The accumulation of Ni in serpentines and garnierites from Falcondo Ni-laterite deposit (Dominican Republic) elucidated by means of μ XAS

Josep Roqué-Rosell^a, Cristina Villanova-de-Benavent^a and Joaquín A. Proenza^a.

Abstract:

The Falcondo Ni-laterite deposit (Dominican Republic) contains a significant amount of garnierites (Ni bearing Mg-phylosilicates) that are being extracted as Ni grade ores. In the present study a set of garnierite samples with different characteristic greenish colors and textures associated to different amounts of Fe-Ni-bearing serpentines, Ni-bearing serpentines, Ni-bearing talc and Ni-bearing sepiolites phases have been studied by means of EMPA, μ XRF and μ XAS in order to elucidate for the first time the accumulation of Ni associated to the development of garnierites. The EMPA showed the presence of Fe-Ni-bearing serpentine in the saprolite fragments and successive generations of garnierites sitting within the compositional ranges of serpentine (lizardite-népouite/chrysotile-pecoraite), talc (kerolite-pimelite) and sepiolite (sepiolite-falcondoite). The elemental maps obtained by means of μ XRF displays the Fe-rich protolith fragments coated and crosscut by Ni-bearing garnierite veins. The Fe K-edge μ XANES acquired on the selected samples demonstrated the presence of iron oxides, relicts of primary hydrothermal Fe-Ni-bearing serpentines within the saprolite and the development of Fe-Ni-bearing serpentines within the garnierite surrounding the saprolite fragments. In parallel the local environment of Ni determined by means of Ni K-edge μ EXAFS confirmed that Ni is initially associated within the primary hydrothermal Fe-Ni-bearing serpentines forming a Ni-Mg solid solution and that during the subsequent weathering process Ni is mobilized from the saprolite to the garnierites precipitating within the newly developed Fe-Ni-bearing serpentines forming Ni-Ni clusters. The Ni K-edge μ EXAFS also confirm that within the subsequent development and precipitation of garnierites Ni is found forming Ni-Ni clusters in Ni-bearing serpentine (lizardite-népouite/chrysotile-pecoraite), talc (kerolite-pimelite) and sepiolite (sepiolite-falcondoite). This paper explains the development and accumulation of Ni in garnierites Ni-laterite deposits, displays how the primary hydrothermal serpentine present in the saprolite fragments are weathered and how Ni is mobilized and accumulated forming clusters within the garnierites.

1. Introduction.

The Ni-laterite deposits are regoliths formed as a result of the weathering process of ultramafic rocks occurring under tropical and subtropical regimes. Under these conditions, with high temperatures and intense precipitations, the most soluble elements from the parent rock-forming minerals are leached. This results in the removal of Si and Mg and the accumulation of the less mobile elements (Elias, 2002; Freyssinet *et al.*, 2005; Golightly, 1981, 2010). During this process, the laterites develop two main horizons, a saprolite zone covered by a limonite zone, which in turn may be subdivided into from bottom to top: protolith (serpentinized peridotite), saprolite (consisting mostly of Ni-bearing serpentines and garnierite), limonite (formed by Fe-oxyhydroxides) and ferricrete.

The Ni-laterites host over 60% of the world land-based Ni resources (Gleeson *et al.*, 2003, Kuck, 2013), and the amount of Ni being extracted from laterite ores is increasing steadily (Mudd, 2010). It is accounted that about 10% of the world's Ni resources are found in the Caribbean region, and the Falcondo deposit is one of the largest hydrous Mg silicate-type Ni-laterite in the Caribbean, with estimated Ni reserves of about 79.2 million dry tons at a grade of 1.3 wt.% Ni (Falcondo Annual Report, 2010: http://www.falcondo.com.do/ES/Publicaciones/brochures/Memoria_FALCONDO_2010.pdf). In addition to its economic importance, Falcondo is an open air laboratory and allows a unique opportunity to study the weathering processes in laterites (Aiglsperger *et al.*, 2015; Villanova-de-Benavent *et al.*, 2014).

In Falcondo the main ores are the Ni-bearing serpentines and the garnierite from the saprolite horizon, the latter being the ones with highest Ni grades (e.g. Villanova-de-Benavent *et al.*, 2014). During weathering the Ni present in the limonite horizon is leached by meteoric solutions and it is incorporated in the serpentines from the saprolite and precipitates as garnierites in open fractures across the saprolite horizon. The term garnierite is a widely used field term to refer to the group of green, fine-grained, poorly crystallized, often intimately mixed nickel bearing magnesium phyllosilicates (e.g. Brindley & Hang, 1973; Springer, 1974; Brindley, 1978; Villanova-de-Benavent *et al.*, 2014). In the Falcondo Ni-laterite, these phyllosilicates include the Mg-Ni series lizardite-népouite and chrysotile-pecoraite (serpentine group minerals with the composition $(\text{Mg,Ni})_3\text{Si}_2\text{O}_5(\text{OH})_4$), kerolite-pimelite (invalid names for hydrated talc-like phases with the formula $(\text{Mg,Ni})_3\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot (\text{H}_2\text{O})$) and sepiolite-falcondoite $(\text{Mg,Ni})_4\text{Si}_6\text{O}_{15}(\text{OH})_2 \cdot 6(\text{H}_2\text{O})$).

These garnierites in the Falcondo Ni-laterite deposit display various shades of green which, in addition to characteristic mineralogy, textural features and chemical composition, have been used to classify them into five groups (Villanova-de-Benavent *et al.*, 2014). Also the secondary Ni-bearing precipitates sequence has been established with the serpentine minerals development first, followed by the precipitation of the talc-like phase, the subsequent formation of the sepiolite-falcondoite series, and finally Ni-free sepiolite and quartz (Galí *et al.*, 2012). This well established sequence of garnierite precipitation in Falcondo provides a unique framework to study the Ni geochemistry and the Ni-serpentine and garnierite development in Ni-laterites.

Pioneering synchrotron radiation studies by Manceau and coauthors dealt with the distribution of nickel in Ni-bearing Mg-phyllosilicates from New Caledonia (Manceau and Calas, 1985), Manceau *et al.*, 1985), Manceau and Calas, 1986). More recently, Fan and Gerson (2011) and

Dublet *et al.* (2012) discussing the distribution of Ni across a laterite profile and the incorporation of Ni in Ni-phyllosilicates in laterites from the Philippines and New Caledonia, respectively.

The results from Dublet *et al.* (2012) indicate that Ni accumulation across the laterite profile is mainly driven by the different weathering stages involved in the lateritization process. This study demonstrated that Fe-oxides (mainly goethite) are accumulating Ni at the most advanced stages of weathering within the limonitic horizon and that phyllosilicates (mainly serpentine) are accumulating Ni within the saprolite horizon. In this study, the EXAFS analysis indicate that the intracrystalline distribution of Ni within the secondary Ni-rich serpentine from the saprolite is not forming a homogeneous Ni-Mg solid solution but is clustered into discrete domains.

