Goethite aging explains Ni depletion in upper units of ultramafic lateritic ores from New Caledonia

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ABSTRACT

An upward loss of Ni is commonly reported in the oxide-rich unit of Ni-laterite deposits developed over ultramafic rocks in tropical regions, especially in freely drained and deeply weathered regoliths. Because goethite is the major mineral constituent of such oxide-rich units, this Ni loss has been linked to compositional changes in goethite. In the present study, we have investigated possible correlations between Ni contents in the bulk laterite, and the evolution of goethite in terms of composition and crystallinity, in two Ni-rich and one Ni-poor lateritic profiles from New Caledonia. Ni K-edge Extended X-ray Absorption Fine Structure (EXAFS) spectroscopy indicates that goethite hosts the main fraction of Ni in the three profiles investigated. Asbolane/lithiophorite identified as accessory minerals by x-ray diffraction (XRD) have little effect on the vertical variations in bulk Ni content in spite of the fact that the Ni contents of these Mn-oxides can be significant at certain depths. The gradual decrease in Ni content from the bottom to the top of the three Ni lateritic profiles correlates with a decrease in the Ni content of goethite as determined by electron probe micro-analysis. In addition, XRD data show that these compositional trends are linked to an increase of the mean coherent domain size of goethite. These observations support the hypothesis that Ni is expelled from goethite as it ages through successive dissolution and recrystallization cycles during the lateritization process. Comparison of laterites having different degrees of weathering suggests that this aging process could also play a significant role in the regional variability of Ni content in Ni-laterite deposits.

1. INTRODUCTION

Ultramafic rocks are characterized by low SiO₂ content (<45 wt%), high Mg and Fe contents, and elevated contents of other first-row transition elements like Ni, Cr, Mn, and Co. Intense weathering of such rocks under tropical conditions usually yields Ni-laterite ore deposits. Various classification schemes for such deposits worldwide have been proposed on the basis of geochemical and mineralogical patterns (Brand et al., 1998; Gleeson et al., 2003), as well as geomorphological history, climate, and drainage conditions (Golightly, 1981; Oliveira et al., 1992; Dalvi et al., 2004; Butt and Cluzel, 2013). Most of these Ni-laterite deposits can be described as consisting of two main units: a lower silicate-rich unit and an upper oxide-rich unit. The silicate-rich unit, also called saprolite, contains mainly Mg,Ni-bearing phyllosilicates including serpentine and, to a lesser extent, talc and smectite, together with variable amounts of residual silicates such as olivine and pyroxene. The oxide-rich unit, also called laterite *sensu stricto*, is dominated by Ni-bearing iron (oxyhydr)oxides, essentially goethite with minor amounts of hematite and maghemite, locally accompanied by Ni/Co-bearing manganese oxides such as lithiophorite and asbolane.

The Ni grade of oxide ores (below 1.5–2 wt% Ni) is lower than that of Ni silicate ores (between 1.5 and 2.5 wt% Ni). Moreover, these deposits usually exhibit a regular decrease in bulk Ni content upwards in the regolith (Trescases, 1973; 1979; Elias et al., 1981; Colin et al., 1990; Gleeson et al., 2004; Gaudin et al., 2005; Lewis et al., 2006; Soler et al., 2008; Thorne et al., 2009; Wells et al., 2009; Yongue-Fouateu et al., 2009; Sagapoa et al., 2011; Dublet et al., 2012). This geochemical trend could be related to a vertical change in Ni speciation. However, the mineralogical composition of the oxide-rich unit in Ni-laterite deposits worldwide is dominated by Ni-bearing goethite, which has long been proposed as the main Ni host, based on selective chemical extractions (Trescases, 1975; Schwertmann and Latham, 1986; Trolard et al., 1995; Oliveira et al., 2001; Chen et al., 2004), and micro-analyses

(Trescases, 1975; Som and Joshi, 2012; Zu et al., 2012). Bulk EXAFS spectroscopy studies have confirmed that Ni-substituted goethite is the major Ni-species in Ni oxide deposits from West Africa, the Philippines, and New Caledonia (Manceau et al., 2000; Fan and Gerson, 2011; Dublet et al., 2012).

Ni has been shown to stabilize amorphous ferric oxide precipitates and to retard their transformation into goethite in laboratory syntheses (Cornell et al., 1992). In addition, Ni for Fe substitution was limited to 5.5 mol% NiOOH in most of the synthetic and natural goethites reported in the literature (Gerth, 1990; Cornell et al., 1992; Singh et al., 2002; Carvalho-e-Silva, 2002; 2003), even for low-crystallinity, except in one study which suggested a substitution of 10 mol% Ni (Wells, 1998). Although the difference between the ionic radius of $^{VI,HS}Fe^{3+}$ (0.645 Å) and $^{VI}Ni^{2+}$ (0.69 Å) is rather small (Shannon, 1976), Ni substitution in the goethite structure induces a small but significant change in the cell parameters compared to that of other substituting elements (Gerth, 1990). However, the valence of Ni^{2+} is different than that of Fe^{3+} , and hydroxylation and local distortion of the goethite lattice have been observed upon isomorphous substitution of Ni^{2+} for Fe^{3+} . These changes have been explained by charge and size mismatch compensation effects (Gerth, 1990; Cornell et al., 1992; Singh et al., 2002; Carvalho-e-Silva, 2002; 2003). Incorporation of Ni^{2+} in goethite thus favors the formation of defects and is limited in highly crystalline goethite. Goethite usually forms from dissolution-reprecipitation reactions of more soluble ferric oxide precursors (Schwertmann and Murad, 1983; Cornell and Giovanoli, 1987). These formation processes as a function of goethite aging are thought to affect the extent of Ni incorporation in goethite. Such aging processes are likely to have occurred in thick lateritic profiles. For example, Kühnel et al. (1975) found an increase in the crystallinity of goethite with decreasing depth in two Ni-laterites from the Philippines and Indonesia, and Trescases (1975) reported an evolution from poorly crystalline Fe-oxides to better ordered goethite from the bottom to the uppermost part

of Ni deposits in New Caledonia. The above findings suggest that the decrease in bulk Ni content with decreasing depth in Ni laterite deposits worldwide could result from the aging of goethite upon lateritization. Such a hypothesis was proposed by [Oliveira et al. \(2001\)](#) in their study of nickel ore from Punta Gorda (Cuba). [Schellmann \(1983\)](#) combined data from many Ni-laterite deposits and showed a correlation between Ni substitution in goethite and goethite crystallinity. However, scarce evidence has been reported to date for a direct correlation between bulk Ni content and goethite crystallinity in thoroughly described Ni-laterite profiles.

In the present study, compositional changes of goethite were determined as a function of depth in three Ni laterite deposits from distinct geomorphological settings with different Ni contents. EXAFS spectroscopy at the Ni-K-edge, Rietveld refinement of powder XRD patterns, and Electron Probe Micro-Analysis (EPMA) were combined to determine Ni-speciation and content, crystallite size, and structural strain in goethite.

