardt, 2002). At the PZC, a dispersion of particles exhibits its maximum flocculation  
570 rate. In the profile, this range of pH is encountered in the saprolite, towards the limonitic horizon, where it  
571 might well favor the flocculation/aggregation of the goethite particles that could prevent desorption of Ni.

572 In the model, nesquehonite is always subsaturated (saturation indices below -2) while quartz presents  
573 saturation indices about 0.7 in the partially serpentinized peridotite horizon and close to 0.4 in the  
574 saprolite horizon.

575

#### 576 4.2 Sensitivity analyses

577 Different ~~sensitivity~~ cases have been investigate~~calculate~~ to evaluate the effect of the uncertainty of  
578 some key parameters on the model results. As ~~can be seen shown in in~~ Table Table 76, ~~where the~~

579 ~~differences between these sensitivity cases and the Reference case (RC) are highlighted,~~ sensitivity  
580 ~~analyses~~ explore the effect of not considering sorption of Ni onto goethite (*No\_ads* case), of using  
581 different chemical compositions for serpentine II (*Srp II\** and *Srp II<sup>s</sup>* cases), of considering faster  
582 dissolution rates of Fo<sub>90</sub> and En<sub>90</sub> (*Rate* case), of considering a smaller carbonate concentration  
583 (*Less\_carb* case), ~~and of or~~ allowing the precipitation of quartz (*Qt* case).

584 In the *No\_ads* sensitivity ~~case~~ analysis, the formation of surface species onto goethite is not considered.  
585 After 10<sup>6</sup> years of elapsed time, the same horizons developed as in the RC, with a goethite horizon with  
586 pH 4.5, a saprolite horizon with serpentine II and goethite at pH 8.3, and a partially weathered peridotite  
587 with serpentine I and II and goethite at pH 8.6, ~~are also obtained.~~ Mg and Si are also significantly  
588 leached (Fig. 7); but as ~~shown in~~ Fig. 8, the saprolite horizon is thicker than in the RC. This is due to  
589 the fact that, on one hand, all Ni is available to precipitate in *Srp II* whereas (in RC, sorption of Ni was  
590 dominant and *Srp II* formed once the goethite surface was saturated), and on the other, the pH of  
591 porewater is not affected by the (de)protonation of goethite. In the RC, pH was lower in the saprolite  
592 horizon because sorption of Ni displaced H<sup>+</sup> from the goethite surface, while in the *No\_ads* case, the pH  
593 in the saprolite horizon is maintained at 8.3, the same pH that is achieved in the RC when goethite  
594 becomes saturated in Ni (Fig. 9).

595 To account for the variability of compositions of *Srp II* observed in the field, two more chemical  
596 compositions ~~of *Srp II*~~ have been used in the sensitivity ~~cases~~ analyses *Srp II\** and *Srp II<sup>s</sup>* (Table 54).

597 These two *Srp II* have been chosen as they are the compositions having the lowest and the highest  
598 solubility constants, respectively. Results indicate that the same main processes are occurring ~~are the~~  
599 ~~same~~ as in the RC (Fig. 7, Fig. 9), but that the composition of *Srp II* ~~has effectively some effect~~ on the  
600 final distribution of the profile horizons (Fig. 8). On one hand, the thickness of the saprolite horizon,  
601 dominated by *Srp II*, decreases as the solubility of this mineral increases (*Srp II<sup>s</sup>* in Fig. 8). On the other  
602 hand, the amount of leached Ni is higher in the sensitivity case *Srp II\**, that is, the one considering the *Srp*  
603 *II* with the lowest ~~poorest in~~ Ni content (Table 54).

604 ~~In As already mentioned when discussing the RC results, in~~ the *Rate* case, the reactive areas of Fo<sub>90</sub> and  
605 En<sub>90</sub> are set equal to 0.1 m<sup>2</sup>/g to obtain dissolution rates of Fo<sub>90</sub> and En<sub>90</sub> that are 200 and 20 times faster,  
606 respectively, than in the RC. Results show that these faster dissolution rates increase the amounts of Si,  
607 Ni, Mg and Fe released, which also leads to increased goethite precipitation and Ni adsorption. Fo<sub>90</sub> and  
608 En<sub>90</sub> are completely consumed before (1000 and 1.5×10<sup>5</sup> years respectively), without further effects on

609 ~~and therefore, their control on~~ laterite formation, ~~finishes soon~~. After  $10^6$  years of elapsed time,  
610 differences with the RC are minor (Fig. 7-9).

611 In the sensitivity ~~ease~~ analysis *Less\_carb*, only the infiltrating rain water ~~at the inlet~~ is in equilibrium with  
612 atmospheric  $O_2(g)$  and  $CO_2(g)$ . ~~By doing this change, t~~The model reproduces a case in which the system  
613 is fully saturated (water table at the surface), limiting the input of  $O_2(g)$  and  $CO_2(g)$  to the system (Butt  
614 and Cluzel 2013). As ~~can be seen~~ shown in Fig. 8, the advancement of the weathering front after  $10^6$  years  
615 is ~~very~~ small compared to the RC. The main reason for such big difference is the availability of carbonate,  
616 which affects pH. In this sensitivity analysis ~~ease~~, the lack of dissolved  $CO_2(g)$  (~~a weak acid~~) does not  
617 buffer pH and, as a result of Srp I dissolution, pH goes up ~~very~~ quickly and the solution becomes  
618 saturated ~~s~~ with respect to primary minerals (Fig. 8). In the RC, where atmospheric  $CO_2(g)$  is always  
619 available in the column, dissolution of  $CO_2(g)$  provides enough acidity to buffer the increase in pH caused  
620 by silicate mineral dissolution. This observation agrees with Golightly (1981) that identified carbonate as  
621 one of the principal agents of weathering. When carbonate is not available, the solubility of serpentines is  
622 lower and the reaction front moves slowly. As a consequence, in  $10^6$  years of elapsed time, Mg and Si  
623 leaching is not as important as for equivalent to the other cases (Fig. 7) and pH is around 10 (Fig. 9). The  
624 *Less\_carb* and RC results suggest that the aqueous carbonate concentration is, in fact, an important key  
625 parameter controlling the rate of laterite formation. Any phenomena preventing  $CO_2(g)$  equilibration with  
626 porewater would lessen laterite profile development.

627 As reported previously in the RC, saturation indices of quartz indicated a slight oversaturation, especially  
628 along the saprolite and peridotite horizons. In the *Qt* sensitivity ~~ease~~ analysis, quartz is allowed to  
629 precipitate ~~in case it oversaturates~~ according to local equilibrium. Results show that quartz precipitation is  
630 significant because Si is preferentially retained as quartz rather than being incorporated in Srp II and,  
631 consequently, the weathering front is advancing faster. After  $10^6$  years of elapsed time, the profile  
632 presents two different horizons (Fig. 8). The first 11.5 m are of goethite, with a porosity of 91% and a pH  
633 of 4.5; and the other 75 m are composed of 43% (in vol.) of quartz and 9% (in vol.) of goethite with a  
634 porosity of 48% and a pH of 6 (Fig. 9). All Mg and nearly 40% of Ni have been leached from the system,  
635 while leaching of Si is reduced to 15% (Fig. 7). ~~Microcrystalline quartz in laterite profiles has been~~  
636 reported in some profiles (e.g. Golightly 1981; Tauler et al. 2009; Villanova-de-Benavent et al. 2014) and  
637 observed ~~to occur in some~~ cases with small lixiviation rates (Butt and Cluzel 2013), but it does not form  
638 in those cases where weathering rate is fast (Golightly 2010). In the RC, quartz saturation indicates ~~s~~ its

639 possible precipitation but the results obtained when quartz is allowed to precipitate are not consistent with  
640 field observations. An explanation to this might be found in the value of the saturation indices calculated  
641 for quartz, that were not higher than 0.76. These small saturation indices might not be enough to  
642 ~~overcome a kinetic barrier for~~allow the precipitation of quartz. Instead of the precipitation of quartz under  
643 local equilibrium, the precipitation of ~~an more~~ amorphous phase such as SiO<sub>2</sub>(am), or a kinetically  
644 ~~controlled-limited~~ precipitation of quartz should have been -considered.

645

## 646 ~~5.~~ Conclusions

647 This paper presents a reactive transport model of the formation of the Punta Gorda Ni--laterite deposit of  
648 Moa mining district (northeast of Cuba). The model is based on the ~~direct formation~~ conceptual model  
649 ~~described in of~~ Butt and Cluzel (2013), according to which laterite deposits form due to a continuous  
650 weathering of a partially serpentinized peridotite under tropical climate. Numerical model considers a 1D  
651 column of 88 m length initially composed of Fo<sub>90</sub>, En<sub>90</sub>, Srp I and Mag. Due to the interaction with  
652 rainwater, these primary minerals dissolve, and a Fe(III) and Ni bearing serpentine (Srp II) and goethite  
653 ~~are left to~~precipitate. Ni is allowed to sorb onto goethite. ~~Models are run for 10<sup>6</sup> y.~~

654 Although some of the assumptions made in the numerical model are ~~a~~ simplifications of the real system,  
655 results of the model ~~are consistent with validate~~ the conceptual model about the formation of oxide type  
656 Ni-laterite ~~this kind of~~ deposits:

- 657 • After 10<sup>6</sup> years of elapsed time, simulations reproduce the three main horizons observed in the  
658 field: a) a thick limonite horizon, ~~placed~~ at the top of the profile, composed of goethite, b) a  
659 narrow saprolite horizon, in the middle, composed of Srp II and Gth, and c) a partially weathered  
660 serpentinized peridotite horizon, at the bottom, in which ~~Srpserpentine I, serpentineSrp II and~~  
661 ~~goethiteGth~~ coexist.
- 662 • Simulations show the increase of porosity from values close to 5% at the bottom to values close to  
663 90% at the top of the profile, due to the dissolution of silicate minerals (~~collapse of limonite~~  
664 ~~horizon is not simulated~~) and the pH increase from 4.5 at the top (rainwater pH) to values close to  
665 8.6 at the bottom, being 8.3 at the saprolite horizon.
- 666 • Sorption of Ni onto goethite can explain the field observations. Ni sorption onto goethite is linked  
667 to pH ~~profile~~, showing its maximum ~~in the -at~~ saprolite horizon ~~profile~~, as observed in the field.  
668 Sorption onto goethite in the limonite horizon decreases because of the acidic pH, which displaces

669 Ni<sup>2+</sup> from the surface sites. In the serpentinized peridotite horizon, sorption is negligible because  
670 Ni is preferentially ~~retained~~ located in Srp I.

671 • During the laterization process, Mg and Si are leached out the system, while Fe and Ni are  
672 conserved.

673 This simulation exercise has been useful not only to identify but also, to quantify, the effect that some  
674 variables can have on the formation of laterites:

675 • The saprolite reaction front does not advance while there is Srp I in the system.  
676 • Protonation/desprotonation of goethite surface exerts a significant control on porewater pH as it  
677 increases acidic pH of entering rainwater but also decreases pH of saprolite horizon porewater to  
678 values below 8.3, preventing the development of saprolite horizon. Nevertheless, this control  
679 finishes when goethite surface sites saturate.

680 • Aqueous carbonate concentration is an important key parameter as it controls the rate of  
681 laterization process, ~~being faster as higher the concentration is~~ with laterization increasing with  
682 carbonate concentration. This is due to carbonic acid buffering capacity, which buffers the increase  
683 of pH due to silicate dissolution.

684 • Forsterite is the main mineral providing Ni to the system. The dissolution rate ~~at which it dissolves~~  
685 ~~but also of Fo and the rate of En enstatite dissolution~~ affects the thicknesses of the different  
686 horizons.

687 • Serpentine II composition influences the development of laterite profile, from two perspectives: ~~a~~  
688 serpentine II poor in Ni causes an increase of the % of Ni leached after 10<sup>6</sup> years of elapsed time  
689 and since composition determines the solubility constant of serpentine, the more soluble the  
690 serpentine is, the narrower the saprolite horizon is. In any case, its effect is minor and must be  
691 further evaluated.

692 • Precipitation of quartz significantly enhances the formation of the limonitic horizon and inhibits  
693 the formation of the saprolite horizon. The inclusion of quartz or even an amorphous silica phase  
694 must be ~~further~~ evaluated in more details.

695 Results of this ~~study paper~~ provide new valuable insights to the understanding of the differences between  
696 Ni-laterite deposit types and show the capabilities of reactive transport simulations to test and validate  
697 conceptual models.

698 ~~Nevertheless,~~ The model ~~could an still~~ be improved by increasing either the complexity of the  
699 geochemical system (more minerals, solid solutions, incorporation of Ni into goethite structure,-...) or the  
700 physical system (2D or 3D, matrix diffusion to simulate corestones structures, mineral heterogeneity...  
701 Finally, investigations on the PZC of goethite under the hydrochemical conditions of the Moa profile  
702 would account for flocculation of particles that may preserve Ni all along the goethite horizon.

703

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709

#### 710 **Conflict of interest**

711 The authors declare that they have not conflict of interest.

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929 **Figure captions**

930 **Fig.1** Location and simplified geological map of the Moa Bay mining area (Cuba) showing the location of  
931 the Punta Gorda Ni-laterite deposit. Modified from Marchesi et al. (2006).

932 **Fig. 2** Schematic representation of the studied profile of the Punta Gorda Ni-laterite deposit (a) and  
933 mineral composition of the analyzed samples (b). Mineral abbreviations taken from Whitney and Evans  
934 (2010) (Fo: forsterite, En: enstatite, Srp: serpentine, Mgh: maghemite, Gth: goethite, Hem: hematite, Gib:  
935 gibbsite, Qz: quartz), except pyrochroite (Prc). Modified from Galí et al. (2007).

936 **Fig. 3** ~~Powder X-Ray~~ diffraction diagram profile of sample M4 from Punta Gorda. ~~In blue: the measured~~  
937 ~~profile; in red: the total calculated profile; in purple: the calculated profile for goethite; in grey: the~~  
938 ~~difference profile between observed and calculated profiles.~~ Agreement index  $R_{wp} = 10.31$ . Triangles at  
939 bottom are the position of the reflections used for calculating  $D_{hkl}$  values from measured  $2\theta$  and  $FWHM_{hkl}$   
940 values.

941 **Fig. 4** Evolution of the amount of mineral (in wt.%) (areas) and of the amount of Ni sorbed onto goethite  
942 (in wt.% of Ni in goethite) (solid line) and porosity in the profile at initial time (0 y) and at different  
943 model elapsed times (from  $10^3$  to  $10^6$  years) for the Reference case.

944 **Fig. 5.** pH distribution at the profile at different time steps ~~Evolution of pH in the profile at different~~  
945 ~~model elapsed times~~ for the Reference case.

946 **Fig. 6** Distribution of Mg, Si, Fe and Ni aqueous concentration (a), goethite surface species (b), and pH  
947 (c) along the modeled profile after 1My of elapsed time.