This is also in agreement with the results presented previously in garnierites by Manceau and Calas (1985) where bulk EXAFS measurements on lizardite-népouite and kerolite-pimelite samples demonstrate the heterogeneous solid solution of Ni within their structures. This paper also pointed out that the Ni distribution within lizardite-népouite was probably derived from the transformation of earlier serpentines by a Ni-enrichment and a subsequent Mg loss. But in the case of kerolite-pimelite it suggested that Ni heterogeneity takes place when these phases precipitate from solution, leading to the existence of distinct Mg- and Ni-octahedral layers within their structure (Manceau and Calas, 1985, Manceau *et al.*, 1985, Manceau and Calas, 1986).

Nevertheless, there are still missing gaps in the study of Ni in Ni-bearing phyllosilicates. Up to now most of the XAS work has been done by means of bulk analysis across several meters of a laterite profile, without taking into account the garnierites and their textures and not paying much attention to their relationship with the host saprolite. Only few studies have been published on sepiolite-falcondoite (Tauler *et al.*, 2009; Galí *et al.*, 2012, Villanova-de-Benavent *et al.*, 2014). In addition, despite the amount of research done, the majority of publications are mostly focused on Ni-laterites from New Caledonia (Manceau and Calas, 1985, Manceau *et al.*, 1985, Manceau and Calas, 1986, Dublet *et al.*, 2012), Philippines (Fan and Gerson, 2011) Indonesia (Golightly, 1979; Fu *et al.*, 2014), Australia (Elias *et al.*, 1981) and Africa (Dzemua *et al.*, 2013). Only being very few papers that have been published recently from the laterites in Caribbean region (Tauler *et al.*, 2009; Roqué-Rosell *et al.*, 2010; Galí *et al.*, 2012; Villanova-de-Benavent *et al.*, 2014).

Thus this paper aims to widen the understanding of the lateritization process, focusing on the garnierite development in Falcondo and bringing up to light the understudied laterites from the Caribbean. The aim of this contribution is to understand the Ni-crystal chemistry in serpentines and garnierites with the ultimate goal to achieve a better understanding on the supergene enrichment of Ni in laterite profiles.

In the present work, a set of samples containing Ni-bearing serpentines and garnierites are studied in an attempt to correlate their texture and the Ni enrichment that takes place during the lateritization in the Falcondo deposit. Initially a representative sample from each garnierite type was selected and characterized by means of optical microscopy (OM). Subsequently, the elemental compositions were obtained and the crystalline phases were identified by means of electron microprobe analysis (EPMA) and micro X-ray fluorescence (μ XRF). Then, representative points of interest were defined within these regions, and synchrotron radiation microfocus X-ray absorption spectroscopy (μ XAS) was deployed in order to acquire Fe K-edge micro X-ray absorption near edge structure (μ XANES) and the Ni K-edge micro Extended X-Ray Absorption Fine Structure (μ EXAFS). The μ XAS measurements were used to both identify the Fe-bearing minerals

present and to elucidate the chemistry and local environment of Ni within the phyllosilicates constituting the garnierites.

The results from each technique are combined to present the picture of the mineralogy and the Ni accumulation in Ni-bearing serpentines and garnierites and its speciation in the different garnierite types in Falcondo. This paper highlights the importance of the application of μ XAS in ore deposits and provides for the first time a detailed μ XAS study of garnierite development from the Caribbean Ni-laterites.

2. Materials and methods

2.1. Sampling

In the present work, five samples from the saprolite horizon exposed in the mining pit of the Falcondo Ni-laterite deposit were selected (**Fig. 1**). These samples are thought to be the most representative from each one of the five garnierite types described and studied in detail by Villanova-de-Benavent *et al.* (2014). The samples LC101A, LC100B and GAR2C on **Fig. 1a, b** and **c** do correspond to saprolite breccias and samples GAR6 and FALC3 on **Fig. 1d** and **e** correspond mostly to a massive block of garnierite. Samples L101A (type I), LC100B (type II), GAR2C (type III) consist of saprolite fragments crosscut by millimeter to centimeter thick garnierite veins (**Fig. 1a-c**) and samples GAR6 (type IV) and FALC3 (type V) represent massive garnierite aggregates with some remarkable differences in texture and green tonality (**Fig. 1d-e**).

2.2. Optical microscopy (OM)

Polished thin sections of the selected samples have been studied by means of optical microscopy with plane polarized light. The OM has been used to characterize the mineral textures and to select the representative regions of interest (ROI) to be studied in the samples by means of EMPA and μ XAS. On **Fig.1** each ROI contains one of the five garnierite types described in Villanova-de-Benavent *et al.* (2014) with the respective associated mineral assembly, including fragments of serpentinized peridotite, garnierite veins and quartz crystals.

2.3. Electron Microprobe Analysis (EMPA)

The polished thin sections were analyzed by EMPA in a Cameca SX-50 at the Centres Científics i Tecnològics of the Universitat de Barcelona. The measurement conditions were 20 kV, at 15 nA probe current, a spot size of *ca.* 2 μ m, and a counting time of 20 s per element. The calibration standards used were: hematite (Fe, LIF, K α), rutile (Ti, PET, K α), periclase (Mg, TAP, K α), rhodonite (Mn, LIF, K α), Al₂O₃ (Al, TAP, K α), Cr₂O₃ (Cr, PET, K α), diopside (Si, TAP, K α), NiO (Ni, LIF, K α) and wollastonite (Ca, PET, K α). Point analyses were performed directly on the carbon-coated surface of the sample on selected points corresponding to different regions of interest (ROI) in order to probe both the fragments of the saprolite and the garnierite veins.

Selected chemical analyses obtained by means of EMPA on the different samples are listed in **Table 1**, including the talc fraction (X_{talc}) of garnierites calculated according to Brindley and Hang (1973). The analyzed data points of the five samples are plotted in the ternary (Mg+Fe):Ni:Si diagram showing the composition of the garnierite types and the saprolite fragments (**Fig. 2**). This diagram also displays the compositional fields of the five garnierite types in Falcondo established

by Villanova-de-Benavent *et al.* (2014) to demonstrate the representativeness of the samples selected.

The analyzed spots on the saprolite breccias from the ROI's samples LC101A, LC100B and GAR2C are representative from both the saprolite fragments and the garnierite veins. By comparing the data from the saprolite and the garnierite across the different saprolite breccias the details on the chemical composition changes that take place during the weathering of the saprolite are obtained and the chemical compositions of serpentines and garnierites precipitated from the percolating waters and in contact with the saprolite are elucidated. The analyzed spots on the massive garnierites from the ROI's samples GAR6 and FALC3 are representative of garnierite mineralizations in absence of saprolite fragments and the data obtained provide insights on the chemical composition changes that take place during the dissolution and precipitation of garnierites in contact with the percolating waters from the top of the laterite profile and in absence of saprolite fragments.