2. MATERIALS AND METHODS

2.1. Geological history and description of samples

The New Caledonian peridotitic ophiolite was obducted on the Norfolk ridge during the late Eocene ([Cluzel et al., 2001](#)) and then exposed to cyclic periods of erosion and lateritization that shaped the main landforms of this major geomorphological unit ([Chevillotte et al., 2006](#)). Such landforms cover one third of the island and account for one of the biggest Ni reserves in the world ([Dalvi et al., 2004](#)). Previous studies distinguished the large peneplains isolated by cross-cut ridges in the South from the alignment of klippe in the Center and North of the main island ([Trescases, 1975](#); [Sevin et al., 2012](#)). This differentiation testifies to post obduction tectonic uplift and faulting, leading to relief inversion ([Chevillotte et al., 2006](#); [Sevin et al., 2012](#)). The deeply weathered peneplains of the South are commonly described as endorheic basins or weathering cells, separated by narrow rock outcrops along

the ridges. Erosion led to lacustrine deposits and deep river incisions, initiating the relief inversion and the formation of plateau capped by iron pans, which are similar to those described in the North on higher elevation klippe.

Three drill cores provided by two mining companies, Koniambo Nickel Society (Y5) and Vale NC (S4 and S78), were selected for this study as representative of the freely drained lateritic regoliths developed on the ultramafic rocks of New Caledonia (Figure 1). The three regolith profiles belong to two distinct geomorphological units of the North and South of the main island. Core Y5 (64 m deep) was drilled at the edge of a high elevation plateau (880 m above sea level) capped by a residual iron pan. It belongs to the Koniambo klippe of the Northern Province. The oxide-rich unit has a rather high Ni grade (1.4 wt% NiO on average) and its underlying saprolite unit, mostly formed on harzburgite, is deeply fractured and mineralized (Perrier et al., 2006; Fandeur, 2009; Dublet et al., 2012). The two other cores (S4 and S78) come from the deeply incised peneplain capped by an iron pan of the Goro region in the Southern Province (Figure 1). The corresponding lateritic profiles were developed on layered peridotites with abundant intrusive bodies and belong to a low elevation plateau deeply incised by the Kue River (Figure 1). Located at the edge of a plateau in the Kue watershed, core S4 (217 m above sea level, 67 m deep) represents a rather high Ni grade laterite (average is 1.5 wt% NiO in the oxide-rich part). In contrast, core S78 (236 m above sea level, 43 m deep), which occurs in a zone shaped by dolines near the Xere Wapo Lake, represents a low Ni grade laterite (average is 0.7 wt% NiO in the oxide-rich part).

2.2. Samples preparation and analyses

Each sample chosen for study is representative of a 10 cm to 1 m long section, centered at a specified depth along the cores. One half of each core section was dried at 105°C for 12 to 24 hours, ground to powder, and homogenized. The compositions of powder samples were

then analyzed by ICP-AES. Samples were stored under ambient conditions in sealed containers and were later analyzed by XRD and EXAFS spectroscopy to determine crystalline phases present and Ni speciation. The second half of each core section was used to prepare hand-polished thin sections after impregnation in epoxy resin for scanning electron microscopy-energy dispersive x-ray spectroscopic (SEM-EDXS) analysis and EPMA. In the case of the Y5 core, it was also used to perform complementary x-ray fluorescence (XRF) analyses. The location of samples analyzed by these various techniques is provided in [Figure 2](#).

2.2.1 Chemical and mineralogical analyses

Bulk contents of major (SiO_2 , MgO , Fe_2O_3 , Al_2O_3 , TiO_2 , K_2O , CaO , Na_2O , MnO , P_2O_5) and trace (Ni, Co, Zn, Cu, Cr, V) elements were determined by ICP-AES with a Perkin Elmer optima 3300 DV after alkali fusion of powder samples with lithium tetraborate. Complementary XRF analyses, performed on samples from the other half of the Y5 core, are reported in [Dublet et al. \(2012\)](#). EPMA analyses were performed on thin sections and/or pressed pellets with a CAMECA SX50 equipped with four Wavelength Dispersive Spectrometers (WDS), operating at 15 kV and 30 nA at the Centre d'Analyse des Minéraux de PARIS (CAMPARIS, Université Pierre et Marie Curie, Paris, France).

Mineralogical analyses were performed by XRD with a PANALYTICAL[®] Xpert Pro MPD diffractometer using Co $K\alpha$ radiation in order to minimize x-ray absorption by iron. Data were recorded over the $5\text{--}100^\circ 2\theta$ range, with $0.017^\circ 2\theta$ steps, requiring 4–8 hours per sample. Goethite, hematite, chromite, gibbsite, talc, quartz, asbolane, lithiophorite, chlorite, and enstatite were identified with JCPDS references # 00-017-0536, #00-024-0072, #00-034-0140, #00-029-0041, #00-019-0770, #00-005-0490, #00-043-1459, #00-041-1378, #00-019-0768 and #00-029-0853, respectively.

Rietveld refinement of the powder diffraction patterns was performed with the XND code developed by [Berar and Baldinozzi \(1998\)](#) in order to estimate the mean coherent domain (MCD) size of the goethite crystallites ([Fritsch et al. 2005](#); [Wang et al. 2008](#); [Hohmann et al. 2011](#); [Maillot et al. 2011](#)). Space groups, atomic positions, and isotropic Debye–Waller factors were taken from the following structure refinements: goethite (α -FeOOH: [Forsyth et al. 1968](#)), hematite (α -Fe₂O₃: [Blake et al., 1966](#)), chromite (FeCr₂O₄: [Hill et al., 1979](#)), gibbsite (α -Al(OH)₃: [Saalfeld and Wedde, 1974](#)), and talc (Mg₃Si₄O₁₀(OH)₂: [Gruner, 1934](#)). The asbolane/lithiophorite mixed phase was not included in the model because, to our knowledge, the structure of this complex mineral phase is not yet fully determined. Scale factors and cell parameters were refined for all phases. Unit-cell parameters, iron occupancy factors, and Voigt line-shape parameters were further refined for goethite. Anomalous scattering factors were calculated from Cromer (1983). Using the approach of [Young \(1995\)](#), size and strain broadening effects for goethite were estimated from Lorentzian and Gaussian line-width varying as a function of $1/\cos\theta$ and $\tan\theta$, respectively, and corrected from instrumental line-width (see [Wang et al. \(2008\) for details](#)). An isotropic strain parameter ε (rad) was derived from the refined isotropic Gaussian line-width w_G using the classical formula $\varepsilon = w_G \tan\theta$ taken at $\theta=45^\circ$. Because goethite crystallites are generally elongated along the [001] crystallographic axis (space group *Pbnm*), anisotropic size broadening was considered ([Fritsch et al. 2005](#); [Hohmann et al. 2011](#); [Maillot et al. 2011](#)). Lorentzian line-width parameters at $\theta=0$ (w_{L100} , w_{L010} and w_{L001}) were refined for the three principal crystallographic axes [001], [010], and [001], respectively. According to the XND code procedure ([Berar and Baldinozzi, 1998](#)), these anisotropic parameters were obtained from a decomposition of the Lorentzian line-shape into an isotropic contribution corrected by two anisotropic contributions along the [001] and [010] directions. MCD sizes along the three principal crystallographic axes were then calculated from the w_{L100} , w_{L010} , and w_{L001} values

using the classical Scherrer formula: $\text{MCD} [\text{hkl}] = 0.9 \lambda / w_{\text{Lhkl}} \cos\theta$, taken for $\theta=0$, and with $\lambda = 1.79\text{\AA}$ for Co $\text{K}\alpha_{1,2}$ radiation. The instrumental Lorentzian line-width of $0.076^\circ 2\theta$ limited the maximum measurable MCD to 120 nm, which was much larger than the sized obtained for the samples of this study.