948 **Fig. 7** Amount of Mg, Si and Ni (in wt.%) leached out from the modelled profile after  $10^6$  years of  
949 elapsed time for the RC (Reference case) and the different sensitivity eases analyses reported: *No\_ads\_*  
950 *ease* (without considering sorption of Ni onto goethite), *Srp II\** and *Srp II<sup>s</sup>\_eases* (considering different  
951 serpentine compositions, see Table 54), *Rate\_e* (considering faster dissolution rates of enstatite and  
952 forsterite), *Less\_carb\_e* (considering a smaller concentration of carbonate) and *Qt\_e* (allowing  
953 quartz precipitation).

954 **Fig. 8** Distribution of the horizons along the modelled profile after  $10^6$  years of elapsed time for the RC  
955 (reference-Reference case) and the different sensitivity analyses easing reported (same abbreviations from  
956 than in-Fig.7).

957 **Fig. 9** Evolution of pH along the modelled profile after  $10^6$  years of elapsed time for the Reference case  
958 and the different sensitivity analyses easing reported (same abbreviations from than in-Fig.7).



960

961 **Table captions**

962 ~~Table 1 Structural formulae of serpentine II, calculated on the basis of 7 oxygens from electron~~  
963 ~~microprobe analyses (EMPA) of 8 individual samples.~~

964 **Table 2-1** pH, Eh (in V) and total concentration of components of rainwater and initial porewater (in  
965 mol/L). Mineral abbreviations ~~taken~~ from Whitney and Evans (2010)

966 **Table 3-2** Initial mineral composition considered in the model.

967 **Table 4-3** Solubility constants at 25°C of the pure end-member phases used to calculate solubility  
968 constants of solid solutions used in the simulations. Mineral abbreviations ~~taken~~ from Whitney and Evans  
969 (2010).

970 **Table 5-4** Solubility constants at 25°C calculated for the solid solutions used in the simulations.

971 <sup>\*s</sup>serpentine II used in the sensitivity cases. Mineral abbreviations ~~taken~~ from Whitney and Evans  
972 (2010).

973 **Table 6-5** Equilibrium constants for goethite surface reactions used in the calculations.

974 **Table 7-6** Summary of the main differences between the Reference ~~ec~~ase and the sensitivity  
975 ~~analyses, cases of the modelling exercise.~~

976

# 1        Reactive transport model of the formation of oxide type 2        Ni-laterite profiles (Punta Gorda, Moa Bay, Cuba)

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12

13        ABSTRACT

14        Oxide type Ni-laterite deposits are characterized by a dominant limonite zone with goethite as the  
15        economically most important Ni ore mineral, and a thin zone of hydrous Mg silicate-rich saprolite  
16        beneath the magnesium discontinuity. Fe, less soluble, is mainly retained forming goethite, while Ni is  
17        redeposited at greater depth in a Fe(III) and Ni rich serpentine (serpentine II) or in goethite, where it  
18        adsorbs or substitutes for Fe in the mineral structure.

19        Here, a 1D reactive transport model, using Crunchflow, of Punta Gorda oxide type Ni-laterite deposit  
20        (Moa Bay, Cuba) formation is presented. The model reproduces the formation of the different laterite  
21        horizons in the profile from an initial, partially serpentinized peridotite, in 10<sup>6</sup> years, validating the  
22        conceptual model of the formation of this kind of deposits in which a narrow saprolite horizon rich in Ni-  
23        bearing serpentine is formed above peridotite parent rock and a thick limonite horizon is formed over  
24        saprolite. Results also confirm that sorption of Ni onto goethite can explain the weight percent of Ni  
25        found in the Moa goethite.

26        Sensitivity analyses accounting for the effect of key parameters (composition, dissolution rate, carbonate  
27        concentration, quartz precipitation) on the model results are also presented. It is found that aqueous  
28        carbonate concentration and quartz precipitation significantly affects the laterization process rate, while  
29        the effect of the composition of secondary serpentine or of mineral dissolution rates is minor. The results

30 of this reactive transport modeling have proven useful to validate the conceptual models derived from  
31 field observations.

32

33 **KEYWORDS,**

34 Oxide type Ni-laterites, Reactive Transport Modeling, Sorption, Goethite, Cuba

35

36

## 37 **Introduction**

38 Nickel laterite deposits are an important source of nickel and cobalt (Golightly 1981, 2010; Freyssinet et  
39 al. 2005, Lambiv Dzemua et al. 2013) and have potential for Sc and platinum group element by-products  
40 (Aiglsperger et al. 2016). Ni-laterite deposits formed from the chemical and mechanical weathering of  
41 ultramafic rocks exposed to the surface under favorable topography and climatic conditions. Laterite  
42 formation is controlled by intrinsic or extrinsic factors (Freyssinet et al. 2005, Moore et al. 2012, Butt and  
43 Cluzel 2013). Intrinsic factors include, among others, the chemical and mineralogical composition of  
44 protolith (mainly peridotite), the dissolution rate of minerals and the surface area. The geological context  
45 where laterite develop, the hydrological properties of the terrain (controlling water flow), the climate  
46 (temperature and rainfall) and the duration of the weathering process are examples of extrinsic factors that  
47 may condition laterite formation.

48 According to Golightly (1981, 2010) a typical Ni-laterite profile consists, from bottom to top of: a)  
49 partially or totally serpentinized ultramafic rock (protolith) characterized by unweathered minerals; b)  
50 saprolite horizon with textural features inherited from the protolith and dominated by secondary Si- and  
51 Mg- minerals; and c) limonitic horizon composed mainly of goethite that evolves to hematite with time.  
52 The interaction of slightly acidic meteoric water with the ultramafic bedrock causes the release of Mg, Si  
53 and Ni, which are transported downwards. In particular, Ni, less soluble, is redeposited at depth  
54 producing Ni-enriched zones. In the saprolite zone, Ni is mainly found in garnierite and/or secondary Ni-  
55 rich lizardite (serpentine II) and Ni-smectite (Pelletier 1996, Wells et al. 2009, Villanova-de-Benavent et  
56 al. 2014). In the limonitic horizon, Ni is mainly retained by goethite, either adsorbed or substituting Fe in  
57 the mineral structure, and by minor Mn- oxyhydroxides (Roqué-Rosell et al. 2010; Dublet et al. 2015).

58 Ni-laterites are usually classified according to their dominant Ni-bearing mineralogy in a) hydrous silicate  
59 type, b) clay type and c) oxide type (Brand et al. 1998; Freyssinet et al. 2005). Oxide type deposits,  
60 discussed in this contribution, are characterized by a dominant limonite horizon with goethite as the  
61 economically most important Ni ore mineral. These deposits represent about 60% of the current total Ni  
62 laterite resources, with mean grades ranging from 1.0 to 1.6 wt% Ni (Butt and Cluzel 2013).

63 Ni-laterites formed, or are currently forming (Butt and Cluzel 2013), under humid tropical climate, where  
64 rainfall is higher than 1000 mm/y and temperature ranges between 15-31 °C (Freyssinet et al. 2005;  
65 Thorne et al. 2012). The mechanisms controlling the retention of Ni in goethite determine the mobility of

66 the metal and the supergene enrichment of the Ni-bearing phases in the laterite horizons (Roqué-Rosell et  
67 al. 2010; Dublet et al. 2012). However, the mechanisms controlling Ni mobility remain partly understood.  
68 The Ni-goethite association has been explained either by sorption of Ni onto the goethite surface (Cornell  
69 1991; Rose and Bianchi-Mosquera 1993; Bryce et al. 1994; Coughlin and Stone 1995; Beukes et al. 2000;  
70 Trivedi and Axe 2001; Trivedi et al. 2001; Buerge-Weirich et al. 2002; Fisher et al. 2007; Arai 2008;  
71 Marcussen et al. 2009) or by the incorporation of Ni into the goethite structure or both (Manceau et al.  
72 2000; Singh et al. 2002; Carvalho-e-Silva et al. 2002, 2003; Fan and Gerson 2011; Dublet et al. 2012).  
73 Sorption of Ni on goethite has been studied both in natural and synthetic goethite by means of sorption  
74 experiments and spectroscopic techniques. Ni sorbs onto goethite forming inner-sphere mononuclear  
75 bidentate complexes (Trivedi et al. 2001; Xu et al. 2007), and sorption increases from pH 5 to 8 (Rose  
76 and Bianchi-Mosquera 1993; Beukes et al. 2000; Buerge-Weirich et al. 2002; Arai 2008). Sorption of Ni  
77 onto goethite has been modelled by considering Langmuir isotherms (Trivedi et al. 2001), a Diffuse Layer  
78 Model (Bryce et al. 1994; Buerge-Weirich et al. 2002; Marcussen et al. 2009; Rajapaksha et al. 2012) or a  
79 Triple Layer Model (Coughlin and Stone 1995).

80 The incorporation of Ni in the goethite structure is facilitated by the similar ionic radii between  $\text{Fe}^{3+}$   
81 ( $0.64\text{\AA}$ ) and  $\text{Ni}^{2+}$  ( $0.69\text{\AA}$ ). However, even this small difference changes cell parameters, and together with  
82 the difference in charge between both cations, limits the maximum amount of Ni in goethite (Dublet et al.  
83 2015). According to Cornell (1991), 15% of sites occupied by Fe in goethite can be substituted by other  
84 cations without destabilizing the goethite structure. Manceau et al. (2000) studied natural goethite by  
85 extended X-Ray Absorption Fine Structure (EXAFS) and showed that Ni was partially incorporated in the  
86 goethite structure. Singh et al. (2002) demonstrated up to 5 mol % isomorphic substitution of  $\text{Ni}^{2+}$  in the  
87  $\text{FeOOH}$  structure which was limited by changes in the next-nearest-neighbour coordination environment.  
88 Differential thermal (DTA), thermal gravimetric (TGA) and EXAFS analyses of natural lateritic goethite  
89 (1.8-4.1 mol% Ni) by Carvalho-e-Silva et al. (2002, 2003) suggested that the charge imbalance could be  
90 compensated by the incorporation of  $\text{H}^+$  into the goethite structure. Fan and Gerson (2011) indicated that  
91 Ni associated with goethite in Philippine laterite was substituting Fe within its structure. Dublet et al.  
92 (2012) and Cathelineau et al. (2016) studied the speciation of Ni in a New Caledonian laterite profile and  
93 observed Ni-goethite as the predominant Ni-bearer.

94 Bryce et al. (1994) considered that although sorption should be reversible, because of aging or hysteresis  
95 Ni might not be completely released from goethite surface. Dublet et al. (2015) stated that the

96 incorporation of Ni in goethite may be affected by the sequence of dissolution-precipitation reactions  
97 forming goethite. Therefore, in spite of evidence of both sorption of Ni on the goethite surface and its  
98 incorporation in the structure, there is still a lack of understanding of these processes.

99 In order to test the validity of conceptual models derived from field and/or experimental observations,  
100 reactive transport and geochemical modeling has proven successful (Soler and Lasaga 1998; Corbella et  
101 al. 2004). There are several computer codes available to perform reactive transport or geochemical  
102 calculations (Steeffel et al. 2015), although none of them can consider all hydro-geochemical processes  
103 simultaneously.

104 Soler and Lasaga (1996, 1998) developed one dimensional models of bauxite (Al-laterite) formation,  
105 describing the alteration of a granitic protolith and the formation of the bauxite and saprolite horizons  
106 over long time scales ( $10^6$  years) using mineral reaction kinetics. Fletcher et al. (2006) performed a  
107 simple two-mineral model to study how weathering can transform intact bedrock into saprolite. The  
108 model coupled physical processes (e.g. fracturing) to chemical processes (e.g. mineral dissolution) and  
109 the rate of displacement of the reaction front was shown to depend on the composition of the reactant  
110 fluid where  $O_2$  and  $CO_2$  are the most critical components in the case of a Puerto Rico quartz diorite  
111 regolith. Lebedeva et al. (2007) incorporated saprolite-forming reactions and developed a four-mineral  
112 model to predict rates of formation of saprolite, whereas Fletcher and Brantley (2010) developed a  
113 simplified one dimensional model to study a weathering profile, including vertical fluid transport, kinetic  
114 reaction and erosion.

115 Navarre-Sitchler et al. (2011) used the reactive coupled transport code CrunchFlow to simulate the  
116 chemical and physical transformations during weathering of a basaltic rock and compared their results  
117 with field observations of alluvial terraces in Costa Rica, where erosion was not significant. They used a  
118 1D model of a total length of 100 mm and observed that for porosities higher than 9%, mineral reaction  
119 kinetics dominated over transport, and that the advance of the weathering front was controlled by the rate  
120 at which porosity was created.

121 Moore et al. (2012) modeled the dissolution of minerals in a granitic soil and in a granitic saprolite with  
122 the reactive transport model FLOTRAN. The modeled reaction front depth was highly dependent on the  
123 precipitation rate of secondary minerals and on fluid flow. Moreover, they had to use reduced reaction  
124 rates, compared with rates from laboratory studies, to fit the field observations. They concluded that

125 reactive transport models can be used to understand the long-lived ( $10^6$  years) mineral weathering  
126 processes given that they consider the simultaneous non-linear processes.

127 In this study, a reactive transport model is used to simulate the formation of the oxide type Punta Gorda  
128 Ni-laterite deposit from an initial partially serpentinized peridotite at constant temperature ( $25^\circ\text{C}$ ). The  
129 Punta Gorda deposit is part of the Moa Bay mining area, one of the largest reserves of nickel and cobalt in  
130 the world (Linchenat and Shirakova 1964; Lavaut 1998; Lewis et al. 2006; Proenza et al. 2007;  
131 Aiglsperger et al. 2016), and probably the best known example of Ni-laterite deposits of oxide type  
132 (Gleeson et al. 2003).

133 The main objective of this contribution is to test a conceptual model for the formation of oxide type Ni-  
134 laterite deposits and to identify and quantify, the key parameters affecting the development of the  
135 different laterite horizons. Moreover, by considering that Ni is sorbed onto goethite, we aim to determine  
136 whether this process could account for the amount of Ni found in the goethite at Punta Gorda.

137 In this paper, we present a modeling exercise that provides valuable insights into the understanding of the  
138 formation of Ni-laterite deposits. The modeling consists of a set of one dimensional models in which rain  
139 water infiltrates and flows vertically downwards simulating the infiltration through fractures and cracks.  
140 Formation of the goethite and saprolite horizons is achieved by dissolution of primary minerals and  
141 precipitation of secondary minerals. No solid solutions have been included for simplicity. Porosity  
142 changes reflecting different molar volumes of dissolving/precipitating minerals are taken into account.  
143 Due to fact that the model is one dimensional, it does not account for the formation of typical saprolite  
144 corestones as lateral water flow and matrix diffusion processes are not considered. Water is allowed to  
145 equilibrate with air along the whole domain, simulating unsaturated conditions. Calculations have been  
146 carried out for a time span of  $10^6$  years. Past climatic changes, such as variations in precipitation regime,  
147 erosion, or collapse due to increase in porosity in the upper part of laterite profile are not considered.

148 The 1D models described here differ in values for several parameters that preliminary work had identified  
149 as having a significant role in the formation of laterite profiles, such as solubility constants, dissolution  
150 rates,  $\text{CO}_2(\text{g})$ , precipitation of quartz. A Reference case model is explained in detail whereas the results of  
151 the other models are compared to the results of the Reference case.