2.4. Synchrotron experiments

In the present work the synchrotron experiments were performed on the beamline 10.3.2 at the Advanced Light Source (Marcus *et al.*, 2004). This is a hard X-ray microprobe on a bending magnet, delivering a monochromatic beam with a spot size ranging from about 1 to 15 μm . It is a dedicated beamline for environmental sciences with a 2-bounce Si(111) water cooled monochromator that covers the energy range from 2.45 keV to about 17 keV, and a 7 element Canberra Ge detector. The experiments consisted of three steps as in Mosselmans *et al.*, (2008; 2009) and Roqué-Rosell *et al.*, (2010). The first step allows identifying a good area of the sample by screening it and looking at the X-ray fluorescence counts from the multi-channel analyzer (MCA). The second step consists in performing X-ray fluorescence (μXRF) mapping to obtain the distribution of several elements simultaneously in the chosen ROI. And the third and last step is to collect X-ray absorption spectroscopy (μXAS) spectra on one or more spots of interest identified by the μXRF mapping.

2.4.1. μXRF

The μXRF elemental maps have been obtained by taking into account the intensity of the fluorescence lines corresponding to Cr $K\alpha$ at 5.415 keV, Fe $K\alpha$ at 6.405 keV and Ni $K\alpha$ at 7.48 keV, when rastering 4x4 mm samples' cross sections on selected ROI's at 2° to the beam. This fluorescence geometry was used to minimize overabsorption in the subsequent experiments below. The incident X-ray beam size was $\sim 5 \times 5 \mu\text{m}$ ($v. \times h.$) and the step size of 5 μm (which fits within the mineral aggregate size range from 10 to 500 μm) using an incident excitation energy of 10 keV. The obtained distribution of these elements is shown by the tricolor map in **Fig. 3**.

To assess the relationships between the Fe from the saprolite fragments and the Ni from the garnierite veins the scatter plots corresponding to Ni $K\alpha$ and Fe $K\alpha$ fluorescence intensities from each pixel on the ROI's μXRF mappings have been obtained in **Fig. 4**. When the points represented in the scatter plot are aligned with a positive slope means that both Ni $K\alpha$ and Fe $K\alpha$ intensities are dominant and it is indicative of cross-correlation, when the slope is negative it indicates that Ni $K\alpha$ and Fe $K\alpha$ are excluding each other showing anti-correlation. When more than one cloud of data appears it means that the plotted elements are present in two or more non-related phases.

In addition, a chemical map for Fe has been performed to plot the distribution for the different Fe-bearing phases present in the samples. The Fe chemical map relies on the fact that the Fe-K edge XANES varies with its chemical state, and thus different energies allows to plot the corresponding variations on Fe K α corresponding the different excited species that do have different sensitivities. Thus in the present paper, in order to obtain the Fe⁺² in distribution from the silicates and the Fe⁺³ distribution from the weathering by products, a set μ XRF mappings have been obtained at energies at 7.1, 7.11, 7.113, 7.125, 7.133, 7.35 and 10 keV. This allowed mapping at an energy just below, mapping at a range of energies just after and mapping at an energy far above the Fe K-edge. Then, these maps have been combined into a multi energy map that is capable to provide a rough Fe K-edge XANES spectra on each measured pixel.

The multi energy maps from each ROI in each sample have been subsequently analyzed with weighted sums of the representative species found on the same samples. These representative Fe K-edge spectra have been used as single compounds and have been fitted on every μ XRF pixel across the different energies as in Sutton *et al.* (1995). This allowed us to plot the distribution of the most relevant Fe bearing mineral phases with a ~ 5 μ m spatial resolution. The XY Display and Chemical Mapping scripts for μ XRF acquisition and analysis were used to obtain the elemental and chemical maps respectively. These scripts are freely distributed and available at <https://sites.google.com/a/lbl.gov/microxas-lbl-gov/software>.

2.4.2. μ XAS

In order to identify and quantify the Fe-bearing minerals in the samples, a range of Fe K-edge μ XANES were performed on representative selected spots in fluorescence geometry. A metal Fe foil was measured in transmission mode for calibration prior the experiments. Every measurement was taken by scanning the monochromator about 300 eV above the Fe K-edge (7.112 keV). To optimize the signal to noise ratio, about 40 spectra were acquired at each point. The resulting spectra have been fitted by means of principal components analysis (PCA) using the PCA package that can be found at <https://sites.google.com/a/lbl.gov/microxas-lbl-gov/software>. This software implements the PCA as described by Ressler *et al.* (2000). It analyzes a set of spectra to see if each acquired measurement can be represented as linear combinations of a smaller number of component spectra. In the present study, a range of Fe-bearing mineral standards acquired at the ALS beamline 10.3.2 have been used to fit the measured Fe K-edge μ XANES. The standards used in the PCA fittings are freely available and can be downloaded from the website <https://sites.google.com/a/lbl.gov/microxas-lbl-gov/databases>.

The local environment of Ni within the samples has been determined by means of Ni K-edge μ EXAFS following the same fluorescence geometry. A Ni metal foil has been measured for calibration prior to the experiments. Every single measurement has been taken by scanning the monochromator about 700 eV above the Ni K-edge (8.333 keV). To optimize the signal to noise ratio as many as 500 spectra were acquired at each point in order to achieve sufficient data quality. The EXAFS fittings have been performed using the Athena package (Ravel and Newville, 2005) and the refinement included only single scattering events, to account for the averaged distances and the coordination numbers of Ni within the phyllosilicates. The parameters chosen to be refined corresponded to the atomic potentials, the interatomic distance, the Debye–Waller factor, and the shell occupancy numbers. The length of the EXAFS signal is important to determine the number of parameters available to fit according to the relationship described by Galois

(2004). In the present EXAFS experiments for a data length Δk of $9.5 \text{ \AA}^{-1}$ and a filtering window in real space about $2.1 \text{ \AA}$ the number of independent parameters N_{ind} that can be refined is 12.

The Ni local environment has been fitted taking into account the parameters and constraints of Ni within the original mineral phases constituting the saprolite fragments and the garnierite veins. According to Manceau and Calas (1985), Manceau *et al.* (1985) and Manceau and Calas (1986) the interatomic distances between Ni and the second shell in hydrated phyllosilicates should be close to $3.06 \text{ \AA}$. In addition special attention has been given to the nature of the second coordination shell. In EXAFS the phase shift of the scattered photoelectrons depends on the chemical nature of the backscattering atom. This allows us to distinguish between Ni and Mg second coordination shells in phyllosilicates if some constraints are applied on Ni-Ni and Ni-Mg distances during the EXAFS fitting. However there were not enough N_{ind} parameters to model multiple Ni-Ni and Ni-Mg environments simultaneously on the same spectrum.