2.2.2 Extended X-ray Absorption Fine Structures (EXAFS) spectroscopy

Bulk Ni K-edge EXAFS spectra of lateritic samples selected from the oxide-rich units of the three cores were collected on the high-flux wiggler beamline 11-2 at the Stanford Synchrotron Radiation Lightsource (SSRL, California, USA). Samples were analyzed at 10 K using a modified Oxford Instruments[®] liquid helium cryostat. Data were collected in fluorescence-yield mode with a Canberra[®] high-throughput Ge 30-element solid-state detector. The energy of the incoming x-ray beam was monochromatized using a Si(220) double-crystal monochromator over the energy range 8100 to 9100 eV. Energy was calibrated by setting the position of the first maximum of the first derivative of a Ni metal foil at 8333 eV. Selected lateritic samples from the oxide-rich unit were prepared as pressed pellets of finely hand-ground and homogenized powders without filler material. For each sample, between 4 and 20 scans were necessary to obtain an acceptable signal-to-noise ratio. EXAFS spectra were averaged using the SIXPACK[®] code ([Webb, 2005](#)). Data were then normalized and background subtracted using the XAFS[®] code ([Winterer, 1997](#)) to obtain experimental EXAFS spectra in the form of k^3 -weighted $\chi(k)$ functions. These were Fast-Fourier-transformed over the 2–11 $\text{\AA}^{-1}$ k -range using a Kaiser-Bessel window with a Bessel weight value of 2.5.

Averaged EXAFS spectra were analyzed by Principal Component Analysis (PCA) using the SIXPACK[®] code ([Ressler et al., 2000](#); [Webb, 2005](#)). The minimum number of principal components necessary to fit the whole set of experimental EXAFS spectra was chosen on the

basis of the minimum value of the Factor Indicator Function (Malinowski, 1977; 1991; Webb, 2005). The database of Ni K-edge EXAFS references included the same model compounds as those described in Dublet et al. (2012) (i.e. Ni-substituted goethites, and Ni-bearing phyllosilicates, Mn-oxides, and forsterite). Target Transformation (TT) was then used to select the EXAFS spectra of model compounds that can most likely represent the set of experimental EXAFS spectra (Malinowski, 1978; Ndiba et al., 2008). This selection was based on the quality of the TT fits assessed by the Normalized Sum of Squared Residual (NSSR: $\Sigma(k^3\chi_{\text{target}} - k^3\chi_{\text{transform}})^2 / \Sigma(k^3\chi_{\text{target}})^2$) (Figure A3). EXAFS spectra of the lateritic samples were then fit by linear combinations of the EXAFS spectra of these model compounds using a Linear Combination Least-Squares Fitting (LC-LSF) procedure (Isaure et al., 2002; Scheinost et al., 2002; Sarret et al., 2004; Voegelin et al., 2005; Ndiba et al., 2008). This procedure was performed using a homemade code based on the Levenberg-Marquardt minimization algorithm (Hohmann et al. 2011; Pantke et al. 2012; Dublet et al. 2012). Linear coefficients were only constrained to be positive. The accuracy of this LC-LSF procedure is considered between $\pm 5\%$ and $\pm 25\%$ of the stated values of each individual contribution, depending on the quality of the experimental data and on the occurrence of distinctive features in the data (Ostergren et al., 1999; Cances et al., 2005; 2008; Juillot et al., 2011). The standard deviation of the Ni-goethite component was specifically estimated on the basis of the range of values obtained for successive LC-LSF fits performed with various Ni-containing goethite model compounds in mixtures with the other model compounds (see Dublet et al., 2012 for details). The quality of these fits was assessed using the Normalized Sum of Squared Residual (NSSR: $\Sigma(k^3\chi_{\text{exp}} - k^3\chi_{\text{fit}})^2 / \Sigma(k^3\chi_{\text{exp}})^2$) (Table 1).

3. RESULTS

3.1. Geochemical trends along the oxide-rich unit of the three regolith profiles

Three main units can be distinguished for the three regolith profiles investigated: (1) bedrock, (2) saprolite, and (3) the oxide-rich unit. In order to use a common terminology to compare the three profiles on the basis of macroscopic observations and mineralogy we defined the oxide-rich unit as having a $\text{MgO}/\text{Fe}_2\text{O}_3$ ratio < 0.07 whereas the associated saprolite had a higher ratio. Indeed, the SiO_2 and MgO contents decrease whereas Fe_2O_3 contents increase markedly from the saprolite to the oxide-rich unit (Figure 2). Based on this definition, we estimated the thicknesses of the Y5, S4, and S78 oxide-rich units to be 34 m, 33 m, and 30 m, respectively. Within the oxide-rich units, we distinguished four sub-units: (i) transition laterite defined by $\text{SiO}_2/\text{Fe}_2\text{O}_3$ ratios higher than 0.11, (ii) yellow laterite with $\text{SiO}_2/\text{Fe}_2\text{O}_3$ between 0.11 and 0.23, (iii) red laterite with $\text{SiO}_2/\text{Fe}_2\text{O}_3$ between 0.01 and 0.11, and (iv) iron cap with $\text{SiO}_2/\text{Fe}_2\text{O}_3$ between 0.0 and 0.01. These distinctions correspond to significant geochemical and mineralogical changes observed in the weathering profiles (Figure 2). The transition laterite, which is 4, 1, and 0 meters thick for the Y5, S4, and S78 core samples, respectively, consists predominantly of ferric (oxyhydr)oxides (mainly goethite) and contains residual silica (in the form of phyllosilicates, quartz, and possibly amorphous silica) and often Mn (mostly as Mn oxides) (Figure 3). In contrast, the overlying yellow laterite is almost devoid of such elements (Figure 2); this sub-unit is 19, 36, and 17 meters thick for Y5, S4, and S78, respectively (Figure 2). The red laterite is 9, 3, and 8 meters thick for Y5, S4, and S78, respectively (Figure 2). Finally, the iron cap above the S78 oxide-rich unit is the thickest, reaching 3 m (Figure 2). Although these general chemical trends are similar for the three profiles, the average SiO_2 content in the S78 oxide-rich unit (1.36 wt%) is significantly lower than that in the S4 (3.54 wt%) and Y5 oxide-rich units (3.01 wt%).

There are also differences in the chromium, aluminum, and manganese contents in the three profiles examined (Figure A1).