152

153 **The Punta Gorda Ni-laterite deposit**

154 The Punta Gorda Ni-Co laterite deposit is located in the Moa Bay mining area (northeast of Cuba; Fig.1).  
155 The Moa Bay laterite deposits are part of a larger province of nickel laterite in northeast Cuba. The  
156 deposits developed over serpentized harzburgite of Moa-Baracoa ophiolitic massif (Proenza et al. 1999;  
157 Marchesi et al. 2006) with weathering and laterization commencing during the Miocene (Lewis et al.  
158 2006; Proenza et al. 2007). The elevation of the peneplain surface of the deposits varies from 60 to 950 m  
159 above sea level, and the weathering mantle can reach a total thickness of more than 50 m in the laterite  
160 profile (Linchenat and Shirakova 1964; Golightly et al., 2008b).

161 This deposit can be classified as oxide type (Oliveira et al. 2001; Rojas-Purón et al. 2012; Aiglsperger et  
162 al. 2016). As with many northeastern Cuban deposits, the typical vertical section consists of four principal  
163 horizons, from bottom to top: (1) parent rock serpentized peridotite, (2) saprolite, (3) lower and upper  
164 limonite and (4) ferricrete or duricrust (Lewis et al. 2006; Proenza et al. 2007; Aiglsperger et al. 2016;  
165 Fig. 2a). Occasionally, within a profile some gabbro bodies weather to bauxite. Ni and Co are mainly in  
166 the limonite zone but the siting of metals (adsorbed or in solid solution) remains debated.

167 The Punta Gorda deposit has been extensively studied (Oliveira et al. 2001; Galí et al. 2007; Roqué-  
168 Rosell et al. 2010; Rojas-Purón et al. 2012; Aiglsperger et al. 2016). The mineralogy was characterized  
169 by qualitative and quantitative X-Ray diffraction, optical and scanning electron microscopy (SEM) and  
170 electron probe microanalysis (EPMA; Galí et al. 2007). Concentrations of major and minor elements as  
171 well as trace elements in parent rocks and weathering products of Ni-laterite profiles were measured by  
172 Aiglsperger et al. (2016).

173 The mineralogical composition of the studied profile in Punta Gorda is shown in Fig. 2b. The main  
174 minerals of the parent serpentized peridotite are forsterite, enstatite, serpentine and maghemite (Sample  
175 M10). The saprolite horizon is dominated by serpentine and goethite (Sample M9), whereas in limonite  
176 and ferricrete horizons, goethite and hematite are the main minerals, although other minor phases such as  
177 pyrochroite, gibbsite, quartz, Mn-oxyhydroxide aggregate (lithiophorite, “lithiophorite–asbolane  
178 intermediates”) and asbolane (Roqué-Rosell et al. 2010) are also found (samples M8 to M1).

179 The parent rock from which the Ni-laterite profile in the Moa district originated consists of partially  
180 serpentized ophiolitic harzburgite (70%  $Mg_9Fe_{0.95}Ni_{0.05}Si_5O_{20}$ , 16%  $Mg_9FeSi_{10}O_{30}$ ) including  
181 plagioclase-rich bodies, which was exposed to the surface during the late Miocene ( $\approx 10^7$  years; Lewis et  
182 al. 2006). Serpentine minerals are polymorphs 1T and 2H1 lizardite. Lizardite 1T is the dominant polymorph  
183 whereas lizardite 2H1 is less crystalline and presents many stacking faults in its structure. The cell

184 volume is slightly larger than that corresponding to the ideal end member  $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$ , due to  
185 substitution of Mg by Fe and minor Ni and Mn, as confirmed by chemical analyses. Two different types  
186 of serpentine have been identified. Serpentine I formed by alteration of forsterite and enstatite during a  
187 hydrothermal stage, whereas serpentine II formed after weathering of serpentine I. Serpentine II can be  
188 formed as a thermodynamically stable secondary phase in meteoric conditions, as shown in Villanova-de-  
189 Benavent et al. (2016a). Serpentine I composition, calculated from EPMA data is  
190  $\text{Mg}_{2.85}\text{Fe}_{0.14}\text{Ni}_{0.01}\text{Si}_2\text{O}_5(\text{OH})_4$ . In serpentine II, Mg in octahedral coordination is partially substituted by  
191  $\text{Fe}^{3+}$  and  $\text{Ni}^{2+}$ . Serpentine II structural formulae calculated from EPMA are shown in Online resource 1.  
192 Serpentine II contains more Ni than serpentine I. The Ni-bearing serpentine (Srp-II), in addition to  
193 “garnierite”, is the main Ni ore in saprolite horizon of Ni-laterite deposits (Golightly and Arancibia 1979;  
194 Pelletier 1996; Villanova-de-Benavent et al. 2014, 2016b). In the case of Punta Gorda deposit, this second  
195 generation of serpentine is the major Ni-bearing silicate phase in the saprolite horizon. Nickel content in  
196 Ni-rich serpentine ranges from 1 to 7 wt.% NiO, in contrast with serpentine I, which has the same Ni  
197 content than the olivine (~ 0.4 wt.%).

198 Iron oxides are maghemite, goethite and hematite. The refined cell parameter of maghemite, very similar  
199 to the accepted value of 8.3505 Å, indicates a composition near the ideal  $\text{Fe}_2\text{O}_3$  (Galí et al. 2007). In near  
200 surface conditions, maghemite can form by oxidation of magnetite (Gehring et al. 2009, Lilova et al.  
201 2012) that in turn, results from the hydration of primary olivine and pyroxene. Under atmospheric  
202 conditions, maghemite is transformed into goethite. Hematite ( $\text{Fe}_2\text{O}_3$ ) has almost an ideal composition  
203 and structure, although it has a low crystallite size (30 to 40 nm; Galí et al 2007). Goethite ( $\text{FeOOH}$ ), the  
204 major phase containing most of the Ni in this profile (from 0.8 to 4 wt.% with an average value of 1.23  
205 wt.%), coexists with maghemite and hematite in limonite samples and with lizardite in samples M8 and  
206 M9 (Galí et al. 2007). Crystallographic studies indicate that there is some substitution (2-17%) of Fe by  
207 Al as the cell volume is always smaller than the accepted value for goethite. The analysis of different  
208 diffraction peaks of goethite using the Scherrer’s relation (Klug and Alexander 1962; Langford 1978; De  
209 Keijsers et al. 1982; Louër et al. 1983) and using values for the 110, 020, 120 and 130 peaks in the space  
210 group  $P_{bnm}$  ( $a=4.605$  Å,  $b=9.96$  Å and  $c=3.02$  Å; Fig. 3), and a value of  $\lambda[\text{K}\alpha 1, \text{Cu}]$  of 1.5406 Å, yields an  
211 ideal mean elongated prism in the **c** direction, with 8.7 nm in the **a** direction and 18.1 nm in **b** direction.  
212 The length in **c** could not be determined, but observations have shown that the **c/b** aspect ratio is not less  
213 than 4.5 (Strauss et al. 1997). With these data, the calculated specific surface for goethite is 84.8 m<sup>2</sup>/g. If,

214 instead of adjusting a prismatic shape, an elliptical cylinder elongated in the *c* direction is fitted, a specific  
215 surface of 87.2 m<sup>2</sup>/g is obtained, which is similar to the previous value.

216 The specific surface obtained by the BET (Brunauer-Emmet-Teller) method (Brunauer et al. 1938) for the  
217 same material is 65.2 m<sup>2</sup>/g. As expected, the BET value is lower than the value calculated through X-Ray  
218 diffraction which reflects the dimension of the coherent diffracting domains, rather than the dimension of  
219 the material particle that consists of an aggregate of several domains.

220

## 221 **Materials and methods**

222 The reactive transport model presented in this work is based on the direct formation conceptual model  
223 described in Butt and Cluzel (2013). According to this model, oxide type Ni-laterite deposits form as a  
224 result of continuous weathering of partially serpentinized peridotite under tropical climate. During  
225 weathering, the water table is high and fluctuating, and erosion rates are low. The system is fully  
226 saturated. Meteoric water, in equilibrium with atmospheric O<sub>2</sub> and CO<sub>2</sub>, flows through the profile at a  
227 constant rate. Therefore, Ni is expected to be released from olivine or serpentine I and retained by the  
228 formation of a Fe(III)-rich serpentine II and by sorption onto goethite, while Mg and Si are expected to be  
229 leached out of the system (Ulrich et al. 2014, Villanova-de-Benavent et al. 2016a) because of serpentine  
230 and silicate dissolution. Dissolution can cause an increase in porosity that may accelerate the processes  
231 due to the decreased solid/water ratio.

232 According to Butt and Cluzel (2013), Ni may be leached from goethite to garnierite deeper in the profile,  
233 and goethite may transform to hematite, particularly in the upper most limonite horizon. Neither the  
234 formation of garnierite, nor the formation of hematite, is considered in this model.

235 Temperature is considered constant at 25 °C. According to Thorne et al. (2012), Ni-laterite forms in  
236 tropical areas where monthly temperatures are in the range of 22-31 °C in the summer and between 15-27  
237 °C in the winter.

238 The partially serpentinized unweathered peridotite is composed of Ni-bearing forsterite, enstatite and  
239 serpentine I. In our model, maghemite is not considered given its low stability. Its precursor, magnetite is  
240 considered instead (Gehring et al. 2009). Serpentine I and magnetite formed during a previous  
241 hydrothermal serpentinization event (pre-weathering), that is outside the scope of this study.

242

243 Chemistry solver, modeled domain and hydrodynamic system

244 The computer code used for the simulations is Crunchflow, a software package for simulating reactive  
 245 transport developed by Steefel and co-workers (Steefel and Lasaga 1994; Steefel 2009). This code can  
 246 take into account aqueous speciation, surface complexation, ion exchange, mineral  
 247 dissolution/precipitation and transport processes under fully saturated flow conditions and variable  
 248 temperature (Steefel et al. 2015). All mineral transformations are treated as dissolution and precipitation  
 249 reactions. Kinetic reaction rates, depending on reactive surface area, are used to describe these reactions.  
 250 Transformations in the solid state (without dissolution/precipitation) are not considered. However, if  
 251 reaction rates are fast compared to solute transport by advection, dispersion or diffusion, when the  
 252 dissolution of a mineral can cause supersaturation of the solution with respect to another phase, this new  
 253 phase will precipitate at the same location as that of the dissolving mineral, causing an effect similar to a  
 254 potential solid-state transformation. The code uses an integrated finite difference discretization to solve  
 255 the advection-dispersion-reaction differential equations that link flow, solute transport and geochemical  
 256 processes. Total porosity ( $\phi_T$ ) is updated after each time step according to eq. 1, where  $N_m$  is the number  
 257 of minerals in the model (Navarre-Sitchler et al. 2011) and  $\phi_m$  the volume fractions of minerals.

$$258 \quad \phi_T = 1 - \sum_{k=1}^{N_m} \phi_m \quad (1)$$

259 The  $\phi_m$  values are updated after each time step according to eq. 2, where  $t-1$  indicates the parameter value  
 260 of the previous time-step,  $\Delta t$  is the time step length (s),  $V_m$  the molar volume of the mineral ( $\text{m}^3/\text{mol}$ ) and  
 261  $R_m$  the mineral reaction rate ( $\text{mol}/\text{m}^3/\text{s}$ ). Rate equations follow the Transition State Theory (Lasaga 1998)  
 262 and are calculated according to eq. 3 where  $A_m$  is the mineral surface area ( $\text{m}^2/\text{m}^3_{\text{rock}}$ ),  $k_{25}$ , the reaction rate  
 263 constant ( $\text{mol}/\text{m}^2/\text{s}$ ) at 25°C,  $R$  is the gas constant (8.3144 J/mol/K),  $E_a$  is the activation energy (J/mol),  $T$   
 264 is temperature (K),  $a_i^{n_i}$  is the term describing the effect of species  $i$  on the rate, and  $f_m(\Delta G)$  is the function  
 265 describing the dependence of the rate on the solution saturation state (Soler 2013). This function is  
 266 calculated with eq. 4 where IAP is the ionic activity product of the solution with respect to the mineral,  
 267  $K_{eq}$  is the equilibrium constant of that mineral, and  $m_1$ ,  $m_2$  and  $m_3$  are empirical parameters defining the  
 268 shape of this function (assumed to be equal to 1 if no experimental data are available).

$$269 \quad \phi_m = \phi_{m,t-1} + V_m(R_m \Delta t) \quad (2)$$

$$270 \quad R_m = A_m \sum_{\text{terms}} k_{25} e^{\frac{-E_a}{R} \left( \frac{1}{T_{25}} - \frac{1}{T} \right)} \left( \prod_i a_i^{n_i} \right) f_m(\Delta G) \quad (3)$$

$$271 \quad f_m(\Delta G) = \left[ 1 - e^{\left( m_2 \left( \frac{\text{IAP}}{K_{eq}} \right)^{m_3} \right)^{m_1}} \right] \quad (4)$$

272 The mineral surface area ( $A_m$ ) is calculated according to eq. 5 where,  $A_{specific}$  is the mineral specific surface  
273 area ( $m^2/g$ ) and  $MW_m$ , the mineral molecular weight ( $g/mol$ ). A threshold mineral volume fraction value  
274 must be provided for secondary minerals not initially present in the system to calculate the bulk surface  
275 area until the computed time-evolving volume fraction exceeds the threshold value.

$$276 \quad A_m = \frac{\phi_m A_{specific} MW_m}{V_m} \quad (5)$$

277 Activity coefficients for aqueous species are calculated according to the extended Debye-Hückel equation  
278 (Steefel 2009).

279 The physical system chosen to conduct the reactive transport model is a 1D column of 88 m length  
280 representing the laterite profile. In the model, rainwater flows from top to bottom. The column is  
281 discretized into a mesh of 250 elements of 0.35 m length each. Models are run for  $10^6$  years, with a  
282 maximum time step of 1 year. Meteoric water has a constant composition (Table 1), typical of rainwater  
283 from tropical areas (Veneklaas 1990; Williams et al. 1997; Bertolo et al. 2006). It has an ionic strength of  
284  $1.4 \times 10^{-4}$  mol/L. pH has been set to 4.5, accounting for both the acidic pH of rainwater and the acidity  
285 generated in soils due to the formation of organic acids as a consequence of organic matter decomposition  
286 (Soler and Lasaga, 1996). Rainwater is flowing along the column at a constant rate during modeling. The  
287 average annual rainfall at Moa in the period 1900-2009 is 1360 mm, of which 990 mm fall during the two  
288 wet seasons (data from <http://sdwebx.worldbank.org/climateportal>). This value agrees with the values  
289 between 900 and 1800 mm/y reported by Butt and Cluzel (2013) as summer rainfall for laterite deposit in  
290 Caribbean areas. Assuming retention by the soil of 15% (Veneklaas, 1990) the infiltration flow rate is  
291 1156 mm/y ( $4.0 \times 10^{-8}$  m<sup>3</sup>/m<sup>2</sup>/s).

292 Neither dry periods nor changes in the infiltration rate are considered during the modeling. Transport is  
293 mainly advective. A water diffusion coefficient for solutes of  $1.0 \times 10^{-10}$  m<sup>2</sup> s<sup>-1</sup> is used and dispersivity is  
294 assumed to be equal to 1 m based on the length of the domain (88 m). Diffusive and dispersive transport  
295 is not significant.