Thus to model the partial substitution of Ni by Mg within the crystalline structure the N_{ind} impose some limitation in terms of the EXAFS fittings. This has been overcome by performing simultaneously a lineal combination with k^3 -weighted $\chi(k)$ for second shells one corresponding to Ni and another to Mg. This implied refining the Ni and Mg shells with the constraint that these two components are made to add to one to account for Ni local environment. When doing that the same degree of disorder has been also defined in both shells by forcing them to share the same Debye-Waller factor. This additional last assumption kept the N_{ind} acceptable, and allowed the accounting for the amount of Ni and Mg second shells within the phyllosilicates.

3. Results.

3.1. Mineral textures observed by OM.

On **Fig.1** the two groups of samples can be seen, the one corresponding to fragments of saprolite cemented with a fine green garnierites **Fig. 1 a-c** and the one corresponding to massive green garnierites **Fig. 1 d-e**. All samples exhibit changes in color and texture in function of the garnierite assemblies and types as described by (Villanova-de-Benavent *et al*, 2014) and each selected ROI within each sample contain a representative selection of the mineral assemblies that correspond to the different garnierite types in Falcondo.

Under the OM the ROI from sample LC101A on **Fig. 1a** corresponds to saprolite fragments that are cemented mostly by type I garnierite. This sample corresponds to saprolite fragments surrounded by yellowish pale green garnierite veins with some relict chromian spinel grains. The ROI from sample LC100B on **Fig. 1b** corresponds to saprolite fragments cemented mostly by greenish type II garnierite and with euhedral quartz crystals filling the voids. The ROI from sample GAR2C on **Fig. 1c** corresponds to a saprolite fragments cemented mostly by type III garnierite. This garnierite has an intense green color, forming coatings with botryoidal features and it is intergrown with quartz crystals. The development of the garnierite type II, and III coatings accompanied by the presence of euhedral quartz confirms that these garnierites have been precipitated in open spaces from an aqueous solution.

The saprolite fragments from the ROI's on samples LC101A, LC100B and GAR2C on **Fig. 1** display a distinctive heterogeneous degree of serpentinization and weathering at millimeter scale. Most of the saprolite fragments on sample LC101A on **Fig. 1a** display pale yellow veinlets possibly related

to primary hydrothermal serpentine that are associated to green-brown color material which is thought to be a highly serpentinized Fe-rich fragments. The saprolite on sample LC100B on **Fig. 1b** display a pale yellow serpentinization mesh corresponding to the least serpentinized regions associated to green-brown central cores corresponding to highly serpentinized Fe-rich regions. On sample GAR2C on **Fig. 1c** the saprolite consists mostly of heavily weathered and highly serpentinized Fe-rich fragments.

Under the OM the massive garnierites samples GAR6 and FALC3 are mostly free of saprolite fragments. The ROI from sample GAR6 on **Fig. 1d** can be described as fragments of turquoise-colored garnierite cemented by a later garnierite precipitate with minor amounts quartz grains. The GAR6 is mostly identified as type IV garnierite breccia. The ROI from sample FALC3 on **Fig. 1e** has the most distinct texture when compared to all the garnierites described above. Sample FALC3 is identified as type V and displays light green undulated bundles of fibers accompanied only by tiny quartz veinlets with no traces of saprolite.

3.2. Chemical composition obtained by means of EMPA.

The composition for the saprolite breccias ROIs corresponding to samples LC101A, LC100B and GAR2C display two groups of analyzed points corresponding to the saprolite fragments and sitting on the lizardite-chrysotile compositional domain and the the garnierite veins sitting on a compositional domain corresponding to a mixture of serpentine (lizardite/chrysotile-népouite/pecoraite) and talk-like (kerolite-pimelite) (**Table 1, Fig. 2**). The selected ROIs from the massive garnierite samples GAR6 and FALC3 are saprolite free and their corresponding analyzed spots are clustered in a single compositional domain (**Table 1, Fig. 2**). The overall analyzed compositional spots show a trend that is characteristic of the development of the five types of garnierites in the Falcondo Ni-laterite deposit described on Villanova-de-Benavent *et al.*, (2014).

The composition from sample LC101A displays the lizardite-chrysotile compositions from the saprolite fragments and a mixture of serpentine (lizardite/chrysotile-népouite/pecoraite) and talk-like (kerolite-pimelite) compositions corresponding to type I garnierite. The garnierite on LC101A has a remarkable content of Ni (1.2-8.9 wt.% NiO) and Fe (2.7-8.9 wt.% Fe₂O₃) (**Table 1, Fig. 2**). The sample LC100B also displays the lizardite-chrysotile compositions corresponding to the saprolite fragments and a mixture of a serpentine (lizardite/chrysotile-népouite/pecoraite) and talk like (kerolite-pimelite) corresponding to type II garnierites. The garnierite on LC100B has a higher Ni content (21.6-25.2 wt.% NiO) and much lower Fe content (around 0.5 wt.% Fe₂O₃) than sample LC101A (**Table 1, Fig. 2**). The saprolite breccia GAR2C also displays the lizardite-chrysotile compositions corresponding to the saprolite fragments and a mixture of serpentine (lizardite/chrysotile-népouite/pecoraite) and talk-like (kerolite-pimelite) corresponding to type III cgarnerites. The garnierite from sample GAR2C is closer to the kerolite-pimelite Ni-dominant end members with a Ni content ranging from 29 wt.% to 41 wt.% NiO and no significant amounts of Fe were detected (**Table 1, Fig. 2**).

The selected ROIs from the massive garnierite samples GAR6 and FALC3 are saprolite free (**Fig. 1, 3**) and their corresponding analyzed spots are clustered in a single compositional domain. The compositions for sample GAR6 correspond to a mixture of serpentine (lizardite/chrysotile-népouite/pecoraite) and talk like (kerolite-pimelite) sitting within the type IV garnierite domain with a variable Ni content ranging from 24.2 wt.% to 31.8 wt.% NiO and with almost no Fe (**Fig. 2; Table 1**). The compositions for sample FALC3 do not sit on serpentine or talk-like compositions

but on the sepiolite-falcondoite series sitting within the type V garnierite domain and with the lowest Ni content in garnierites ranging from 12.3-26.8 wt.% NiO and without significant amounts of Fe (**Fig.2; Table 1**).

3.3. Elemental Fe, Cr and Ni distribution obtained by means of μ XRF.

The elemental maps obtained on the saprolite breccias ROIs corresponding to samples LC101A, LC100B and GAR2C display differences and variations of the elemental distribution of Ni, Cr and Fe that highlight the chemical and textural relationship between the saprolite fragments and the garnierite veins (**Table 1, Fig. 2**). In addition some differences are observed between the massive garnierites GAR6 and FALC3 on Ni distribution providing important hints on garnierites composition and texture (**Table 1, Fig. 2**).