The vertical changes in the NiO content are consistent with a division into two groups. Indeed, the NiO contents are rather similar in the Y5 (1.4 wt%) and S4 (1.5 wt%) oxide-rich units and lower in the S78 oxide-rich unit (0.7 wt%) (Figure 4; Table A1). However, in the three profiles, the bulk NiO content progressively decreases towards the surface of the oxide-rich units, reaching contents of 0.53, 0.48, and 0.28 wt% NiO at the top of the Y5, S4, and S78 profiles, respectively (Figure 4; Table A1). In the present study, the origin of the progressive Ni depletion from the bottom to the top of the oxide-rich units is the main emphasis of our investigation. For this reason the following sections focus on the analysis of Ni speciation and on goethite crystal chemistry in the oxide-rich units of the three profiles investigated.

3.2. EXAFS analysis of Ni speciation in the oxide-rich units

PCA analysis of the EXAFS spectra for 12 samples selected from the three oxide-rich units (black arrows in Figure 2) indicates that the Ni speciation is well represented by one to three principal components (Figure A2; Table A2). As indicated by Target transform analysis, the best candidates for these principal components are four synthetic Ni-goethites (Ni-Gt; Ni,Al-Gt; Ni,Al,Mn-Gt; and Ni-Gt “from Fe²⁺”), a natural sample with mixed asbolane and lithiophorite (Asb/Lit), a synthetic Ni-sorbed birnessite at pH 7, and two natural Ni-bearing serpentines (one Ni-rich and one Ni-poor) (Figure A3; Dublet et al., 2012).

The EXAFS spectrum of Ni-goethite alone reasonably matches the EXAFS spectra of some of the samples from the shallowest depths, but this is not the case for the deeper samples. Additional model compounds were included in the fit, provided that (i) they

accounted for more than 10 % of total Ni-bearing phases and (ii) they improved the quality of the fit by more than 10 % (Figure 5; Table 1).

Based on this fitting procedure, LC-LSF results indicate that Ni-goethite is the major Ni-bearing phase (Ni-Gt component = 61 to 84 % of total Ni), compared to Mn-oxides (Asb/Lit component = 16 to 39 % of total Ni) or serpentine (Ni-rich serpentine = 0 to 14 % of total Ni), in the three oxide-rich units (Figure 5; Table 1). These results also indicate significantly larger contributions of the minor model compounds in the deepest samples compared to the shallowest ones (at least 1.5 times more; Table 1). Moreover, addition of the Asb/Lit model compound to the LC-LSF procedure improves significantly the goodness of fits for the transition and yellow laterites (+ 27 to 68 %), whereas the improvement in fit is much lower in the red laterite or iron cap samples (+13 to 19 %; Table 1).

Although the asbolane/lithiophorite (Asb/Lit) and the Ni-poor serpentine (Ni-poor Srp) model compounds have rather similar spectra (see Supporting Information in Dublet et al., 2012), the Asb/Lit EXAFS spectrum gave clearly better fits than the Ni-poor Srp EXAFS spectrum, especially for the Y4 and S5 samples. This result is consistent with the predominance of Asb/Lit phases over serpentine in most samples of the oxide-rich unit, as determined by XRD (Figure 3). Accordingly, adding Ni-poor Srp to the Asb/Lit and Ni-Gt components did not improve the goodness of fit by more than 10%. The Ni-poor Srp component was not retained in the final fit solutions (Figure 5, Table 1).

3.3. Changes in Ni contents of goethites in the oxide-rich units

Fe-rich zones of the samples were analyzed in thin sections by EPMA in order to assess the variability of their composition at the micrometer scale (Table A3, Table A4). EPMA analyses approaching goethite stoichiometry were used to assess changes in the composition of goethite in the oxide-rich units of the profiles. Large standard deviations in these analyses

are due to the chemical heterogeneity of the analyzed materials that consist of intimately mixed and finely divided minerals. The association of goethite with minor proportions of other minerals identified by XRD such as Mn-oxides, hematite, gibbsite, phyllosilicates, or chromite cannot be excluded. Nevertheless, EPMA results indicate that Ni contents in goethite zones increase with depth (Figure 4b, Table A4). Indeed, these contents range from around 2.0 wt% NiO in goethite from the deepest samples to around 0.5 wt% NiO in goethite from the shallowest ones (Figure 4b; Table A4). Globally, the NiO content in goethite (Figure 4b; Table A4) is very close to the NiO content in the corresponding bulk samples from the oxide-rich unit (Figure 4a; Table A1), which is in agreement with the predominant incorporation of Ni into goethite, as indicated by EXAFS data (Table 1).

3.4. Crystallinity of goethite in the oxide-rich units

Rietveld refinement of powder XRD patterns from the three oxide-rich units confirm the major occurrence of goethite in the samples suggested by visual inspection of the patterns (Figure 3). An example of multiphase Rietveld full pattern fitting of goethite, hematite, and chromite in the bulk sample collected at 10.5 m depth in the S4 profile is displayed in Figure 6. The proportion of hematite determined from such a refinement ranges between 0.2 and 2 wt%, with the maximum value corresponding to the uppermost sample of the S4 regolith (i.e. at 2.7 m depth).

Interestingly, the Full Width at Half Maximum (FWHM) of the (110) XRD peak of goethite (i.e. the most intense) tends to decrease towards the surface for the three oxide-rich units (Figure A5). For S4 and Y5, the decrease in FWHM values is clearly more pronounced in the upper red laterite than in the lower yellow laterite (Figure A5). In addition to this general trend, FWHM values in the S78 samples were found to be lower on average than in

the S4 and Y5 samples. FWHM values are in the range reported by [Schellmann \(1983\)](#) for several oxide-rich deposits worldwide (0.4 to 1.05 °).

The Rietveld refinement of XRD patterns gave a good fit quality, with Rwp values ranging between 0.9% and 1.8%. The calculated MCD sizes range between 7 and 23 nm and tend to increase from the bottom to the top of the oxide-rich units ([Figure 4c](#)), irrespective of crystallographic direction (i.e. [001], [010], and [100]; [Figure A7](#)). This range of MCD sizes of goethite is consistent with those already reported in the literature. For example, [Schwertmann and Latham \(1986\)](#) reported MCD sizes ranging from 14 to 30 nm in the [110] direction for goethite from a toposequence in New Caledonian Ni-laterites. Other studies indicate MCD sizes ranging from 12 to 22 nm and from 11 to 18 nm in the [110] direction for goethite from Cuban and Brazilian Ni-laterites, respectively ([Oliveira et al., 2001](#); [Carvalho-e-Silva et al., 2002](#)). In our study, we also refined a strain parameter, which is related to unit cell deformation that can be caused, for instance, by structural defects. Strain was found to decrease from the bottom to the top of the oxide-rich units ([Figure A7](#)), except for the low values found for deeper samples of the S4 profile. Rietveld results thus indicate an increase in MCD size and a decrease in the amount of structural defects from the bottom to the top of the oxide-rich units investigated. In addition, consistent with FWHM results, MCD [100] sizes are significantly larger for S78 than for Y5 and S4, above 15 meters depth ([Figure A7](#)). Although less marked, this difference is also observed above 10 m depth, for the MCD [010] values.