296

297 Geochemical system

298 Initially, the system has a homogeneous mineralogical composition, representing the partially  
299 serpentinized peridotite (Table 2). Initial mineral volume fractions are based on field observations in the  
300 Punta Gorda laterite deposit (M10 sample in Fig. 2b). An initial porosity of 12 % is used to account for

301 the fracture porosity. En<sub>90</sub> and Fo<sub>90</sub> are chosen as representative of the pyroxene and olivine from the  
302 unaltered peridotite, respectively.

303 Initial porewater composition is calculated to be in equilibrium with this set of minerals (Table 1). It has  
304 an ionic strength of  $1.1 \times 10^{-4}$  mol/L. K and Na are found as free ions, Si is forming aqueous H<sub>4</sub>SiO<sub>4</sub> (68%)  
305 and H<sub>3</sub>SiO<sub>4</sub><sup>-</sup> (32%). The most abundant aqueous species of carbonate at pH 9.5 is HCO<sub>3</sub><sup>-</sup> (86%) although  
306 CO<sub>3</sub><sup>2-</sup> is also significant (13%), together with minor amounts of MgCO<sub>3</sub>(aq) and FeCO<sub>3</sub>(aq) (<1%). All  
307 iron is found as Fe(II), and is present as Fe<sup>2+</sup> (50%), FeOH<sup>+</sup> (48%) and Fe(OH)<sub>2</sub>(aq) (2%). Mg aqueous  
308 speciation is dominated by Mg<sup>2+</sup> (99%) although a small amount of MgOH<sup>+</sup> (1%) is computed. Finally,  
309 the main Ni aqueous species are Ni(OH)<sub>2</sub> (83%), Ni<sup>2+</sup> (9%) and NiOH<sup>+</sup> (8%).

310 Besides the primary minerals considered in the initial composition, serpentine II and goethite are included  
311 in the calculations and are allowed to precipitate in the case where porewater is saturated with respect to  
312 those minerals. Although several compositions for serpentine II are available (Online resource 1), only  
313 one composition was used in the model for sake of simplicity. In the Reference case, the composition is  
314 set to Mg<sub>2.798</sub>Fe<sub>0.102</sub>Ni<sub>0.049</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub> but the effect of different compositions has been studied in  
315 sensitivity analyses.

316 In many oxide deposits abundant secondary silica has been observed in the form of chalcedony or quartz  
317 (Butt and Cluzel 2013). In the model presented here, the saturation index of quartz is monitored and the  
318 formation of quartz is considered in a sensitivity analysis.

319 Moore et al. (2012) highlighted the role of weathering of silicate mineral as a sink for atmospheric  
320 CO<sub>2</sub>(g). Magnesite deposits associated to serpentine bodies have been reported (Foster and Eggleton  
321 2002; Ulrich et al. 2014; Quesnel et al. 2016). However, magnesite precipitation, although  
322 thermodynamically stable, is inhibited in near surface environments given the strong hydration shells that  
323 form around Mg<sup>2+</sup> ions (Power et al. 2013; Morgan et al. 2015). In these conditions, Königsberger et al.  
324 (1999) suggested that hydrated magnesium carbonate minerals, such as nesquehonite (MgCO<sub>3</sub>·3H<sub>2</sub>O)  
325 form instead. Power et al. (2013) reported that CO<sub>2</sub>(g), in turn, may affect the weathering rate of silicate  
326 mineral. In order to elucidate the effect of CO<sub>2</sub> in the formation of this type of deposits, the saturation  
327 index of nesquehonite is monitored and the effect of different CO<sub>2</sub>(g) concentrations is considered in  
328 sensitivity analysis.

329

330 Thermodynamic and kinetic data

331 Thermodynamic data used in the calculations for aqueous species and for the dissolution/precipitation of  
332 quartz and goethite are from ThermoChimie v.9 database (Giffaut et al. 2014). The total list of solute  
333 species included in the simulations is shown in Online resource 2.

334 Solubility constants for  $En_{90}$ ,  $Fo_{90}$ , serpentine I and serpentine II have been modified given that they are  
335 not pure magnesium end member minerals. An ideal solid solution between pure end members has been  
336 considered for each mineral. For an ideal solid solution  $A_{\chi}B_{(1-\chi)}C$ , where the pure end members are AC  
337 and BC, the solubility constant of a given discrete composition can be calculated using eq. 6, where  $K_{AC}$  is  
338 the solubility constant of pure AC,  $K_{BC}$  is the solubility constant of pure BC and  $\chi$  the molar fraction of A  
339 in the solid solution.

$$340 \quad K = (K_{AC}\chi)^{\chi} (K_{BC}(1-\chi))^{1-\chi} \quad (6)$$

341 The pure end members considered for  $Fo_{90}$  are fayalite ( $Fe_2SiO_4$ ), forsterite ( $Mg_2SiO_4$ ) and the phase  
342  $Ni_2SiO_4$ ; for  $En_{90}$ , the pure end members are enstatite ( $MgSiO_3$ ) and ferrosilite ( $FeSiO_3$ ). In the case of  
343 serpentine I the pure end members are lizardite ( $Mg_3Si_2O_5(OH)_4$ ), népouite ( $Ni_3Si_2O_5(OH)_4$ ) and  
344 greenalite ( $Fe_3Si_2O_5(OH)_4$ ) while in the case of serpentine II, Fe(III)-lizardite ( $Fe_2Si_2O_5(OH)_4$ ) is  
345 considered instead of greenalite to account for the difference of the valence state of Fe in the octahedral  
346 site. The log K values of these pure end members are taken from ThermoChimie v.9 when available.  
347 Additional log K values (e.g. forsterite) are calculated from  $\Delta G_f^{\circ}$  or  $\Delta G_f$  values from literature (Villanova-  
348 de-Benavent et al. 2016a). Selected log K values for pure end-members are listed in Table 3, whereas log  
349 K values calculated for the solid solutions are in Table 4.

350 In CrunchFlow, dissolution/precipitation of minerals is kinetically controlled. As dissolution and/or  
351 precipitation of serpentine I, serpentine II, goethite and magnetite is considered to occur under local  
352 equilibrium, the rates for these minerals have been modified in order to rapidly achieve equilibrium (large  
353 surface areas and/or large rate constants). The threshold volume fraction considered is  $10^{-8}$  and  $10^{-4}$  for  
354 goethite and serpentine II, respectively.

355 Dissolution rates for  $Fo_{90}$  and  $En_{90}$  are assumed equal to those for pure forsterite and enstatite reported in  
356 Palandri and Kharaka (2004). The assignment of a value for the reactive area of forsterite and enstatite is  
357 not straightforward. Dissolution rates measured in the laboratory are 2 to 5 orders of magnitude faster  
358 than in field due to a variety of factors such as the presence/absence of inhibitors or catalyzers such as  
359 organic acids, hydrologic regimes, armoring of natural surfaces or the affinity of secondary minerals  
360 (Navarre-Sitchler et al. 2011). After preliminary calculations, a reactive area of  $0.0005 \text{ m}^2/\text{g}$  for  $Fo_{90}$  and

361 of 0.005 m<sup>2</sup>/g for En<sub>90</sub> is considered in the model. These values give results comparable to field  
 362 observations. Nevertheless, the effect of higher surface areas is studied in sensitivity analyses. Mn-  
 363 oxyhydroxides have not been considered.

364 The Ni content in the goethite from Punta Gorda ranges from 0.8 to 4.0 wt.% Ni. In the model presented  
 365 here, this Ni is sorbed onto the goethite surface. Assuming that when the Ni content is 4.0 wt.% all  
 366 surface sites are occupied by Ni, the maximum sorption capacity of goethite can be calculated, being 6.5  
 367 sites/nm<sup>2</sup> for a surface area of 65.2 m<sup>2</sup>/g. This value is consistent with the values proposed by Davis and  
 368 Kent (1990) (2.6-16.8 sites/nm<sup>2</sup> for Fe oxyhydroxides), or Hayes and Leckie (3-11 sites/nm<sup>2</sup>).

369 Information concerning the sorption of Ni onto goethite is scarce (Marcussen et al. 2009; Rajapaksha et  
 370 al. 2012). Sorption of Ni onto the goethite surface is modeled following a one-site non electrostatic  
 371 sorption model based on Marcussen et al. (2009) (Table 5), where Ni sorbs onto goethite surface forming  
 372 the surface complex >Fe\_ONi<sup>+</sup>. These authors used a log K for goethite surface  
 373 protonation/deprotonation from Richter et al. (2005) but an update of these values (Richter and Brendler  
 374 2008) is used in our study. The original log K values were provided for a density site of 2.31 sites/nm<sup>2</sup>  
 375 and they have been recalculated to account for the site density of Punta Gorda goethite according to eq. 7  
 376 (Richter et al. 2005), where K are the sorption equilibrium constants,  $\Gamma$  the site density (sites/nm<sup>2</sup>), and  
 377 the subscript *o* stands for the new values calculated for 6.5 sites/nm<sup>2</sup>. Total sorption capacity of goethite is  
 378 0.0625 moles sites/moles goethite.

$$379 \log K_o = \log K + \frac{\Gamma}{\Gamma_o} \quad (7)$$

380

### 381 **Results and discussion**

382 The modeling results presented in this paper consists of a Reference case whose initial and boundary  
 383 conditions have been detailed above and a set of Sensitivity analyses in which some parameters have been  
 384 modified with respect to those of the Reference case.

385

386 Reference case

387 The residence time of water in the profile is 2.7 years. This residence time is very short compared to the  
 388 total time of modeling (10<sup>6</sup> years) and indicates, as expected, that the influence of the initial porewater  
 389 composition on the final results can be neglected.

390 Fig. 4 shows the evolution of the mineral composition (% wt), sorbed Ni concentration, and porosity as a  
391 function of depth at different elapsed times. When looking at Fig. 4 the reader must take into  
392 consideration that the weight percentage of a given mineral can increase either because of its precipitation  
393 or because of the dissolution of other minerals without precipitation. In order to simulate the effect of  
394 unsaturated flow, once the model run starts, porewater is equilibrated with atmospheric O<sub>2</sub>(g) and CO<sub>2</sub>(g)  
395 all along the profile. Due to O<sub>2</sub>(g) equilibrium, magnetite becomes unstable and is transformed into  
396 goethite, serpentine II precipitates, and porosity decreases before 1000 years of elapsed time to values  
397 down to 5% (Fig. 4). Although this is realistic, changes at the bottom of the weathering profile are an  
398 artifact caused by the assumption of equilibrium with atmospheric O<sub>2</sub>(g) and CO<sub>2</sub>(g). Given the  
399 impossibility of fixing a realistic depth in which the system changes from unsaturated to saturated  
400 conditions, we have carried out the *Less\_carb* sensitivity case in which only the infiltrating rainwater (not  
401 along the profile) is in equilibrium with atmospheric O<sub>2</sub>(g) and CO<sub>2</sub>(g).

402 During the first 1000 years, two different reactions are observed to occur in the profile. Dissolution of En  
403 and Fo occurs all along the profile, while precipitation of Srp I and Srp II occurs along the profile, except  
404 at the top. pH is buffered to 8.6 (Fig. 5) and Ni aqueous concentration is low (<10<sup>-15</sup> mol/L). The main  
405 species occupying the goethite surface is >FeOH (>95%).

406 However, at the top of the profile, where rainwater is acidifying the system, Srp I dissolves together with  
407 Fo<sub>90</sub> and En<sub>90</sub> and the saprolite horizon begins to develop. Srp II and goethite precipitate removing Ni and  
408 Fe from solution. In fact, the amount of Srp II precipitating depends on the amount of Ni released from  
409 the dissolution of Fo<sub>90</sub> and Srp I. Fe released by En<sub>90</sub>, Fo<sub>90</sub> and Srp I that has not been incorporated into  
410 Srp II, precipitates as goethite. The presence of both Srp I and Srp II buffers pH at a value of 8.6 and  
411 causes Ni aqueous concentration remain at very low values. Goethite surface speciation is dominated by  
412 >FeOH.

413 Between 1000 and 10000 years of elapsed time, no significant changes are observed, except that, at the  
414 top of the profile, Srp I has been exhausted. As a consequence, porosity has significantly increased.

415 However, as Fo<sub>90</sub> and En<sub>90</sub> are still in the system, they dissolve and Srp II and goethite precipitate.

416 Although in the model Fo<sub>90</sub> is the first silicate mineral to dissolve followed by En<sub>90</sub>, as observed by  
417 Freyssinet et al. (2005), Golightly (2010) and Hewawasam et al. (2013), their coexistence with Srp II and  
418 Gth without Srp I is not in agreement with the paragenesis observed in the field in which neither enstatite  
419 nor forsterite are in contact with Srp II. One of the most uncertain parameters in reaction kinetics is the

420 choice of reactive area, which suggests that the reactive areas used in the Reference case could be too  
421 low. In any case, this is a transitory effect that is not observed after  $10^6$  years of elapsed time.

422 Between 1000 and 10000 years of elapsed time, a new horizon starts to develop in the model first node, in  
423 contact with the infiltrating rainwater. The precipitation of goethite has increased its sorption capacity and  
424 causes the dissolution of Srp II because Ni is preferentially sorbed onto the goethite surface ( $>FeONi^+$ ).  
425 pH decreases from 8.6 to a buffered value of 8.3. Ni aqueous concentration is close to  $10^{-8}$  mol/L.

426 During the period  $10^4 - 10^5$  years, two significant observations can be made. On one hand,  $Fo_{90}$  is  
427 exhausted, which means that the only processes controlling Ni concentration in solution are the formation  
428 of Srp II and the sorption of Ni onto goethite surface. On the other hand, a new oxide horizon is starting  
429 to form at the top of the profile because Srp II has been dissolved. pH is no longer buffered at 8.3.

430 Enstatite is dissolving yielding Fe that precipitates as goethite. As a consequence, the porosity increases  
431 up to 75%. The formation of  $>FeONi^+$  displaces  $H^+$  from the goethite surface (Table 5) and contributes to  
432 the decrease of pH together with the input of acidic water. Ni aqueous concentration is about  $3 \times 10^{-7}$   
433 mol/L.

434 At  $10^5$  years of elapsed time, the three main horizons of a typical laterite profile have formed (Fig. 4). At  
435 the top of the column, there is the goethite-dominated horizon; below 10 m depth, Srp I is in equilibrium  
436 with Srp II and Gth at pH 8.6 in a partially weathered peridotite horizon, and between both layers, there is  
437 a narrow horizon in which serpentine II is in equilibrium with a goethite with Ni sorbed, the saprolite  
438 horizon (Fig. 4).

439 From  $10^5$  years on, slight changes are predicted. The oxide and saprolite horizons develop and the  
440 interfaces are displaced towards greater depths. At the top of the profile, there is no more forsterite  
441 providing Ni to the system and the pH is acid, such that desorption of Ni increases Ni aqueous  
442 concentration. At  $4 \times 10^5$  years of elapsed time, enstatite is exhausted and goethite becomes the only phase  
443 in this horizon. pH is 4.5 and porosity is high, about 91% (Fig. 4). Ni released from the goethite surface is  
444 sorbed downflow on the goethite in the saprolite horizon until its surface is saturated (at  $8 \times 10^5$  years of  
445 elapsed time). From this moment, saprolite horizon develops faster given that no more Ni can sorb onto  
446 goethite and it is available for serpentine precipitation.