The elemental distribution of Ni, Cr and Fe within the LC101A ROI shows that Fe is found associated to the saprolite fragments, Ni is localized mostly in the garnierite veins and Cr is found within the saprolite fragments probably as chromian spinel relicts. The obtained Ni:Fe scatter plot from LC101A in **Fig. 4** displays three clouds of pixels the first corresponding to one cloud of Fe K α fluorescence intensities not related to Ni K α , the second correspond to pixel fluorescence intensities of Ni K α not related to Fe K α and the third group of pixels where the fluorescence of Ni K α is anti-correlated to the fluorescence of Fe K α . The first cloud represents the Fe-bearing serpentine from the saprolite fragments, the second cloud is related to the presence the Ni-bearing serpentine and talc-like phases constituting the type II garnierite and the third cloud is thought to correspond to Ni and Fe-bearing serpentine and talc-like phases constituting the type I garnierite in which Ni and Fe are excluding each other.

As in LC101A the elemental distribution of Ni, Cr and Fe within the LC100B ROI on **Fig. 3** shows that Fe is found principally associated to the saprolite fragments, Ni is found in the garnierite veins and that Cr is also present in chromian spinel relicts. The mapping on LC100B displays some voids corresponding to the secondary precipitated quartz. The obtained Ni:Fe scatter plot from LC100B in **Fig. 4** displays two clouds of pixels corresponding to one cloud of pixel fluorescence intensities of Fe K α not related to Ni K α and a second cloud of pixel fluorescence intensities of Ni K α non related to Fe K α . However the inset graph shows that there is still a small third group of pixels where the fluorescence of Ni K α is anti-correlated to the fluorescence of Fe K α but much less significant than in LC101A. The first cloud represents the Fe-bearing serpentine from the saprolite fragments, the second cloud is related to the presence the Ni-bearing serpentine and talc-like phases constituting the type II garnierite and the residual third cloud corresponds to Ni and Fe-bearing serpentine and talc-like phases constituting the what is left of type I garnierite.

The elemental distribution of Fe, Cr and Ni within the GAR2C ROI on **Fig. 3** shows a heavily weathered and fragmented saprolite that contains most of the Fe. The saprolite fragments are enclosed within a Ni rim and contain some tiny Cr hotspots corresponding to chromian spinel relicts. The elemental map displays a complete separation between Fe and Ni-bearing phases which is also confirmed with the Ni:Fe scatter plot in **Fig. 4** in which unlike LC101A and LC100B samples no anti-correlation between Ni K α and Fe K α has been observed. On GAR2C scatter plot there are only two groups of pixels corresponding to fluorescence intensities of Fe K α non-correlated to Ni K α and fluorescence intensities of Ni non-correlated to Fe. The first cloud represents the heavy weathered Fe-bearing serpentine from the saprolite fragments and the

second cloud is related to the presence the Ni-bearing serpentine and talc-like phases constituting the type III garnierite.

The elemental distribution of Ni, Cr and Fe within the saprolite free samples GAR6 and FALC3 ROIs are shown in **Fig. 3**. Sample GAR6 show a high content of Ni across the ROI with no detectable amounts of Fe or Cr. However some variations in Ni concentrations can be seen in the elemental map depicting a garnierite breccia with lower Ni content garnierite fragments (in dimmer green color) surrounded by a garnierite cement with higher contents of Ni (in a brighter green color). The elemental distribution within the FALC3 ROI shows a high content of Ni with no significant amounts of Fe or Cr. But differently to GAR6 the Ni is mostly uniformly distributed across the entire ROI, except for the rims of some fibrous aggregates. The elemental mapping on FALC3 shows a Ni distribution matching a distinctive elongated texture consistent with the crystalline habit to a mineral from the sepiolite-falcondoite series.

3.4. Fe-bearing mineral phases identification obtained by means of Fe K-edge XANES.

The Fe-bearing mineral phases have been identified on the saprolite breccias ROIs on samples LC101A, LC100B and GAR2C (**Fig. 3**). The mineral composition of the saprolite fragments and the associated garnierite show a trend across which is agreement with the observed mineralogy and texture associated to the weathering process the saprolite during the garnierite development.

The Fe chemical map on LC101A to plot the distribution of Fe^{+2} and Fe^{+3} has been obtained in **Fig. 3**. The map demonstrates that the chemical reduced fraction of Fe is confined into veinlets within the saprolite and that the oxidized fraction of Fe constitutes the rest of the saprolite fragments and the surrounding type I garnierite. In addition the texture displayed in the chemical maps in **Fig. 3** indicates that the Fe^{+2} rich veinlets probably correspond to relics of primary serpentines of hydrothermal origin. According to the Fe K-XANES fittings on **Table 2** the more reduced Fe associated to primary hydrothermal serpentine corresponds to 61% serpentine, 9.7% maghemite and 29% forsterite (**5a**) and the more oxidized Fe corresponding to the bulk of the saprolite corresponds to 65.7% serpentine, 28.2% maghemite and 6.3% forsterite (**5b**) in agreement with a weathered hydrothermal serpentine. The Fe-K edge XANES fitting on type I garnierite confirms that Fe is completely oxidized with a content of 57% serpentine, 39.6% maghemite and 1.9% goethite (**5c**).

The distribution of Fe^{+2} and Fe^{+3} on LC100B shows that the reduced Fe fraction is confined into a vein within the saprolite and that the oxidized Fe fraction constitutes the rest of the saprolite fragment (**Fig. 3**). As in sample LC101A the texture displayed on the chemical map indicates that the Fe^{+2} rich veinlet probably corresponds to a relic of primary serpentines of hydrothermal origin. Two Fe K-edge XANES have been acquired to identify the main phases constituting the Fe^{+2} rich vein and the bulk of the saprolite fragment with a high content of Fe^{+3} . According to the fittings in **Table 2** the more reduced Fe associated to vein corresponds to 60% serpentine, 30.9% maghemite and 18.2% forsterite (**5c**) and the more oxidized Fe corresponding to the bulk of the saprolite corresponds to 13.2 % serpentine, 51 % maghemite and 37.7 goethite (**5d**).

The distribution of Fe^{+2} and Fe^{+3} rich phases on GAR2C in **Fig. 3** shows that the oxidized fraction of Fe constitutes the overall of the saprolite remains and no unweathered primary hydrothermal serpentine relicts with reduced Fe are detected. A Fe K-edge μ XANES has been acquired on one representative point of the protolith fragment (**5e**) and according to the fitting data on **Table 2** the

Fe is mostly in an oxidized form with a composition of maghemite 42.8%, serpentine 27.8% and goethite 29.6%. This data confirms that on GAR2C significant amounts of goethite started to develop suggesting an advanced weathering stage of the saprolite fragments.