4. DISCUSSION

4.1. Vertical evolution of Ni content and Ni speciation.

From the bottom to the top of the oxide-rich units of the three profiles, Ni contents decrease by a factor of 5 to 10, which suggests a significant loss of this element upon lateritization. This finding is in agreement with previous studies of similar Ni-laterite deposits (Trescases, 1973; 1979; Elias et al., 1981; Colin et al., 1990; Gleeson et al., 2004; Gaudin et al., 2005; Lewis et al., 2006; Soler et al., 2008; Thorne et al., 2009; Wells et al., 2009; Yongue-Fouateu et al., 2009; Sagapoa et al., 2011).

LC-LSF analysis of EXAFS data indicates that Ni is mainly hosted by goethite (~ 60 to 85 %; Table 1) in the three oxide-rich units S4, S78, and Y5, with the remaining proportion of Ni hosted by Mn-oxides (~15 and 40%; Table 1). However, the relative proportions of these two Ni species (Table 1) are not correlated with the decrease in bulk Ni contents towards the surface (Figure A8; Figure 4; Table A1). Similarly, the observed variations in Ni speciation (Table 1) do not correlate with the Ni contents observed for the three oxide-rich units.

These observations indicate that the vertical variation of the bulk Ni content observed for the three oxide-rich units is not well explained by a change in Ni speciation.

4.2. Correlation between Ni depletion and goethite crystallinity

Bulk NiO contents are roughly positively correlated with the NiO content in goethite, as estimated from EPMA analyses of Fe-rich zones (Figures 4 and 7). This correlation is also confirmed by the significant value of the correlation parameter ($\rho = 0.69$; Table 2) obtained after a Spearman correlation test between these two parameters. This likely relies on the fact that goethite is the major Ni-host in the oxide-rich units, as indicated by EXAFS analysis (Figure 5; Table 1). Such a correlation is consistent with the results reported for two Cuban lateritic samples (Oliveira et al., 2001). In that study, sequential chemical extractions indicate

that the ore sample with the lowest bulk NiO content was composed of goethite with the lowest bulk Ni content. Our results are also in agreement with those of [Becquer et al. \(2006\)](#) who reported the occurrence of goethite populations with distinct Ni contents in New Caledonian lateritic soils.

In the present study, the Ni depletion in goethite was found to be correlated with a significant increase of the MCD size of goethite from the bottom to the top of the oxide-rich units, as determined by Rietveld analysis ([Figure 4; Table A4](#)). This result is consistent with that of [Trescases \(1975\)](#), who also reported a decrease of the Bragg peak width of goethite from the “fine saprolite” (which corresponds to our definition of transition laterite and yellow laterite) to the red laterite in regoliths from New Caledonia. Combining these observations with sequential chemical extraction data, [Trescases \(1975\)](#) proposed that Fe-oxides were poorly crystalline in the “fine saprolite” and well crystallized in the red laterite. Our results are also consistent with those of [Kühnel et al. \(1975\)](#), who proposed an increase in the crystallinity of goethite from the bottom to the top of laterites from Philippines and Indonesia on the basis of XRD analysis of a few samples. Furthermore, our results show that the increase in the MCD size of goethite is observed in the three unit-cell directions with similar orders of magnitude ([Figure A7](#)), which suggests that the shape of the goethite particles is not significantly different from the bottom to the top of the New Caledonian laterites. This observation is consistent with TEM observation of goethites reported by [Trescases \(1975\)](#), who indicated no morphological change along the “fine saprolite” unit of a lateritic regolith from New Caledonia.

The results of a Spearman correlation test performed between the bulk NiO contents and the MCD size of goethite for our three oxide-rich units confirm that these two parameters are negatively correlated at 76 % for the [100] direction, 82 % for the [001] direction, and 90 % for the [010] direction ([Table 2](#)).

The above considerations indicate that the upward decrease of the bulk Ni content observed in the three oxide-rich units is related to both a decrease of the Ni content of goethite and an upward increase of the MCD size of this mineral species.

4.3. Role of goethite aging on the bulk Ni content as a function of depth

Because the lateritic regoliths investigated are freely drained (Trescases, 1975; Latham, 1986; Join et al., 2005), the intensity and duration of weathering are most likely to increase towards the surface. Vertical changes in the crystallinity and Ni content of goethite could thus be related to aging processes, which are known to influence the crystallinity and composition of synthetic goethite (Schwertmann and Cornell, 1991; Tufo et al., 2012; Liu et al., 2012). In addition, the lateritic regoliths show vertical changes in the physico-chemical characteristics of pore water that may also influence the crystallinity and/or composition of goethite. For example, a previous study of the Y5 regolith by Fandeur et al. (2009) found that pH values vary from 9 in the bedrock to 5 at the top. Because both acidic and alkaline pH values are known to favor goethite crystal growth (Schwertmann and Murad, 1983), pH may have an effect on goethite crystallinity in the New Caledonian laterites. However, pH values were found to vary only from 6 to 5 between the bottom and the top of the oxide-rich units, suggesting that pH alone cannot explain the observed changes in crystallinity as a function of depth.

The composition of the pore water is also susceptible to changes in the lateritic regoliths because it is influenced by mineralogy and by drainage conditions. For example, Join et al. (2005) observed a decreasing in conductivity from 400 $\mu\text{S}/\text{cm}$ in the bedrock to 25 $\mu\text{S}/\text{cm}$ in the iron crust in a regolith from the Tiebaghi massif (West coast of New Caledonia). In addition, the high pH values found in the silicate-rich unit of the regolith are likely to favor a significant dissolution of silicates into the aqueous form H_3SiO_4^- . Several laboratory studies

have demonstrated the possible influence of elements present in the aging solution on the crystallinity of goethite. Silica ions, for example, have been found to hinder the growth of goethite through sorption on the surfaces of growing goethite particles in both synthetic (Cornell and Giovanoli, 1987; Quin et al. 1988; Hiemstra et al., 2007) and natural (Kühnel et al., 1975) samples. Concentrations as low as 10^{-4} M of H_3SiO_4^- would be sufficient to stabilize any precursor phase against transformation to more stable phases such as goethite (Doelsch et al. 2000; Jones et al., 2009). In the present study, silicates occur at the bottom of the oxide-rich units and they are not detected upward in these units. Weathering of silicates can result in the release of significant amounts of dissolved silica in the pore water of the transition laterite, which could contribute to the poor crystallinity of goethite in samples collected at these depths compared with those collected at shallower depths. Among the impurities associated with goethite in the laterites (Figure 4; Figure A4; table A4), Al and Ni are also known to slow down goethite crystal growth (Schulze, 1984; Schulze and Schwertmann, 1984; Ruan and Gilkes, 1995; Cornell and Schwertmann, 1996; Krehula et al., 2005; Liu et al., 2012), whereas Mn has been shown to favor higher crystallinity (Stiers and Schwertmann, 1985). Surprisingly, chromium has been shown to either limit (Schwertmann et al., 1989) or favor (Kaur et al., 2010; Tufo et al., 2012) goethite growth. Nevertheless, only Ni shows a significant and regular decrease in content with decreasing depth in the oxide-rich units (Figures 4 and A4; Table A1), which could be related to the concomitant increase in the MCD size of goethites.