447 The model results obtained agree with the laterite formation rates reported in literature. In  $10^6$  y, the  
448 thickness of weathered laterite might be 10-20 m (Freyssinet et al. 2005), 29-58 m (Golightly 2010) or 2-  
449 75 m (Hewawasam et al. 2013). Hewawasam et al. (2013) observed that in Sri Lanka laterites, weathering

450 processes are occurring at the reaction front, and are displaced towards greater depths as minerals become  
451 weathered. According to Goodfellow et al. (2011) this is because weathering reactions are inhibited in  
452 those areas where porewater is saturated with respect to weathering products that is, far from the water  
453 table, and in contrast, weathering is enhanced in the vadose zone. In agreement with those authors, in the  
454 model presented here, the reaction front starts at the top of the profile and is moving downward with time  
455 as weathering reactions progress.

456 The model satisfactorily explains the formation of the three different horizons observed in the field in a  
457 period of time around  $10^6$  y. The first one, with a thickness of 61 m, is at the top of the profile and is  
458 composed of goethite. In this horizon, the porosity is high (Fig. 4), porewater composition is poor in Mg,  
459 Si, Fe and Ni, pH is around 4.5 and the goethite surface is saturated with  $H^+$  (Fig. 6).

460 The second horizon is formed by goethite and serpentine II. It has a thickness of 11 m with an average  
461 porosity of 40%, although it increases at the bottom. pH increases up to 8.3 and goethite contains up to 4  
462 wt.% Ni sorbed onto its surface. The main surface species is  $>Fe\_ONi^+$ . (Fig. 6). In this saprolite horizon,  
463 the ratios between Mg/Si and  $CO_3/Mg$  in solution are 1.4 and 2.0 respectively, in agreement with the  
464 observations of Golightly (1981). pH values also agree with those reported for saprolite horizons  
465 (Golightly 1981, 2010; Pelletier 1996).

466 Another similitude with field observations is the difference between the development of the limonitic and  
467 saprolite horizons. The larger thickness of the limonitic horizon in relation to that of saprolite has been  
468 observed in areas with maximum lixiviation (Butt and Cluzel 2013), and unsaturated conditions, i.e.  
469 porewater in equilibrium with atmospheric  $O_2(g)$  and  $CO_2(g)$ . Nevertheless, the goethite horizon is  
470 significantly thicker (61 m) than the saprolite horizon (11 m), due to the fact that the model does not take  
471 into account the collapse of this horizon. In case of collapsing, the thickness of the goethite horizon will  
472 be smaller and similar to that observed in the Punta Gorda deposit (30m, Fig. 1).

473 The third and deepest horizon, with a depth limited by model dimensions, represents a partially weathered  
474 serpentinized peridotite, with serpentine I in equilibrium with serpentine II and goethite. pH is 8.6 and Ni  
475 is not sorbed onto goethite (Fig. 6). Porosity is low, close to 5%.

476 After  $10^6$  y, 76% of Mg and 80% of Si have been leached from the profile, in agreement with  
477 observations reported in Golightly (1981) and Butt and Cluzel (2013) (RC in Fig. 7). A significant  
478 increase of Mg aqueous concentration is observed between the goethite and saprolite horizons. Fe and Ni  
479 are scarcely leached out of the system.

480 The model results suggest that sorption of Ni onto the goethite surface can explain the amount of Ni  
481 found in the goethite at Moa. In the model, however, sorption of Ni occurs only on goethite in contact  
482 with serpentine II. This distribution, in accordance with the observations of Dublet et al. (2015) of a  
483 regular decrease in bulk Ni content upwards in the profile and of Soler et al. (2008) in the goethite  
484 horizon of Loma de Hierro deposit, is directly linked to the evolution of pH. Sorption of Ni onto goethite  
485 depends on pH, and as can be seen in Fig. 6, when pH decreases below 7, sorption of Ni significantly  
486 decreases achieving values around 10% or less at pH 5 (Dublet et al. 2015). In natural conditions,  
487 however, goethite particles with Ni sorbed onto their surface might flocculate or form aggregates. For  
488 goethite, the point of zero charge (PZC) is between pH = 6.5 to 9.5 (Strauss et al. 1997; Gaboriaud and  
489 Ehrhardt, 2002). At the PZC, a dispersion of particles exhibits its maximum flocculation rate. In the  
490 profile, this range of pH is encountered in the saprolite, towards the limonitic horizon, where it might well  
491 favor the flocculation/aggregation of the goethite particles that could prevent desorption of Ni.  
492 In the model, nesquehonite is always subsaturated (saturation indices below -2) while quartz presents  
493 saturation indices about 0.7 in the partially serpentinized peridotite horizon and close to 0.4 in the  
494 saprolite horizon.

495

#### 496 Sensitivity analyses

497 Different cases have been investigated to evaluate the effect of the uncertainty of some key parameters on  
498 the model results. As shown in Table 6, sensitivity analyses explore the effect of not considering sorption  
499 of Ni onto goethite (*No\_ads* case), of using different chemical compositions for serpentine II (*Srp II\** and  
500 *Srp II<sup>s</sup>* cases), of considering faster dissolution rates of Fo<sub>90</sub> and En<sub>90</sub> (*Rate* case), of considering a smaller  
501 carbonate concentration (*Less\_carb* case), or allowing the precipitation of quartz (*Qt* case).

502 In the *No\_ads* sensitivity analysis, the formation of surface species onto goethite is not considered. After  
503 10<sup>6</sup> years of elapsed time, the same horizons developed as in the RC, with a goethite horizon with pH 4.5,  
504 a saprolite horizon with serpentine II and goethite at pH 8.3, and a partially weathered peridotite with  
505 serpentine I and II and goethite at pH 8.6. Mg and Si are also significantly leached (Fig. 7) but as shown  
506 in Fig. 8, the saprolite horizon is thicker than in the RC. This is due to the fact that, on one hand, all Ni is  
507 available to precipitate in Srp II whereas in RC, sorption of Ni was dominant and Srp II formed once the  
508 goethite surface was saturated, and on the other, the pH of porewater is not affected by the  
509 (de)protonation of goethite. In the RC, pH was lower in the saprolite horizon because sorption of Ni

510 displaced  $H^+$  from the goethite surface, while in the *No\_ads* case, the pH in the saprolite horizon is  
511 maintained at 8.3, the same pH that is achieved in the RC when goethite becomes saturated in Ni (Fig. 9).  
512 To account for the variability of compositions of Srp II observed in the field, two more chemical  
513 compositions have been used in the sensitivity analyses *Srp II\** and *Srp II<sup>s</sup>* (Table 4). These two Srp II  
514 have been chosen as they are the compositions having the lowest and the highest solubility constants,  
515 respectively. Results indicate that the same main processes are occurring as in the RC (Fig.7, Fig. 9), but  
516 that the composition of Srp II affects the final distribution of the profile horizons (Fig. 8). On one hand,  
517 the thickness of the saprolite horizon, dominated by Srp II, decreases as the solubility of this mineral  
518 increases (*Srp II<sup>s</sup>* in Fig. 8). On the other hand, the amount of leached Ni is higher in the sensitivity case  
519 *Srp II\**, that is, the one considering the Srp II with the lowest Ni content (Table 4).

520 In the *Rate* case, the reactive areas of  $F_{O90}$  and  $E_{N90}$  are set equal to  $0.1 \text{ m}^2/\text{g}$  to obtain dissolution rates of  
521  $F_{O90}$  and  $E_{N90}$  that are 200 and 20 times faster, respectively, than in the RC. Results show that these faster  
522 dissolution rates increase the amounts of Si, Ni, Mg and Fe released, which also leads to increased  
523 goethite precipitation and Ni adsorption.  $F_{O90}$  and  $E_{N90}$  are completely consumed before ( $1000$  and  
524  $1.5 \times 10^5$  years respectively), without further effects on laterite formation. After  $10^6$  years of elapsed time,  
525 differences with the RC are minor (Fig. 7-9).

526 In the sensitivity analysis *Less\_carb*, only the infiltrating rain water is in equilibrium with atmospheric  
527  $O_2(g)$  and  $CO_2(g)$ . The model reproduces a case in which the system is fully saturated (water table at the  
528 surface), limiting the input of  $O_2(g)$  and  $CO_2(g)$  to the system (Butt and Cluzel 2013). As shown in Fig. 8,  
529 the advancement of the weathering front after  $10^6$  years is small compared to the RC. The main reason for  
530 such big difference is the availability of carbonate, which affects pH. In this sensitivity analysis, the lack  
531 of dissolved  $CO_2(g)$  does not buffer pH and, as a result of Srp I dissolution, pH goes up quickly and the  
532 solution becomes saturated with respect to primary minerals (Fig. 8). In the RC, where atmospheric  
533  $CO_2(g)$  is always available in the column, dissolution of  $CO_2(g)$  provides enough acidity to buffer the  
534 increase in pH caused by silicate mineral dissolution. This observation agrees with Golightly (1981) that  
535 identified carbonate as one of the principal agents of weathering. When carbonate is not available, the  
536 solubility of serpentine is lower and the reaction front moves slowly. As a consequence, in  $10^6$  years of  
537 elapsed time, Mg and Si leaching is not as important as for the other cases (Fig. 7) and pH is around 10  
538 (Fig. 9). The *Less\_carb* and RC results suggest that the aqueous carbonate concentration is, in fact, an

539 important key parameter controlling the rate of laterite formation. Any phenomena preventing CO<sub>2</sub>(g)  
540 equilibration with porewater would lessen laterite profile development.

541 As reported previously in the RC, saturation indices of quartz indicated a slight oversaturation, especially  
542 along the saprolite and peridotite horizons. In the *Qt* sensitivity analysis, quartz is allowed to precipitate  
543 according to local equilibrium. Results show that quartz precipitation is significant because Si is  
544 preferentially retained as quartz rather than being incorporated in Srp II and, consequently, the weathering  
545 front is advancing faster. After 10<sup>6</sup> years of elapsed time, the profile presents two different horizons (Fig.  
546 8). The first 11.5 m are of goethite, with a porosity of 91% and a pH of 4.5; and the other 75 m are  
547 composed of 43% (in vol.) of quartz and 9 % (in vol.) of goethite with a porosity of 48% and a pH of 6  
548 (Fig. 9). All Mg and nearly 40% of Ni have been leached from the system, while leaching of Si is reduced  
549 to 15% (Fig. 7). Microcrystalline quartz in laterite profiles has been reported in some profiles (e.g.  
550 Golightly 1981; Tauler et al. 2009; Villanova-de-Benavent et al. 2014) and observed in cases with small  
551 lixiviation rates (Butt and Cluzel 2013), but it does not form in those cases where weathering rate is fast  
552 (Golightly 2010). In the RC, quartz saturation indicates its possible precipitation but the results obtained  
553 when quartz is allowed to precipitate are not consistent with field observations. An explanation to this  
554 might be found in the value of the saturation indices calculated for quartz, that were not higher than 0.7.  
555 These small saturation indices might not be enough to overcome a kinetic barrier for the precipitation of  
556 quartz. Instead of the precipitation of quartz under local equilibrium, the precipitation of an amorphous  
557 phase such as SiO<sub>2</sub>(am), or a kinetically controlled precipitation of quartz should have been considered.

558

## 559 **Conclusions**

560 This paper presents a reactive transport model of the formation of the Punta Gorda Ni-laterite deposit of  
561 Moa mining district (northeast of Cuba). The model is based on the conceptual model of Butt and Cluzel  
562 (2013), according to which laterite deposits form due to a continuous weathering of a partially  
563 serpentinized peridotite under tropical climate. Numerical model considers a 1D column of 88 m length  
564 initially composed of Fo<sub>90</sub>, En<sub>90</sub>, Srp I and Mag. Due to the interaction with rainwater, these primary  
565 minerals dissolve, and a Fe(III) and Ni bearing serpentine (Srp II) and goethite precipitate. Ni is allowed  
566 to sorb onto goethite.

567 Although some of the assumptions made in the numerical model are simplifications of the real system,  
568 results of the model are consistent with the conceptual model about the formation of oxide type Ni-laterite  
569 deposits:

- 570 • After  $10^6$  years of elapsed time, simulations reproduce the three main horizons observed in the  
571 field: a) a thick limonite horizon, at the top of the profile, composed of goethite, b) a narrow  
572 saprolite horizon, in the middle, composed of Srp II and Gth, and c) a partially weathered  
573 serpentinized peridotite horizon, at the bottom, in which Srp I, Srp II and Gth coexist.
- 574 • Simulations show the increase of porosity from values close to 5% at the bottom to values close to  
575 90% at the top of the profile, due to the dissolution of silicate minerals and the pH increase from  
576 4.5 at the top (rainwater pH) to values close to 8.6 at the bottom, being 8.3 at the saprolite horizon.
- 577 • Sorption of Ni onto goethite can explain the field observations. Ni sorption onto goethite is linked  
578 to pH, showing its maximum in the saprolite horizon, as observed in the field. Sorption onto  
579 goethite in the limonite horizon decreases because of the acidic pH, which displaces  $\text{Ni}^{2+}$  from the  
580 surface sites. In the serpentinized peridotite horizon, sorption is negligible because Ni is  
581 preferentially retained in Srp I.
- 582 • During the laterization process, Mg and Si are leached out the system, while Fe and Ni are  
583 conserved.

584 This simulation exercise has been useful not only to identify but also, to quantify, the effect that some  
585 variables can have on the formation of laterites:

- 586 • The saprolite reaction front does not advance while there is Srp I in the system.
- 587 • Protonation/desprotonation of goethite surface exerts a significant control on porewater pH as it  
588 increases acidic pH of entering rainwater but also decreases pH of saprolite horizon porewater to  
589 values below 8.3, preventing the development of saprolite horizon. Nevertheless, this control  
590 finishes when goethite surface sites saturate.
- 591 • Aqueous carbonate concentration is an important key parameter as it controls the rate of  
592 laterization process, with laterization increasing with carbonate concentration. This is due to  
593 carbonic acid buffering capacity, which buffers the increase of pH due to silicate dissolution.
- 594 • Forsterite is the main mineral providing Ni to the system. The dissolution rate of Fo and En affects  
595 the thicknesses of the different horizons.

596 • Serpentine II composition influences the development of laterite profile, from two perspectives:  
597 serpentine II poor in Ni causes an increase of the % of Ni leached after 10<sup>6</sup> years of elapsed time  
598 and since composition determines the solubility constant of serpentine, the more soluble the  
599 serpentine is, the narrower the saprolite horizon is. In any case, its effect is minor and must be  
600 further evaluated.

601 • Precipitation of quartz significantly enhances the formation of the limonitic horizon and inhibits  
602 the formation of the saprolite horizon. The inclusion of quartz or even an amorphous silica phase  
603 must be evaluated in more details.

604 Results of this study provide new valuable insights to the understanding of the differences between Ni-  
605 laterite deposit types and show the capabilities of reactive transport simulations to test and validate  
606 conceptual models. The model could be improved by increasing either the complexity of the geochemical  
607 system (more minerals, solid solutions, incorporation of Ni into goethite structure,...) or the physical  
608 system (2D or 3D, matrix diffusion to simulate corestones structures, mineral heterogeneity...).