3.5. Ni crystallochemistry studied by means of Ni K-edge EXAFS.

To study the Ni local environment on saprolite breccias Ni K-edge μ EXAFS have been acquired on representative points on LC101A, LC100B and GAR2C samples. The analyzed points correspond to saprolite fragments and garnierite veins with significant Ni content with the aim to elucidate differences on the local environment from lizardite-chrysotile within the saprolite and the lizardite/chrysotile-népouite/pecoraite and kerolite-pimelite mixtures constituting the garnierites.

On LC101A sample three Ni K-edge μ EXAFS have been acquired corresponding to the primary hydrothermal serpentine veins within the saprolite fragments labeled LC101A_1, the second point corresponds to the saprolite fragment labeled LC101A_2 and the third point corresponds to the type I garnierite surrounding the protolith fragments labeled LC101A_3 (**Fig. 3** and **6**). Qualitatively the LC101A_1 and LC101A_2 spectra show significant differences when compared to LC101A_3 spectrum, that are clearly seen by the corresponding $FT(\chi(k))$ second shell peaks between ~ 2 and $3.5 \text{ \AA}$. The second shell peak is clearly enhanced in LC101A_3 in contrast to that in LC101A_1 and LC101A_2. This is strongly indicative of different local environment of Ni within the garnierite veins when compared to the local environment within the saprolite fragments. This diversity of Ni local environments has been assessed with the analysis of the Ni K-edge μ EXAFS spectrum.

The $FT(\chi(k))$ prominent second peak at $2.8\text{--}2.9 \text{ \AA}$ on LC101A_3 on **Fig. 6** suggests a second atom shell of higher atomic number than for the second shell in LC101A_1 and LC101A_2 (Dublet *et al.*, 2012). The EXAFS fitting values on **Table 4** demonstrates that the second shell peak for LC101A_3 on the garnierite matrix can be fit with 5.2 Ni at $3.04 \text{ \AA}$ and 3.8 Si at $3.17 \text{ \AA}$. The Ni-Ni distances close to $3.06 \text{ \AA}$ are consistent with edge-sharing NiO_6 and the Ni-Si distance close to $3.3 \text{ \AA}$ is consistent with edge-sharing between SiO_4 tetrahedra and NiO_6 octahedra in kerolite-pimelite mineral series (Manceau and Calas, 1985, Manceau *et al.*, 1985, Manceau and Calas, 1986).

On LC101A_1 and LC101A_2 the second shell peaks have a better fit, not with one site with Ni-Ni and Ni-Si shells, but with a site with Ni-Mg and Ni-Si shells instead. The EXAFS from LC101A_1 on **Fig. 6** shows that $FT(\chi(k))$ peak can be fitted with one shell with 4.6 Mg at $3 \text{ \AA}$ and a second shell with 3.1 Si at $3.3 \text{ \AA}$ as shown on **Table 4**. In this site the Ni-Mg distances and the Ni-Si distances are also consistent with Ni local environment within lizardite/chrysotile-népouite/pecoraite series from New Caledonia (Dublet *et al.* 2012). On LC101A_2 however the second shell peaks have an even better fit not with one site with Ni-Mg and Ni-Si shells, but with a Ni site that has a Ni-Ni shell partially substituted by Mg. The EXAFS from LC101A_2 on **Fig. 6** shows that $FT(\chi(k))$ peak can be fitted with a 2.9 Ni shell partially substituted by 3.1 Mg at $3.06 \text{ \AA}$ as shown on **Table 4**. In this site the Ni-Ni and Ni-Mg distances are close to $3.06 \text{ \AA}$ and the Ni-Si distances are close to $3.3 \text{ \AA}$ which are again consistent with the Ni local environment within lizardite/chrysotile-népouite/pecoraite series from the saprolite studied New Caledonia (Dublet *et al.* 2012).

To study the local environment of Ni within the LC100B the Ni K-edge μ EXAFS have been acquired on two ROI representative points. The first corresponds to the remains of primary hydrothermal serpentine labeled LC100B_1 and the second to the type II garnierite labeled LC100B_2 (**Fig. 3** and **6**). As in sample LC101A the spectrum from sample LC100B shows significant differences in Ni local

environment from saprolite to garnierite that are visible in the corresponding $FT(\chi(k))$ second shell peaks between ~ 2 and $3.5 \text{ \AA}$ consisting in its enhancement from LC100B_1 to LC100B_2. These differences have been assessed with the analysis of the LC100B_1 and LC100B_2 Ni K-edge μ EXAFS spectrum.

The prominent second peak at $2.8\text{-}2.9 \text{ \AA}$ on LC100B_2 suggests a second atom shell of higher atomic number in type II garnierite than that for the second atom shell on LC100B_1 in the primary hydrothermal serpentine as well. The EXAFS fitting values on **Table 4** show that the second shell peak for LC101A_2 can be fit with a combination of 4.8 Ni at $3.04 \text{ \AA}$ and 2.9 Si at $3.17 \text{ \AA}$. The Ni-Ni distances close to $3.06 \text{ \AA}$ are consistent with those kerolite-pimelite mineral series (Manceau and Calas, 1985, Manceau *et al.*, 1985, Manceau and Calas, 1986). On LC100B_1 the second shell peak has a better fit with a Ni site with a second Ni-Ni shell partially substituted by Mg at $3.08 \text{ \AA}$ with 5.7 Ni and 0.3 Mg and 4.24 Si at $3.21 \text{ \AA}$. In this site the Ni-Ni and Ni-Mg distances are close to $3.06 \text{ \AA}$ and the Ni-Si distances are close to $3.3 \text{ \AA}$ which are consistent with the Ni local environment within lizardite/chrysotile-népouite/pecoraite series from New Caledonia (Dublet *et al.* 2012).

To study the local environment of Ni within GAR2C only a single Ni K-edge μ EXAFS has been acquired on the type III garnierite coating labeled GAR2C_1 since no significant amounts of Ni have been detected in the saprolite fragments (**Fig. 3** and **6**). Qualitatively the GAR2C_1 spectra shows similar $FT(\chi(k))$ features to the LC101A_3 and LC100B_2 with a significant shell peak between ~ 2 and $3.5 \text{ \AA}$ which is clearly characteristic of the Ni-Ni clustering within the mixture of lizardite/chrysotile-népouite/pecoraite mineral series and kerolite-pimelite mineral series that constitute the previous garnierites.

The prominent $FT(\chi(k))$ second shell peak at $2.8\text{-}2.9 \text{ \AA}$ on GAR2C_1 can be fit with a combination of 3.72 Ni at $3.08 \text{ \AA}$ and 2.04 Si at $3.24 \text{ \AA}$ as shown on **Table 4**. The Ni-Ni distances close to $3.06 \text{ \AA}$ are consistent with edge-sharing NiO_6 and the Ni-Si distance close to $3.3 \text{ \AA}$ is consistent with edge-sharing between SiO_4 tetrahedra and NiO_6 octahedra in the kerolite-pimelite series (Manceau and Calas, 1985, Manceau *et al.*, 1985, Manceau and Calas, 1986). However, the coordination of Ni-Ni is slightly defective suggesting a highly disordered local environment or partly depleted in Ni.