It is generally accepted that goethite forms via dissolution and reprecipitation reactions upon aging of an amorphous ferric oxide precursor (Schwertmann and Murad, 1983; Cornell and Giovanoli, 1987). In addition, isomorphous substitution of Ni^{2+} for Fe^{3+} in goethite is accompanied by local hydroxylation of the structure, which compensates for the difference in charge between the two cations (Carvalho-e-Silva et al., 2002; 2003). Such a charge mismatch

rather than the difference in effective ionic radii (0.69 and 0.65 Å for Ni^{2+} and Fe^{3+} , respectively) could limit Ni^{2+} incorporation in the goethite structure. In addition, as suggested by Schellmann (1983), the presence of Si^{4+} in goethite at the bottom of the oxide-rich unit could favor the accommodation of Ni^{2+} , while aging of goethite and expulsion of Si^{4+} would imply a concomitant expulsion of Ni^{2+} . Therefore, Ni could be expelled from goethite during its dissolution and precipitation cycles upon aging. The upward decrease of Ni content in goethite in the oxide-rich units (Figure 4; Table A4) could then be explained by aging processes leading to crystal growth and an increase in the MCD size of goethite (Figure 4).

Once expelled from goethite during aging, Ni could either sorb onto goethite particles or be leached from the oxide-rich unit. Ni sorption onto goethite strongly depends on pH, with a sorption capacity that decreases from ~80% of the initial Ni at pH 7 to ~40% of the initial Ni at pH 6 and to roughly 10% of initial Ni at pH 5 (Trivedi and Axe, 2001; Ponthieu et al., 2006; Arai, 2008; Fischer et al., 2007). The pH of the Y5 regolith was shown to range between 5 and 6, with the lower value corresponding to the uppermost samples (Fandeur et al., 2009). In addition, the vertical increase in crystallinity of goethite implies a decrease in specific surface area of goethite upwards in the profiles. As a consequence, the Ni sorption capacity of goethite is expected to be low and to decrease from the bottom to the top of the regolith. During the aging of goethite, Ni may have been leached, resulting in increasing Ni content with depth, which could explain the decrease of Ni content observed from the bottom to the top of the studied lateritic profiles.

4.4. Lateral variability of the bulk Ni content: the role of erosion and deposition of strongly weathered lateritic materials in the S78 profile

Our results show that the Ni contents in the S4 and Y5 oxide-rich units are higher than in S78 (Figure 4; Table A1). When considered together, the bulk NiO concentrations vs. MCD

size data from the three profiles are dispersed around a linear regression model (R^2 between 0.66 and 0.69; [Table 2](#)). However, when considered separately, the data from S4 and Y5 on the one hand, and from S78 on the other hand, better fit a linear regression model (R^2 between 0.66 and 0.94; [Figure 8](#)). The slope of the regression through the data for Y5 and S4 is significantly gentler than that through the data for S78 ([Figure 8](#)), independent of unit-cell direction. This difference in the relationship between Ni content and goethite crystallinity between the S4 and Y5 profiles and the S78 profile is attributed to the fact that goethites in the S78 profile have low Ni contents and large MCD sizes with narrow ranges compared to the two other profiles ([Figure 8](#)). These characteristics of goethites from S78 compare well with the lowest Ni contents found by [Schwertmann and Latham \(1986\)](#) in the most crystalline goethite in oxisols from toposequences in New Caledonia. In addition, goethite cell parameters in S78 are smaller than in S4 and Y5 ([Figure A6](#)). [Gerth \(1990\)](#) suggested that aging parameters such as temperature can induce lower values of a parameter. Goethite in the S78 oxide-rich unit is thus different from goethite in S4 and Y5, and similar to goethite occurring in the uppermost part of the other two oxide-rich units.

Results found by [Dublet et al. \(2014\)](#) on the same lateritic regolith lead to the hypothesis that the S78 regolith is composed of colluvial deposits originating from the uppermost part of the surrounding lateritic covers. This hypothesis is based on (i) color and textural heterogeneities related to materials from the iron cap in the oxide-rich unit down to 30 meters (ii) an atypical relative thickness of the weathering units (a very thick oxide-rich unit on a very thin saprolite, [Figure 2](#)), (iii) the occurrence of a mineralogical discontinuity with siderite (FeCO_3) below 36 meters depth. This earlier study proposed that the S78 lateritic regolith was formed on a former doline that would have been buried by colluvial lateritic materials.

The S78 oxide-rich unit is thus considered to be a reworked profile composed of strongly weathered lateritic materials (i.e. Ni-poor and well-crystalline goethite) that originate from the upper horizons of the surrounding oxide-rich covers. Secondary weathering of these reworked materials is not excluded. Such a process would have contributed to further leaching of Ni downward in this regolith by increasing the crystallinity of goethite and decreasing the capacity of goethite to host Ni. Secondary weathering would be consistent with the fact that compositional and mineralogical trends observed for goethite in the S78 regolith have smaller amplitudes than those observed in the S4 and Y5 regoliths. Crystal chemistry changes observed between *in situ* (S4 and Y5) and reworked (S78) profiles emphasize the importance of erosion/deposition and goethite aging during lateritization in controlling the vertical and lateral distribution of Ni in oxide-rich units of Ni-laterite deposits.

4.5. Comparison with other lateritic systems: the importance of drainage conditions

Our results show an upward increase in crystallinity of the main iron oxide (i.e. goethite) accompanied by a decrease of Ni impurities in its structure. They also show an upward increase in hematite content (Figure 3) that reddens the laterites. Such a reddening has also been reported in other Ni-laterites developed on ultramafic formations in New Caledonia (Trescases, 1975; 1979; Schwertmann and Latham, 1986; Becquer et al., 2001; 2006; Traore et al., 2008; Fandeur et al., 2009; Dublet et al., 2012), as well as in a large number of lateritic systems worldwide (Torrent et al., 1980; 1983; Schwertmann and Kampf, 1985; Ambrosi and Nahon, 1986; Beauvais and Tardy, 1991; Tardy et al., 1991; Beauvais and Colin, 1993; Beauvais, 1999). In addition, an upward decrease of the humidity was observed in the samples collected in S4 and S78 oxide-rich units (Figure A9).

Other lateritic systems have been shown to have changes in the main iron oxides as a function of depth. For example, Fritsch et al. (2005) studied a lateritic system from a humid

tropical region of the Brazilian Amazon Basin and reported an upward yellowing with an increase in the proportion of goethite and a decrease in hematite, in addition to an upward decrease of the crystallinity of hematite and an increase of Al substitution in goethite (from 15 to 33%). In this nearly symmetric system, the shallow horizons are more humid than the deeper ones (Figure A9; Fritsch et al., 2005). Greater water and Al activity in shallow horizons were interpreted as favoring Al-rich goethites over Al-poor ones and crystalline hematites during the dissolution and re-precipitation processes (Fitzpatrick and Schwertmann, 1982; Kampf and Schwertmann, 1983; Tardy and Nahon, 1985; Trolard and Tardy, 1987; 1989; Tardy et al., 1990; Fritsch et al., 2005). Changes in the composition and types of iron oxides can be consistently related to the water and solute activity and their evolution with time in lateritic profiles.