609 Finally, investigations on the PZC of goethite under the hydrochemical conditions of the Moa profile  
610 would account for flocculation of particles that may preserve Ni all along the goethite horizon.

611

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617

## 618 **Conflict of interest**

619 The authors declare that they have not conflict of interest.

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834 **Figure captions**

835 **Fig.1** Location and simplified geological map of the Moa Bay mining area (Cuba) showing the location of  
836 the Punta Gorda Ni-laterite deposit. Modified from Marchesi et al. (2006).

837 **Fig. 2** Schematic representation of the studied profile of the Punta Gorda Ni-laterite deposit (a) and  
838 mineral composition of the analyzed samples (b). Mineral abbreviations taken from Whitney and Evans  
839 (2010) (Fo: forsterite, En: enstatite, Srp: serpentine, Mgh: maghemite, Gth: goethite, Hem: hematite, Gib:  
840 gibbsite, Qz: quartz), except pyrochroite (Prc). Modified from Galí et al. (2007).

841 **Fig. 3** X-Ray diffraction diagram of sample M4 from Punta Gorda. Agreement index  $R_{wp} = 10.31$ .  
842 Triangles at bottom are the position of the reflections used for calculating  $D_{hkl}$  values from measured  $2\theta$   
843 and  $FWHM_{hkl}$  values.

844 **Fig. 4** Evolution of the amount of mineral (in wt.%) (areas) and of the amount of Ni sorbed onto goethite  
845 (in wt.% of Ni in goethite) (solid line) and porosity in the profile at initial time (0 y) and at different  
846 model elapsed times (from  $10^3$  to  $10^6$  years) for the Reference case.

847 **Fig. 5.** pH distribution at the profile at different time steps for the Reference case.

848 **Fig. 6** Distribution of Mg, Si, Fe and Ni aqueous concentration (a), goethite surface species (b), and pH  
849 (c) along the modeled profile after 1My of elapsed time.

850 **Fig. 7** Amount of Mg, Si and Ni (in wt.%) leached out from the modelled profile after  $10^6$  years of  
851 elapsed time for the RC (Reference case) and the different sensitivity analyses reported: *No\_ads*, without  
852 considering sorption of Ni onto goethite, *Srp II\** and *Srp II<sup>§</sup>*, considering different serpentine  
853 compositions, see Table 4, *Rate*, considering faster dissolution rates of enstatite and forsterite, *Less\_carb*,  
854 considering a smaller concentration of carbonate and *Qt*, allowing quartz precipitation.

855 **Fig. 8** Distribution of the horizons along the modelled profile after  $10^6$  years of elapsed time for the RC  
856 (Reference case) and the different sensitivity analyses reported (same abbreviations from Fig.7).

857 **Fig. 9** Evolution of pH along the modelled profile after  $10^6$  years of elapsed time for the Reference case  
858 and the different sensitivity analyses reported (same abbreviations from Fig.7).

859

860 **Table captions**

861 **Table 1** pH, Eh (in V) and total concentration of components of rainwater and initial porewater (in  
862 mol/L). Mineral abbreviations from Whitney and Evans (2010)

863 **Table 2** Initial mineral composition considered in the model.

864 **Table 3** Solubility constants at 25°C of the pure end-member phases used to calculate solubility constants  
865 of solid solutions used in the simulations. Mineral abbreviations from Whitney and Evans (2010).

866 **Table 4** Solubility constants at 25°C calculated for the solid solutions used in the simulations.

867 \*\$serpentine II used in the sensitivity cases. Mineral abbreviations from Whitney and Evans (2010).

868 **Table 5** Equilibrium constants for goethite surface reactions used in the calculations.

869 **Table 6** Summary of the main differences between the Reference case and the sensitivity analyses.

870

## ***Reactive transport model of the formation of oxide type Ni-laterite profiles (Punta Gorda, Moa Bay, Cuba)***

Cristina Domènech, Salvador Galí, Cristina Villanova-de-Benavent, Josep M. Soler and Joaquín A. Proenza

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### ***Answers to the editor-in-chief Prof. Georges Beaudoin***

We appreciate the modifications proposed by Prof. G.Beaudoin. We have accepted all them, except in the following cases, where an alternative text or a response to the reviewer has been proposed. Line numbers refer to the pdf document revised by Prof. G.Beaudoin.

*Line 19. "oxide type Ni-laterite deposit". We have chosen to maintain oxide type Ni-laterite deposit, but we have carefully checked the text to make it uniform.*

*Line 25. "Percentages of Ni" has been changed by "the weight percent of Ni".*

*Line 29. "while the effect of serpentine II composition or dissolution mineral rates is minor" has been changed by "while the effect of the composition of secondary serpentine or of mineral dissolution rates is minor".*

*Line 47. "under favorable climatic and topographic conditions" has been changed by "under favorable topography and climatic conditions".*

*Line 84. "Ni sorbs onto goethite forming inner sphere mononuclear bidentate complexes (Trivedi et al. 2001; Xu et al. 2007)," has been changed by "Ni sorbs onto goethite forming inner-sphere mononuclear bidentate complexes (Trivedi et al. 2001; Xu et al. 2007)".*

*Inner-sphere surface complexes is the name of those surface complexes in which there is a direct bond between the surface and the adsorbed species, in contrast to the outer-sphere surface complexes in which there is a shell of water molecules between the surface and the complex.*

*Line 86. Sorption of Ni onto goethite has been modelled by considering Langmuir isotherms (Trivedi et al. 2001), a Diffuse Layer Model (Bryce et al. 1994; Buerge-Weirich et al. 2002; Marcussen et al. 2009; Rajapaksha et al. 2012) or a Triple Layer Model (Coughlin and Stone 1995).*

*Why is this important? Delete if only information*

*We prefer to leave this text because it introduces the different models that have been used in the literature to explain sorption of Ni onto goethite. In the modelling exercise we have used that of Marcussen et al. (2009).*

*Line 98. "Differential thermal gravimetric (DTA-TGA) and EXAFS analyses" has been changed by "Differential thermal (DTA), thermal gravimetric (TGA) and EXAFS analyses" because De Carvalho et Silva et al. (2002, 2003) performed all these types of analyses.*

*Line 120.* Spheroidal weathering means the “onion type” weathering observed to occur in some granites. We have removed it from the text, as it did not provide relevant information.

*Line 130.* “Navarre-Sitchler et al. (2011) used the reactive coupled transport model CrunchFlow to simulate”. Commas have not been added given that reactive coupled transport model is a term usually used.

*Line 132.* “mineral kinetics dominated over transport, and that weathering front rate was controlled by the rate at which porosity was created” has been changed by “mineral reaction kinetics dominated over transport, and that the advance of the weathering front was controlled by the rate at which porosity was created”.

*Line 136.* “Moreover, they had to reduce the laboratory rates (by decreasing the surface reactive areas) to fit the field observations” has been changed by “Moreover, they had to use reduced reaction rates, compared with rates from laboratory studies, to fit the field observations”.

*Line 137.* “They concluded that reactive transport models can be used to understand the long-lived ( $10^6$  years) mineral weathering processes given that they can cope with simultaneous processes that do not behave linearly” has been changed by “They concluded that reactive transport models can be used to understand the long-lived ( $10^6$  years) mineral weathering processes given that they consider the simultaneous non-linear processes”.

*Line 149.* The word “horizons” has not been changed by laterite facies. It is a common and accepted word that is used in the whole document. We have added the word “laterite” before “horizons”.

*Line 151.* “a first modeling exercise” has not been changed by “modeling experiments” as we have not done experiments but numerical calculations.

*Line 204.* “impregnated by plagioclase, which was exposed to the surface during the late Miocene ( $\approx 10^7$  years) (Lewis et al. 2006).” has been changed by “including plagioclase-rich bodies, which was exposed to the surface during the late Miocene ( $\approx 10^7$  years; Lewis et al. 2006).

*Line 207.* “and lizardite 2H1 is less crystalline and presents many stacking faults” has been changed by “whereas lizardite 2H1 is less crystalline and presents many stacking faults in its structure”.

*Line 262.* “Ni may be further leached from goethite and form garnierite deeper in the profile” has been changed by “Ni may be leached from goethite to garnierite deeper in the profile”.

*Line 278.* “and transport processes under fully saturated flow conditions and different temperatures (Steeffel et al. 2015).” has been changed by “and transport processes under fully saturated flow conditions and variable temperature (Steeffel et al. 2015)”.

*Line 281.* “However, if rates” has been changed by “However, if reaction rates”.

*Line 287.* “Total porosity ( $\phi_T$ ) may be updated” has been changed by “Total porosity is updated”.

*Line 326.* "A diffusion coefficient of  $1.0 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$  is considered" has been changed by "a water diffusion coefficient for solutes of  $1.0 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$  is used".

*Line 352.* "Additional log K values (e.g. forsterite), are calculated from published  $\Delta G_r^\circ$  (e.g.  $\text{Ni}_2\text{SiO}_4$ ) or estimated  $\Delta G_f$  values (e.g. Fe(III)-lizardite, Villanova-de-Benavent et al. 2016a)." has been changed by "Additional log K values (e.g. forsterite) are calculated from  $\Delta G_r^\circ$  or  $\Delta G_f$  values from literature (Villanova-de-Benavent et al. 2016a)."

*Line 441.* "in order to simulate the effect of unsaturated flow, once the model starts," has been changed by "In order to simulate the effect of unsaturated flow, once the model run starts,".

*Line 451.* "Dissolution of En and Fo occurs in all the profile, while precipitation of Srp I and Srp II occurs in all the profile, except at the top" has been changed by "Dissolution of En and Fo occurs all along the profile, while precipitation of Srp I and Srp II occurs along the profile, except at the top."

*Line 454.* "As Srp I and Srp II react at equilibrium" What does react mean?

React means precipitate. The sentence has been removed as it was already said in the sentence before.

*Line 457.* "However, at the top of the profile, where rainwater is acidifying the system," has not been modified as proposed by Prof. G.Beaudoin.

Prof. G.Beaudoin is right in saying that rainwater is slightly acid, but we wanted to emphasize the effect of what this water does on the system.

*Line 480.* "On one hand,  $\text{Fo}_{90}$  is exhausted, which means that the only processes controlling Ni concentration in solution are the formation of Srp I or Srp II and the sorption of Ni onto goethite surface."

But Srp I formed by hydrothermal fluids before weathering.

Text has been changed to "On one hand,  $\text{Fo}_{90}$  is exhausted, which means that the only processes controlling Ni concentration in solution are the formation of Srp II and the sorption of Ni onto goethite surface."

*Line 499.* "From this moment, saprolite horizon develops faster". How?

Text has been changed to "From this moment, saprolite horizon develops faster given that no more Ni can sorb onto goethite and it is available for serpentine precipitation".

*Line 515.* ">Fe\_ONi<sup>+</sup> is the main surface species (Fig. 6)" has been changed by "The main surface species is >Fe\_ONi<sup>+</sup>". Ionic, as Prof. Beaudoin suggested is not added, as surface species can also be neutral.

*Line 521.* "one considered in the model, where despite assuming saturated conditions,  $\text{O}_2(\text{g})$  and  $\text{CO}_2(\text{g})$  are available throughout the column". What do you mean?

As explained previously in “Reference case section”, and in order to simulate the effect of unsaturated flow, once the model run starts, porewater is equilibrated with atmospheric O<sub>2</sub>(g) and CO<sub>2</sub>(g) all along the profile.

The text has been changed to “The larger thickness of the limonitic horizon in relation to that of saprolite has been observed in areas with maximum lixiviation (Butt and Cluzel 2013) and unsaturated conditions, i.e. porewater in equilibrium with atmospheric O<sub>2</sub>(g) and CO<sub>2</sub>(g)”.

*Line 567.* “To account for the variability of compositions observed in the field” of what?

Of serpentine II, it has been modified. “To account for the variability of compositions of Srp II observed in the field, two more chemical compositions have been used in the sensitivity analyses *Srp II\** and *Srp II<sup>S</sup>* (Table 4).”

*Line 605.* “All Mg and nearly 40% of Ni have been leached from the system, while leaching of Si is reduced to 15% (Fig. 7)”. Would imply Mg and Ni go out from the system?

Yes. Leaching of Mg, Si and Ni from laterites profiles developed over peridotites has been observed. (Butt and Cluzel 2013, Ulrich et al. 2014, Villanova-de-Benavent et al. 2016a).

*Line 612.* “These small saturation indices might not be enough to allow the precipitation of quartz” has been changed by “These small saturation indices might not be enough to overcome a kinetic barrier for the precipitation of quartz”.

*Line 614.* “kinetically limited precipitation” Meaning?

It means a kinetically controlled precipitation. Text has been changed by “kinetically controlled precipitation of quartz”.

*Line 620.* “Numerical model considers a 1D column of 88 m length initially composed of Fo90, En90, Srp I and Mag”. The correction proposed by Prof. G.Beaudoin “Numerical models considering a 1D column of 88 m length initially composed of Fo90, En90, Srp I and Mag” has not been accepted as the sentence loses its sense.

*Line 905.* “Fig. 4 Evolution of the amount of mineral (in wt.%) (areas) and of the amount of Ni sorbed onto goethite (in wt.% of Ni in goethite) (solid line) and porosity in the profile at initial time (0 y) and at different model elapsed times (from 10<sup>3</sup> to 10<sup>6</sup> years) for the Reference case”.

We do not change this sentence as we effectively refer to the amount of mineral in wt%.

*Line 908* “Fig. 5. Evolution of pH in the profile at different model elapsed times for the Reference case.” has been changed by “Fig. 5. pH distribution at the profile at different time steps for the Reference case”.

Page 73. Table 1 has been moved to online resources and is referred as Online resource 1. The text has been modified accordingly.