To study the Ni local environment on saprolite free garnierites Ni K-edge μ EXAFS have been acquired on representative points on GAR6 and FALC3 samples. The analyzed points correspond to characteristic heterogeneities in Ni content within the ROIs that have been selected with the aim to elucidate if Ni content variations correspond to distinctive Ni local environments in garnierites constituted by kerolite-pimelite and sepiolite-falcondoite series.

On GAR6 four Ni K-edge EXAFS have been acquired corresponding to the garnierite type IV fragments with lower Ni content labeled GAR6_1, GAR6_3, GAR6_4 and GAR6_5 and two corresponding to the garnierite type IV veins with higher Ni content labeled GAR6_2 and GAR6_6. Their $FT(\chi(k))$ show the distinctive second shell peaks between at $2.8\text{-}2.9 \text{ \AA}$ with no significant qualitative differences across the selected points. Their second shell peak is as prominent as in LC101A_3, LC100B_2 and GAR2C being indicative of GAR6 sharing the same similarities in terms of Ni local environment as in type I, II and III garnierites.

All the analyzed spots on GAR6, independently of their Ni content, show $FT(\chi(k))$ prominent second shell peaks between ~ 2 and $3.5 \text{ \AA}$ that can be fit with a combination of $\sim 6 \text{ Ni}$ at $\sim 3.06 \text{ \AA}$ and

~4 Si at ~3.3 Å as shown on **Fig. 7** and **Table 5**. Thus on type IV garnierite as in the type I, II and III garnierites the coordination numbers and the distances obtained are consistent with edge-sharing NiO₆ and with edge-sharing between SiO₄ tetrahedra and NiO₆ octahedra in the kerolite-pimelite series determined by Manceau and Calas (1985), Manceau *et al.* (1985) and Manceau and Calas (1986). No remarkable differences on the Ni local environment could be observed between the type IV garnierite constituting the fragments and the coatings on the GAR6 breccia.

On FALC3 four Ni K-edge EXAFS have been acquired corresponding to the garnierite type V with low Ni content labeled FALC3_2, FALC3_3, FALC3_5 and FALC3_6 and two corresponding to the garnierite type V with high Ni content labeled FALC3_1 and FALC3_4. Their FT($\chi(k)$) show the distinctive second shell peak at 2.8-2.9 Å with no significant qualitative differences across the analyzed points. However its FT($\chi(k)$) show some specificities when compared to the previous garnierites with a second shell peak less prominent than the garnierites in LC101A_3, LC100B_2 and GAR2C_1 and GAR6_1-6 but remarkably more prominent than the saprolite in L101A_1-2 and LC100B_1. Thus second FT($\chi(k)$) peak suggests some specific differences in the Ni local environment within the sepiolite-falcondoite series constituting the type V garnierite when compared to the local environment within the mixture of lizardite/chrysotile-népouite/pecoraite series and kerolite-pimelite mineral series constituting the previous types I, II, III and IV garnierites.

The height of the FT($\chi(k)$) second shell peak at 2.8-2.9 Å on FALC3 still suggests that the second shell atoms are of Ni and it has been confirmed with the subsequent EXAFS fittings. The obtained values listed in **Table 6** demonstrate that this second peak can be fit with a combination of Ni and Si with coordination numbers close to ~3 and ~4 and with the Ni-Ni distances close to 3.06 Å and the Ni-Si distance close to 3.3 Å. As on the previous samples on type V garnierite the distances obtained are consistent with edge-sharing NiO₆ and with edge-sharing between SiO₄ tetrahedra and NiO₆ octahedra the determined by Manceau and Calas (1985), Manceau *et al.* (1985) and Manceau and Calas (1986) however the low coordination values for the second coordination shell suggest that the second shell is consistently depleted in Ni within the sepiolite-falcondoite mineral series when compared to the lizardite/chrysotile-népouite/pecoraite series and kerolite-pimelite mineral series constituting the previous types I, II, III and IV garnierites.

4. Discussion.

4.1. The garnierite development at Falcondo Ni-laterite deposit.

The garnierite veins display a diversity of Ni content and textures corresponding to the different precipitation and dissolution episodes that took place during their development. Coupling the OM and EMPA measurements provided an opportunity to study the garnierites' texture and chemical composition during the maturing process of the Falcondo Ni-laterites. In addition the chemical compositions obtained on the selected ROI's helped to determine not only the Ni content but the mineralogical composition of the garnierites. The evolution of the mineral phases and their textures in the garnierites helped to elucidate their precipitation process and the factors determining their development within the samples.

Following the garnierite types from Villanova-de-Benavent *et al.* (2014) it is seen that type I garnierite is constituted by Fe-Ni-bearing mixture of lizardite/chrysotile-népouite/pecoraite and kerolite-pimelite that is surrounding the saprolite and by Ni-bearing primary hydrothermal serpentine within the saprolite fragments. The type II garnierite veins are constituted

predominantly by a mixture of Fe-free Ni-bearing lizardite/chrysotile-népouite/pecoraite and kerolite-pimelite mixture with relicts of Ni-bearing primary hydrothermal serpentine found within the saprolite fragments. The type III garnierite is mostly constituted by Fe-free Ni-bearing lizardite/chrysotile-népouite/pecoraite and kerolite-pimelite mixture veins and the saprolite fragments with Fe completely oxidized and no primary hydrothermal serpentine left. The saprolite free type IV garnierite is constituted mostly by a mixture of Fe-free Ni-bearing kerolite-pimelite and low amounts of Fe-free Ni-bearing lizardite/chrysotile-népouite/pecoraite. The saprolite free type IV garnierite corresponds to a massive Fe-free Ni-bearing sepiolite-falcondoite mineralization.

Accordingly the chemical composition from type I, to type II and III garnierites show an increase of the content of NiO from 1.19 wt.% up to 41.1 wt.% at expenses of FeO from 8.9 wt.% down to 0.1 wt.% and MgO from 40.38 wt.% down to 6.88 wt.% with an average constant content of SiO₂ about 41.94 wt.%. It is worth to notice that the accounted amounts of FeO in type I, II and III correspond to the FeO present within the lizardite/chrysotile-népouite/pecoraite and kerolite-pimelite mixtures and not to the saprolite fragments. The chemical compositions for the saprolite free type IV and V garnierites are completely FeO free and display an increase of SiO₂ from 45.53 wt. % to 52.28 wt. % and a decrease of NiO from 31.76 wt.% to 12.25 wt. %. The reported compositions are consistent with the mechanism of supergene enrichment with dissolution of Ni-poor primary hydrothermal serpentines followed by precipitation of secondary Ni-enriched hydrated phyllosilicates process described by Galí *et al.* (2012).