5. CONCLUSIONS

The results reported in this study provide direct evidence for a negative correlation between the bulk Ni content and the crystallinity of goethite as a function of depth in the New Caledonian Ni laterites. The upward decrease of the bulk Ni content observed in the lateritic regoliths from New Caledonia is proposed to be directly linked to an increase in crystallinity and a decrease in the Ni-hosting capacity of goethite, resulting from aging during lateritization under drier conditions. The upward decrease in bulk Ni content is also observed in several other Ni oxide deposits over ultramafic rocks. Therefore, this mineralogical and geochemical evolution of goethite is considered to likely reflect a generic process responsible for the vertical variability of Ni content in lateritic deposits. Finally, this evolution can also play a significant role in the spatial variability of Ni content, as illustrated by the difference observed between the lateritic regoliths consisting of *in situ* lateritic materials vs. those resulting from colluvial accumulation of already differentiated lateritic materials.

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ACKNOWLEDGMENTS

568 This study was supported by the Centre National de Recherche Technologique Nickel et
569 son Environnement (CNRT) in Noumea (New Caledonia) under the Project *Ni/Co*
570 *mineralization factors of laterites derived from ultramafic rocks of New-Caledonia*. CNRT is
571 a Public Interest Group funded by the French and New Caledonian authorities and research
572 organizations, as well as by international mining companies, for promoting local research
573 programs in the field of sustainable mining of geological resources. The authors wish to thank
574 the Koniambo Nickel Society (KNS) and the Vale NC Company for providing the core
575 samples. Michel Fialin and Frederic Couffignal (CAMPARIS center, UPMC) are
576 acknowledged for assistance during EPMA analyses. The technical staff at SSRL (Stanford,
577 USA) is acknowledged for providing good beam conditions during EXAFS measurements.
578 Portions of this research were carried out at the Stanford Synchrotron Radiation Lightsource,
579 a national user facility operated by Stanford University on behalf of the U.S. Department of
580 Energy, Office of Basic Energy Sciences. M. Wells and M. Economou-Eliopoulos are also
581 acknowledged for their advice that helped improving the quality of the manuscript.

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Figure A1: Bulk MnO, Cr₂O₃, and Al₂O₃ contents as a function of depth in the oxide-rich units of the profiles. See Figure 2 for complementary information on the NiO, Fe₂O₃, MgO, and SiO₂ contents in the profiles. The errors on the values are within the size of the points. Chromium content is essentially constant, in agreement with the persistence of chromite observed by XRD (Figure 3). Aluminum contents are constant in the Y5 and S78 oxide-rich units, whereas positive aluminum “anomalies” correlated with the presence of gibbsite are observed at the bottom of the S4 oxide-rich unit (Figure 3), which is likely related to gabbroic intrusions. Manganese contents remain below 0.41 wt% in the S78 oxide-rich unit, whereas in the S4 and Y5 oxide-rich units they reach much higher values in the yellow and transition laterites (3.6 wt% and 21.7 wt% MnO, respectively; Figure 2). These differences among the three profiles are consistent with XRD results that indicate the absence of Mn-oxides in the S78 oxide-rich unit, whereas in the two other regoliths these mineral species are detected in variable amounts (Figure 3).

Figure A2: Reconstruction of the Ni K-edge EXAFS spectra of selected samples from the three profiles with the first, the first two, the first three, and the first four components extracted from the PCA analysis. NSSR values correspond to: $\sum (k^3\chi_{\text{experimental}} - k^3\chi_{\text{reconstructed}})^2 / \sum (k^3\chi_{\text{experimental}})^2$. Adding the fourth principal component improved the reconstruction by less than 10% (Table A2). The IND parameter obtained from the PCA analysis increased with the number of components, indicating that a single component explains a large part of the variance of the data set (Malinowski, 1977; 1991; Webb, 2005). This result is explained by the similar shapes of the EXAFS spectra (Figure 5). However, only 64% of the variance is explained with the first component. The second and third components help explain 8% and 7% additional variance, respectively, whereas the fourth component explains only 1%. Therefore, the number of principal components for the LC-LSF is likely between one and three.

Figure A3: Results of the Target Transform performed on the relevant Ni-bearing model compounds within the 3 - 11.6 Å⁻¹ k-range with the 3 first principal components extracted from the PCA analysis of the whole set of experimental EXAFS spectra. * Ni co-precipitated goethite model compounds were synthesized following different procedures (see Dublet et al., 2012 for further details). ** Ni sorbed on birnessite at pH 7. The target transform analysis was performed by considering the three first components extracted from the PCA analysis and yield 10 probable Ni-bearing phases on the criteria of a R factor < 0.4. The best R factor values (≤0.2) were obtained for all synthetic Ni-goethites (Ni-Gt; Ni,Al-Gt; Ni,Al,Mn-Gt and Ni-Gt from Fe²⁺), a natural sample with mixed asbolane and lithiophorite (Asb/Lit), and a synthetic Ni-sorbed birnessite at pH 7 (Bir pH7). In addition to these good results of Target-Transform, barely acceptable results (R factor ≤ 0.31) were also obtained with the two Ni-rich and Ni-poor natural serpentine model compounds (Ni-rich srp and Ni-poor srp, respectively).

Figure A4: Contents of the main elements (Mn, Cr and Al) associated with goethite, as measured by EPMA on Fe-rich spots at various depths in the three oxide-rich units. The horizontal error bars represent the standard deviation of the content in goethite estimated by EPMA for each sample (see Table A4).

Figure A5: (top) Superposition of the normalized (110) XRD peaks of goethite in selected samples from the yellow laterite (YL), red laterite (RL), and iron cap (ICP) sub-units of the three oxide-rich units. (bottom) Vertical changes of the FWHM of the normalized (110) XRD peaks of goethite for all samples. The horizontal error bars represent a 10% error for each FWHM value. FWHM were measured on the diffraction patterns of the laterite samples after normalization of the intensity of the (110) peaks. The error is estimated of ± 0.01° for the red laterites, and ± 0.05° for the yellow and transition laterites, whereas the FWHM values were in ranges of 0.4 to 0.8° and 0.8 to 1°, respectively.

Figure A6: Unit-cell parameters (*a*, *b*, *c*) and unit-cell volume values determined by Rietveld refinement of the goethite XRD diffraction patterns, as a function of Ni bulk contents. Values of the *b* parameter, that are considered as the most sensitive to the Ni content (Gerth, 1990), are compared

with those obtained by Carvalho-e-Silva et al. (2002) (ref1) for synthetic Ni-goethites and natural goethites from Brazil, and with the relation $b=f(\text{Ni mol}\%)$ proposed by Gerth et al., 1990 (ref2). The cell parameters that we found vary within a significant range of values, which are however not correlated with the Ni content. This result indicates that the observed variations are likely related to the effect of other substituting atoms in the goethite studied, especially Al, Cr, Mn, and Co. In addition, cell parameters are found smaller in goethite from S78 compared to S4 and Y5. This is likely due to lower contents in Ni and in other impurities, in agreement with our interpretation that these goethites are further aged.