Table 1

	<b>Boundary porewater</b>		<b>Initial porewater</b>	
	Concentration (mol/L)	Constraint	Concentration (mol/L)	Constraint
pH	4.5	Fixed	9.5	Equilibrium with Mag and Srp I
O <sub>2</sub> (g)		Equilibrium O <sub>2</sub> (g) (0.21 atm)		Equilibrium with Mag
Eh (V)	0.9		-0.4	
CO <sub>3</sub> <sup>2-</sup>	1.4×10 <sup>-5</sup>	Equilibrium with CO <sub>2</sub> (g) (10 <sup>-3.4</sup> atm)	1.0×10 <sup>-8</sup>	Fixed
Cl	4.3×10 <sup>-5</sup>	Fixed	1.0×10 <sup>-4</sup>	Fixed
Fe	1.0×10 <sup>-10</sup>	Fixed	2.1×10 <sup>-8</sup>	Equilibrium with Mag
Si	1.0×10 <sup>-10</sup>	Fixed	3.1×10 <sup>-5</sup>	Equilibrium with Srp I
K	5.0×10 <sup>-6</sup>	Fixed	1.0×10 <sup>-9</sup>	Fixed
Mg	5.0×10 <sup>-7</sup>	Fixed	1.5×10 <sup>-5</sup>	Equilibrium with Srp I
Na	1.0×10 <sup>-4</sup>	Charge balanced	1.0×10 <sup>-4</sup>	Charge balanced
Ni	1.0×10 <sup>-15</sup>	Fixed	4.6×10 <sup>-8</sup>	Equilibrium with Srp I

Table 1

Table 2

<b>Mineral</b>	<b>Formula</b>	<b>% volume</b>
Srp I	$Mg_{2.85}Fe_{0.14}Ni_{0.01}Si_2O_5(OH)_4$	50
En <sub>90</sub>	$Mg_9FeSi_{10}O_{30}$	27
FO <sub>90</sub>	$Mg_9Fe_{0.95}Ni_{0.05}Si_5O_{20}$	6
Mag	$Fe_{2.97}Ni_{0.03}O_4$	5

Table 2

Table 3

mineral	reaction	log K	reference
Fa	$\text{Fe}_2\text{SiO}_4 + 4\text{H}^+ = 2\text{Fe}^{2+} + \text{H}_4\text{SiO}_4$	19.11	Wolery (1992)
Fo	$\text{Mg}_2\text{SiO}_4 + 4\text{H}^+ = 2\text{Mg}^{2+} + \text{H}_4\text{SiO}_4$	27.86	
En	$\text{MgSiO}_3 + 2\text{H}^+ + \text{H}_2\text{O} = \text{Mg}^{2+} + \text{H}_4\text{SiO}_4$	11.33	
Fs	$\text{FeSiO}_3 + 2\text{H}^+ + \text{H}_2\text{O} = \text{Fe}^{2+} + \text{H}_4\text{SiO}_4$	7.45	
Ni <sub>2</sub> SiO <sub>4</sub>	$\text{Ni}_2\text{SiO}_4 + 4\text{H}^+ = 2\text{Ni}^{2+} + \text{H}_4\text{SiO}_4$	19.43	This study, from data of Gamsjager et al. (2005)
Lz	$\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4 + 6\text{H}^+ = 3\text{Mg}^{2+} + 2\text{H}_4\text{SiO}_4 + \text{H}_2\text{O}$	$33.100 \pm 0.900$	Giffaut et al. (2014)
Gre	$\text{Fe}_3\text{Si}_2\text{O}_5(\text{OH})_4 + 6\text{H}^+ = 3\text{Fe}^{2+} + 2\text{H}_4\text{SiO}_4 + \text{H}_2\text{O}$	21.77	
Nep	$\text{Ni}_3\text{Si}_2\text{O}_5(\text{OH})_4 + 6\text{H}^+ = 3\text{Ni}^{2+} + 2\text{H}_4\text{SiO}_4 + \text{H}_2\text{O}$	$19 \pm 4$	Villanova-de-Benavent et al. (2016a)
Fe(III)-Lz	$\text{Fe}_2\text{Si}_2\text{O}_5(\text{OH})_4 + 6\text{H}^+ = 2\text{Fe}^{3+} + 2\text{H}_4\text{SiO}_4 + \text{H}_2\text{O}$	$-1 \pm 4$	

Table 3

Mineral	Reaction	Log K
Fo90	$\text{Mg}_9\text{Fe}_{0.95}\text{Ni}_{0.05}\text{Si}_5\text{O}_{20} + 20 \text{H}^+ = 9 \text{Mg}^{2+} + 0.95 \text{Fe}^{2+} + 0.05 \text{Ni}^{2+} + 5 \text{H}_4\text{SiO}_4$	134.8
En90	$\text{Mg}_9\text{FeSi}_{10}\text{O}_{30} + 20 \text{H}^+ + 10 \text{H}_2\text{O} = 9 \text{Mg}^{2+} + \text{Fe}^{2+} + 10 \text{H}_4\text{SiO}_4$	109.3
Srp I	$\text{Mg}_{2.85}\text{Fe}_{0.14}\text{Ni}_{0.01}\text{Si}_2\text{O}_5(\text{OH})_4 + 6 \text{H}^+ = 2.85 \text{Mg}^{2+} + 0.14 \text{Fe}^{2+} + 0.01 \text{Ni}^{2+} + 2 \text{H}_4\text{SiO}_4 + \text{H}_2\text{O}$	32.5
Srp II	$\text{Mg}_{2.798}\text{Fe}_{0.102}\text{Ni}_{0.049}\text{Si}_2\text{O}_5(\text{OH})_4 + 6 \text{H}^+ = 2.798 \text{Mg}^{2+} + 0.102 \text{Fe}^{3+} + 0.049 \text{Ni}^{2+} + 2 \text{H}_4\text{SiO}_4 + \text{H}_2\text{O}$	31.0
Srp II*	$\text{Mg}_{2.789}\text{Fe}_{0.114}\text{Ni}_{0.040}\text{Si}_2\text{O}_5(\text{OH})_4 + 6 \text{H}^+ = 2.789 \text{Mg}^{2+} + 0.114 \text{Fe}^{3+} + 0.040 \text{Ni}^{2+} + 2 \text{H}_4\text{SiO}_4 + \text{H}_2\text{O}$	30.8
Srp II <sup>§</sup>	$\text{Mg}_{2.821}\text{Fe}_{0.084}\text{Ni}_{0.053}\text{Si}_2\text{O}_5(\text{OH})_4 + 6 \text{H}^+ = 2.821 \text{Mg}^{2+} + 0.084 \text{Fe}^{3+} + 0.053 \text{Ni}^{2+} + 2 \text{H}_4\text{SiO}_4 + \text{H}_2\text{O}$	31.3

Table 4

Table 5

	<b>log K</b> (2.31 sites/nm <sup>2</sup> )	<b>reference</b>	<b>log K<sub>o</sub></b> (6.5 sites/nm <sup>2</sup> )
$>\text{Fe\_OH} + \text{H}^+ = >\text{Fe\_OH}_2^+$	7.0	Richter and Brendler (2008)	6.6
$>\text{Fe\_OH} = >\text{Fe\_O}^- + \text{H}^+$	-9.4	Richter and Brendler (2008)	-9.8
$>\text{Fe\_OH} + \text{Ni}^{2+} = >\text{Fe\_ONi}^+ + \text{H}^+$	-0.4	Marcusen et al.(2009)	-0.8

Table 5

Table 6

	Reference case	Sensitivity analyses					
		No_ads	Srp II*	Srp II <sup>§</sup>	Rate	Less-carb	Qt
Sorption Ni	Yes	No	Yes	Yes	Yes	Yes	Yes
Srp II composition	Srp II	Srp II	Srp II*	Srp II <sup>§</sup>	Srp II	Srp II	Srp II
Reactive area En <sub>90</sub> /Fo <sub>90</sub> (m <sup>2</sup> /g)	5×10 <sup>-3</sup> / 5×10 <sup>-4</sup>	10 <sup>-1</sup> / 10 <sup>-1</sup>	5×10 <sup>-3</sup> / 5×10 <sup>-4</sup>	5×10 <sup>-3</sup> / 5×10 <sup>-4</sup>			
Equil. with atm O <sub>2</sub> (g) and CO <sub>2</sub> (g)	All nodes	All nodes	All nodes	All nodes	All nodes	Only rainwater	All nodes
Precipitation of Qt	No	No	No	No	No	No	Yes

Table 6

Figure 1

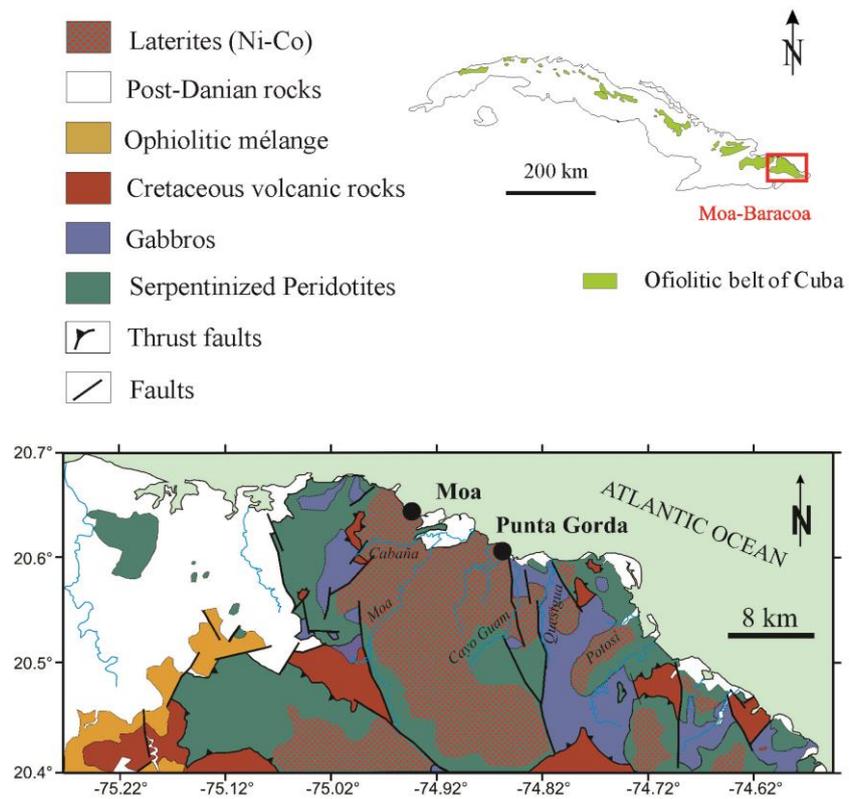


Figure 1

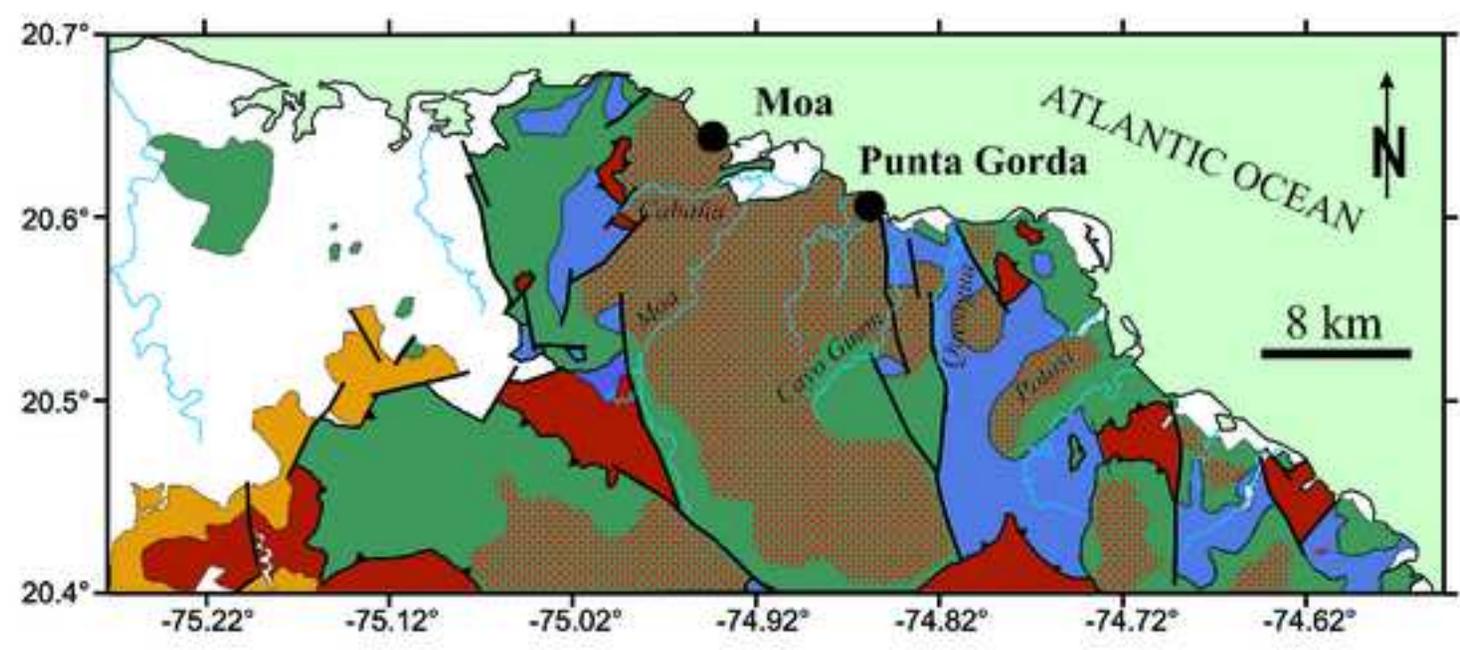
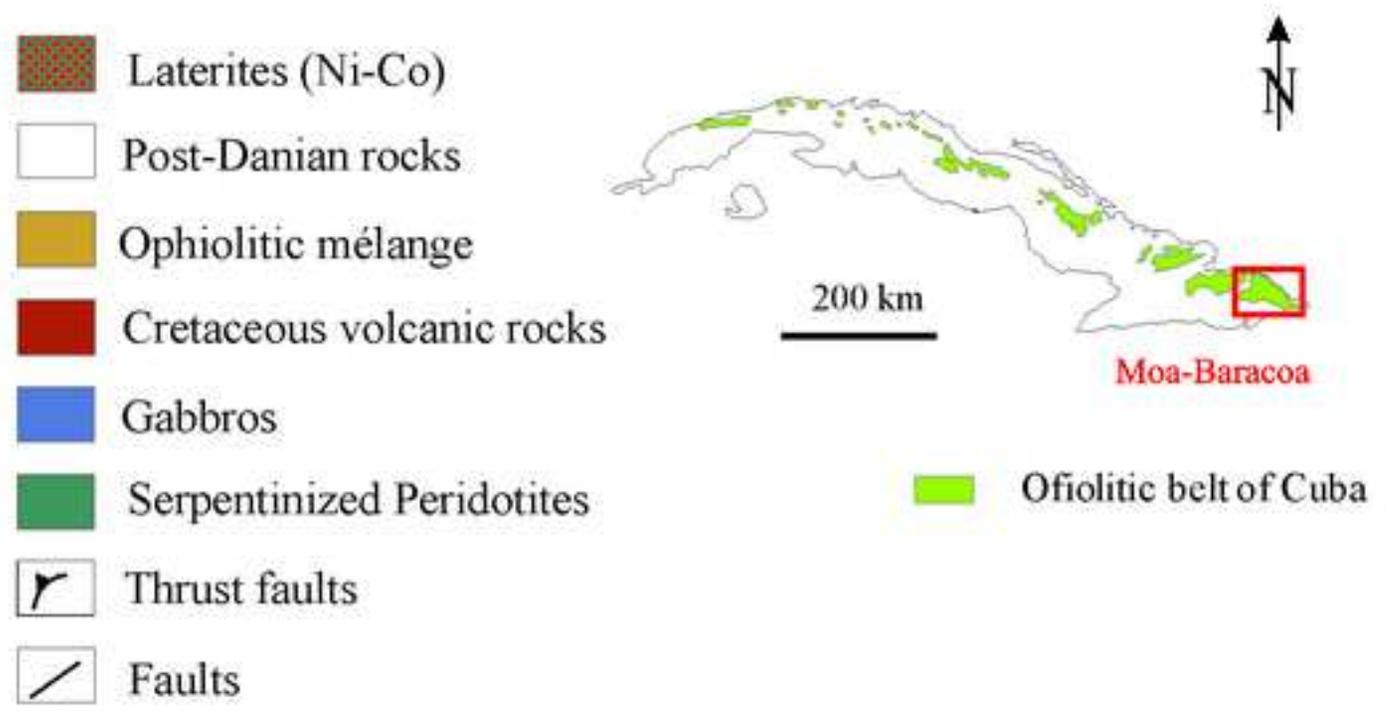