Figure A7: Vertical changes of the Mean Coherent Domain (MCD) size, along the crystallographic axes directions, and of an isotropic strain parameter determined for goethite, by Rietveld refinement of the bulk XRD patterns of samples collected in the oxide-rich units from the three profiles. The horizontal error bars represent the error on the MCD and Strain values estimated on Rietveld refined parameters.

Figure A8: Proportion of Ni associated with Mn-oxides, as assessed by LCF of Ni K-edge EXAFS spectra, as a function of the bulk Ni contents measured by ICP-AES, for the three oxide-rich units.

Figure A9: Comparison of the humidity profiles of the oxide-rich units of the S4 and S78 cores (blue lines) with those from a set of 650 cores drilled in the Goro area (grey dots). The various units indicated are: saprolite (SP), transition laterite (TL), yellow laterite (YL), red laterite (RL), and iron cap (ICP).

Table A1: Chemical composition (ICP-AES after acid digestion) of the three oxide-rich units, for the depths corresponding to EXAFS analyses.

Table A2: NSSR values* obtained for the reconstruction of the experimental EXAFS spectra of the samples from the three profiles with the 1st, the two 1st, the three 1st, and the four 1st components extracted from the PCA analysis.

Table A3: EPMA analyses on various mineral species in the oxide-rich units.

Table A4: Average content (Av., wt%) and standard deviation (SD) for NiO, MnO, Cr₂O₃, and Al₂O₃ in goethite as estimated by EPMA in the oxide-rich units of the three profiles. The *italicized* numbers in the first column indicate the number of analyses for each sample.

Table 1: Results of the LC-LSF fits of experimental EXAFS spectra.

Sample	Ni-Gt*	Asb/Lit*	Ni-rich Srp*	NSS R	SUM* *	%Imp ***
Y5 laterite						
Y5 - 3 m	83	17	/	0.05	90	19
Y5 - 11 m	81	19	/	0.06	99	17
Y5 - 15 m	70	30	/	0.04	109	44
Y5 - 27 m	71	29	/	0.04	102	43
Y5 - 34 m	65	21	14	0.04	101	45
S4 laterite						
S4 - 2.7 m	75	25	/	0.07	98	13
S4 - 10.5 m	84	16	/	0.03	102	19
S4 - 29.5 m	66	34	/	0.07	104	35
S4 - 32.5 m	61	39	/	0.03	104	68
S78 laterite						
S78 - 7.3 m	76	24	/	0.06	104	18
S78 - 15.4 m	79	21	/	0.06	107	18
S78 - 28.7 m	69	31	/	0.07	108	27

*Refers to the model compounds described in [Dublet et al. \(2012\)](#): Ni-Gt is a synthetic Ni-substituted goethite, Asb/Lit is a natural sample of mixed asbolane and lithiophorite from New Caledonia, Ni-rich srp is a natural Ni-bearing serpentine from garnieritic veins from New Caledonia

**Because proportions have been normalized to 100, the SUM column gives the actual sum of the LC-LSF fitting components.

***Percentage of improvement of the NSSR [(NSSR 2 – NSSR 1) / (NSSR 2)] when the Asb/Lit model compound is added (NSSR 2) compared to the LC-LSF fits with only Ni-Gt (NSSR 1). For the Y5 – 34m sample, the improvement of the NSSR with Ni-Gt, Asb/Lit, and Srp is 11% compared to that with only Ni-Gt and Asb/Lit.

Table 2: Results of the ρ correlation tests performed with the Spearman rank method between the bulk NiO content and various crystallographic and chemical parameters of goethite for the three lateritic profiles.

	FWHM	MCD (001)	MCD (010)	MCD (100)	NiO goethite
3 laterites – $N(FWHM) = 48$, $N(MCD, strain) = 22$, $N(wt\% NiO goethite EPMA) = 26$					
ρ corr. with bulk NiO (wt%)	0.80 **	-0.82*	-0.90**	-0.76**	0.69**
R^2	0.62	0.68	0.69	0.66	0.49

** Very significant test (p-value < 10^{-6})

* Significant test (p-value < 10^{-4})

The test with the strain parameter was not significant (p-value > 10^{-2})

Figure 1: Location of the three lateritic profiles at the scale of the New Caledonian peridotitic formations (a) and at the regional scale on altimetric maps (b and c). Maps (b) and (c) were generated by the Generic Mapping Tools (GMT) of the New Caledonian government (www.georep.nc, Sept. 2012). Darker colors correspond to higher altitudes. The map of New Caledonia (a) is adapted from [Cluzel and Vigier \(2008\)](#).

Figure 2: Vertical changes in the bulk content of SiO_2 , MgO , and Fe_2O_3 in the three lateritic profiles. The silicate-rich units are defined as bedrock (BR) and saprolite (SP), and the oxide-rich unit is subdivided in transition laterite (TL), yellow laterite (YL), red laterite (RL), and iron cap (ICP). SP-TL stands for a unit whose composition varies at the meter scale between that of transition laterite and saprolite units. Arrows indicate samples analyzed by EXAFS, EPMA, and XRD (Rietveld refinement).

Figure 3: XRD patterns of selected samples from the three profiles. gt= goethite, hem= hematite, chr= chromite, g= gibbsite, a/l= asbolane/lithiophorite, tlc= talc, srp= serpentine, kaol= kaolinite, qtz= quartz, en= enstatite, trem= tremolite, chl= chlorite, *= signal of a Kapton foil used for this sample only. The grey line for the S78 regolith corresponds to a unit of mixed saprolitic and lateritic materials (SP-TL on Figure 2), whereas black, orange, red, and brown lines for the three profiles correspond to samples from the transition laterite (TL), yellow laterite (YL), red laterite (RL) and iron cap units (ICP), respectively.

Figure 4: Content of NiO in the bulk samples (a) and in goethite, as determined by EPMA analyses (b), compared with the evolution of the MCD (001) of goethite determined by Rietveld refinement (c). Data are reported for the three oxide-rich units of the Y5, S4 and S78 profiles.

Figure 5: Ni K-edge experimental EXAFS spectra obtained for samples from different depths in the three profiles (black lines) and their LC-LSF best fits (red lines). See [Table 1](#) for quantitative results of LC-LSF fits.

Figure 6: Example of multiphase Rietveld refinement performed on the powder XRD pattern of the sample collected at 10.5 m depth in the S4 profile. Unit cell parameters, Mean Coherent Domain (MCD) size, strain parameters and cell parameters of goethite derived from these refinements are reported in [Figure A6](#) and [A7](#).

Figure 7: NiO contents in goethite measured by EPMA as a function of the bulk NiO content in the three profiles. The vertical error bars represent the standard deviation of the NiO content in goethite estimated from EPMA for each sample (see [Table 2](#)). The errors for the bulk NiO values are less than the size of the points.

Figure 8: Correlations between the Mean Coherent Domain (MCD) size of goethite in the [001], [100], and [010] directions obtained from Rietveld refinement of XRD patterns and the bulk NiO content in the three profiles. The dotted lines correspond to the linear regressions through the Y5 (gray), S4 (black), and S78 (blue) data. The vertical error bars represent the estimated 10% error on each MCD value. The errors for the bulk NiO values are less than the size of the points.