Figure 2

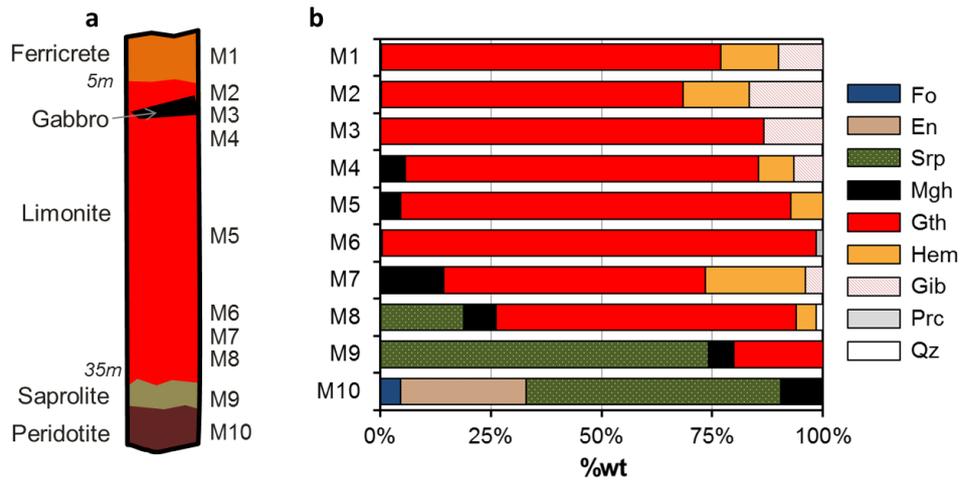


Figure 2

Figure 3

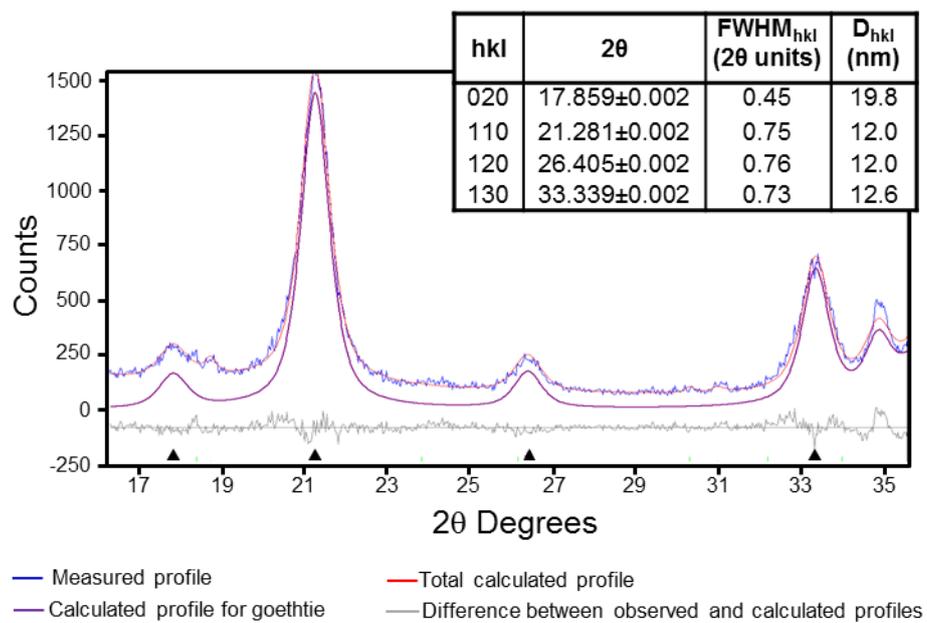


Figure 3

Figure 4

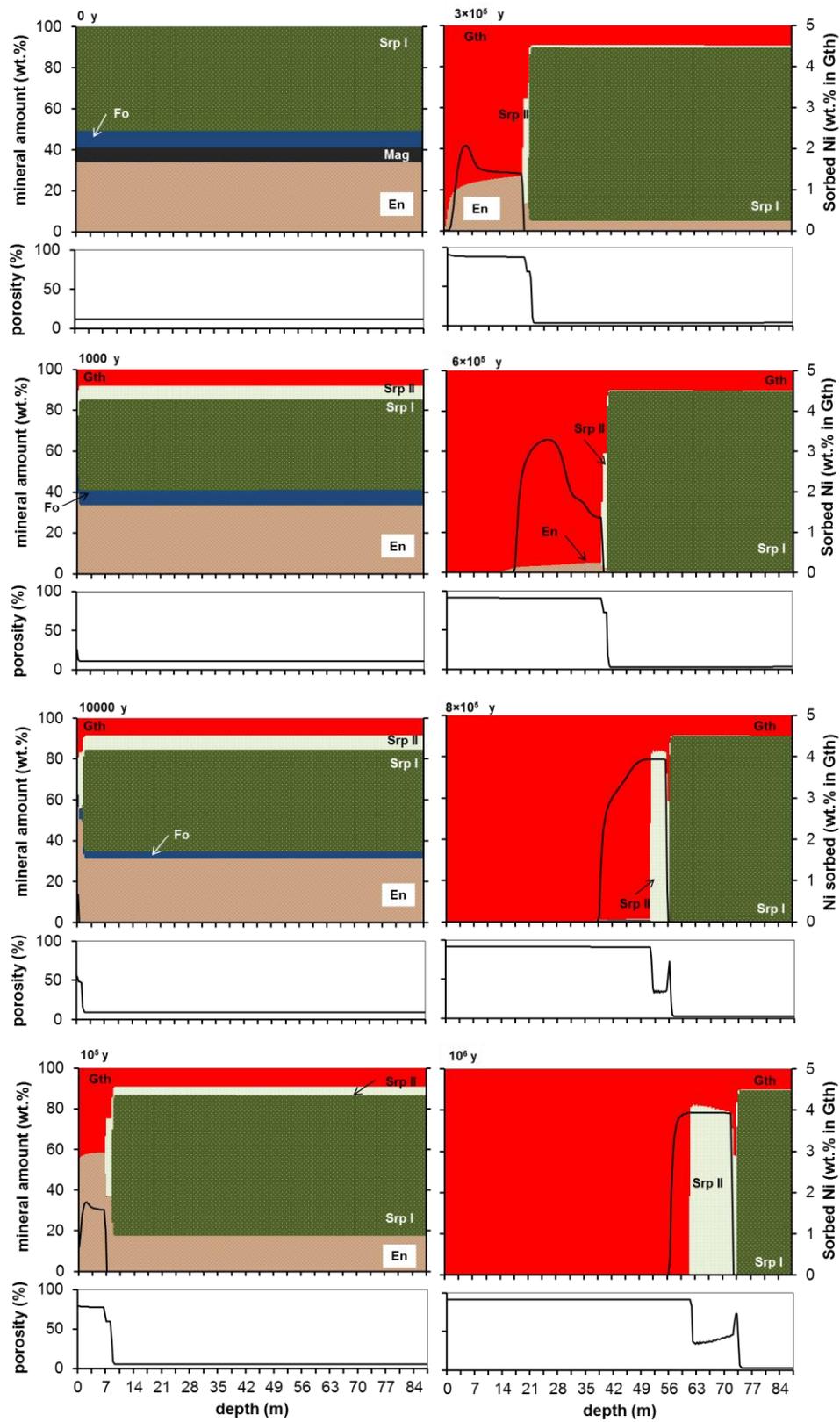


Figure 4

Figure 5

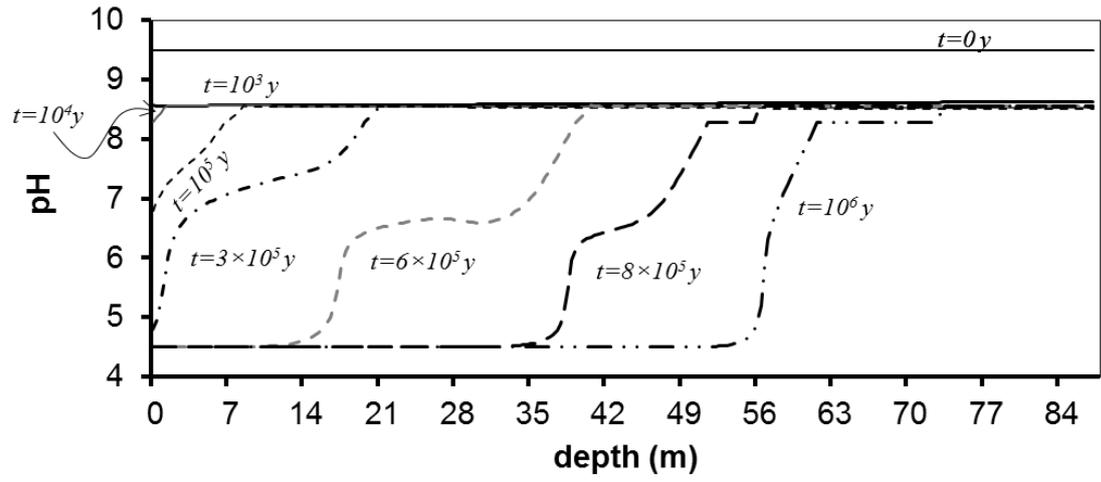


Figure 5

Figure 6

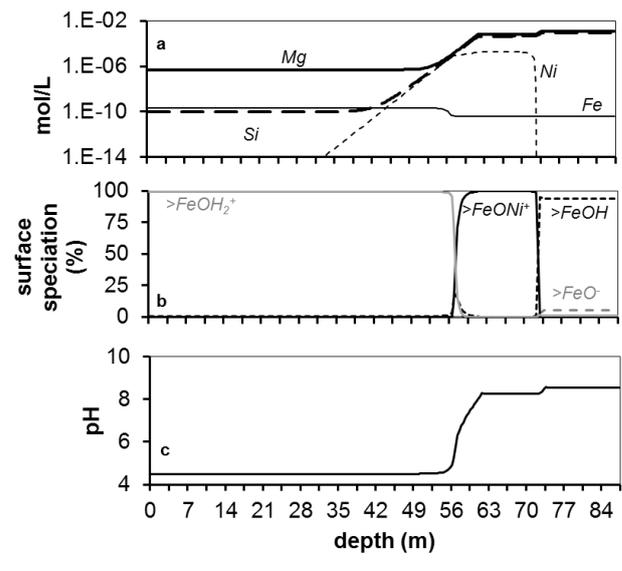


Figure 6

Figure 7

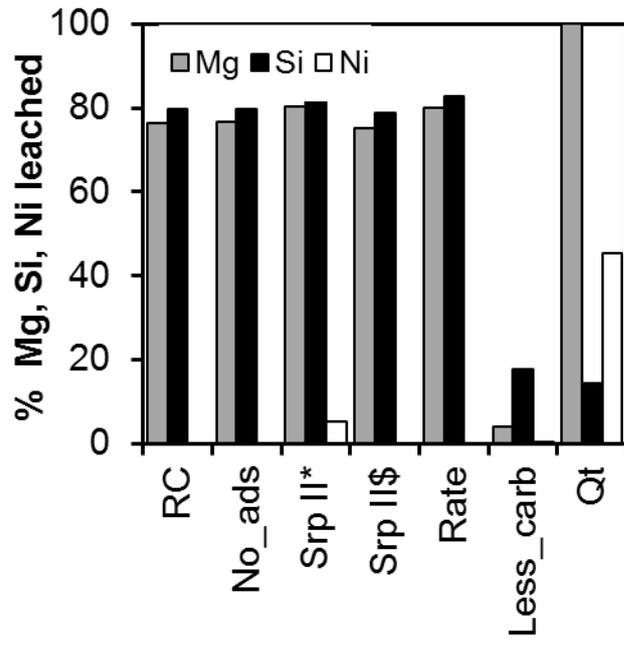


Figure 7

Figure 8

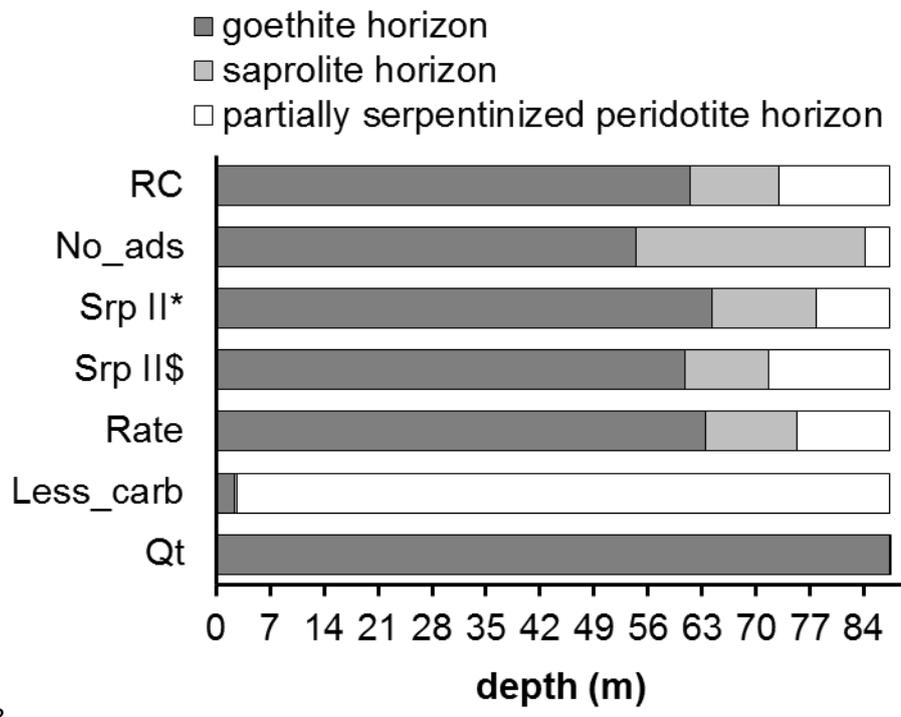


Figure 8

Figure 9

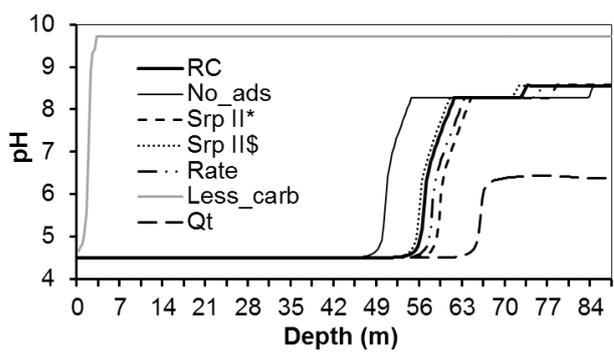
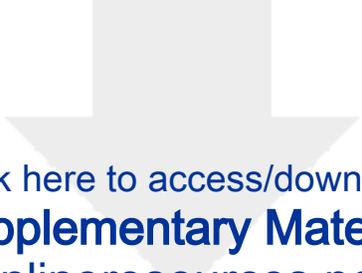


Figure 9



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