The increase of the SiO₂ content from type I to type V garnierites is in agreement with dissolution of the primary hydrothermal serpentines leading to the progressive silicification within the laterites. According to Trescases (1975), Golightly (1981), Freyssinet *et al.* (2005) and Soler *et al.* (2008) there is an increase of the silica activity during the formation of garnierites linked to the preferred release of Mg and Ni in phyllosilicates and the development of silica rich surfaces. During this process the dissolving events under the appropriate pH mobilize the accumulated silica increasing the silica activity in the aqueous solutions. These combined and repeated cycles of dissolution and precipitation in Falcondo explain the observed disappearance of primary hydrothermal serpentines and the development of mineralizations from Ni-bearing lizardite/chrysotile-népouite/pecoraite to Ni-bearing kerolite-pimelite and finally Ni-bearing sepiolite-falcondoite in garnierite as described in Galí *et al.* (2012).

The successive enrichment of Ni observed through type I, II and III garnierites can be explained because of the increase of Ni⁺² through the percolating waters due to the leaching of Ni from goethite in the limonitic horizon by meteoric waters and/or the leaching of Ni during the dissolution of the primary hydrothermal serpentines as predicted by Galí *et al.* (2012). Thus the drop of the Ni content in Falcondo on type IV and V massive garnierites in comparison to type I, II and III garnierite breccias seems to be related to the absence of saprolite fragments. The absence of the later would limit the contribution of Ni exclusively to the percolating water from the top of the profile the resulting in a reduction of the overall amount of Ni⁺² available within the solution from which type IV and V garnierites precipitate.

4.2. The saprolite fragments weathering at Falcondo Ni-laterite deposit.

The original saprolite fragments present in the Falcondo Ni-laterite deposit display abundant serpentine veining corresponding to the oceanic serpentinization that affected the original protolith. Coupling the EMPA, μ XRF and μ XAS and the Fe K-edge measurements provided an

opportunity to study the saprolite fragments, the associated serpentine veins and the changes that took place during the maturing process of the Falcondo Ni-laterite deposit. The obtained results on the selected ROI's helped to assess the weathering process according to the mineral phases present, their Fe oxidation degree and the associated Ni crystallochemistry. This provided a rough estimation that helped to understand the relationship between the weathering of the saprolite fragments and the garnierite development.

The chemical compositions from the saprolite fragments mostly remain similar when associated to type I, II and III garnierites corresponding to the lizardite/chrysotile-népouite/pecoraite mineral series (**Fig.2**) with the only exception of the NiO content that drops significantly to almost disappear in saprolite fragments associated to type III garnierite (**Table 1**). The type I garnierite veins are constituted by Ni and Fe-bearing talc-like phases and are found mostly surrounding the saprolite grains. The texture corresponding to the distribution of type I garnierite seems to indicate that type I garnierite is tightly related to the ongoing weathering process of the protolith fragments. On the other hand the texture displayed by type II and III garnierites where garnierite is found filling cracks suggest that they do appear at later stages of the garnierite development. When combining these results it can be suggested that type I Fe-bearing garnierite is developed from the direct weathering of the protolith fragments whilst type II and III garnierite are mostly related to the percolating waters running from the top across the profile.

The chemical distribution of Fe rich phases displays a texture with the most reduced forms of Fe associated to the primary serpentines meanwhile the more oxidized forms of Fe are found to be associated to a mixture of advanced stages of serpentinized minerals and phases related to the weathering process that take place during the laterization. On the saprolite fragments the account of certain amounts of forsterite into the Fe K-edge fittings is explained of the lesser degree of oxidation of Fe in the preweathering serpentines with a hydrothermal origin when compared to the oxidation degree of Fe within the bulk of saprolite and garnierite type I. This texture corresponds to a highly serpentinized saprolite fragments affected by a weathering process that took place during the laterization of the profile.

4.3. The Ni mobilization and accumulation at Falcondo Ni-laterite deposit.

The local environment of Ni has been studied not only on the saprolite fragments but on all types of garnierite present on the samples. The Ni K-edge μ EXAFS measurements provided an opportunity to study the mobilization of Ni from the saprolite fragments to and through all the successive generations of garnierite veins present at Falcondo Ni-laterite deposit. It has been observed that the local environment of Ni displays specific features from the original serpentines and garnierites that are distinctive of different stages of Ni-laterite development. The changes on the Ni local environment are in agreement with the observed differences on the mineralogy and texture of the garnierites across the Ni-laterite profile in Falcondo. These provide valuable insights that help to understand not only the relationship between the saprolite fragments and the garnierite but changes within the garnierite during its development.

The Ni crystallochemistry within the saprolite fragments show differences which are proposed to be related to its weathering process and it is thought to be partly associated to garnierite development. The $FT(\chi(k))$ second peak at 2.8-2.9 Å from Ni K-edge μ EXAFS shows a steady increase in height linked to the Ni local environment changes that take place by the weathering process affecting the primary hydrothermal serpentines on LC101A_1 to LC100B_1 and the

development of the garnierite matrix on LC101A_3. The $FT(\chi(k))$ second peak from Ni-bearing serpentines on LC101A_1 and the $FT(\chi(k))$ second peak from the advanced serpentized saprolite LC101A_2 do share the same features with Ni as a homogeneous solid solution with Mg as seen on **Fig. 9**. However the $FT(\chi(k))$ second peak from LC100B_1 compared to LC101A_1 depicts a decrease of the amount of Mg in the second coordination shell which is balanced with an increase of the Ni on **Fig. 9**. The $FT(\chi(k))$ second peak from type I garnierite on LC101A_3 completes trend observed on LC100B_1 with the Ni local sites completely surrounded with Ni and Ni forming a heterogeneous solid solution as seen on Fig 9. These transformations are thought to be the result of partly dissolving the primary hydrothermal serpentines and the subsequent precipitation and clustering of Ni in discrete domains within the secondary Fe-bearing phyllosilicates.

At the later stages of garnierite development corresponding to samples GAR2C, GAR6 and FALC3 the $FT(\chi(k))$ second peak at 2.8-2.9 Å from the Ni K-edge μ EXAFS is at full height. However, some minor differences appear between the Ni local environments from the kerolite-pimelite garnierite matrix on samples GAR2C and GAR6 on **Fig. 7** when compared to the Ni local environment from the sepiolite-falcondite garnierite matrix on sample FALC3 on **Fig. 8** and summarized on **Fig. 9**. These differences in this case are thought to be related to the intrinsic crystal structure of the secondary phyllosilicates. The local environment of Ni in garnierites is only surrounded by Ni and forming clusters and thus the differences seen in the $FT(\chi(k))$ second shell peak from type V garnierite when compared to type II, III and IV garnierites are related to Ni depleted shells which is intrinsic of the structure of a sepiolite.

The small decrease of the $FT(\chi(k))$ second peak in FALC3 is related to the important discontinuities associated to the Ni octahedral site configuration within the sepiolite structure. The channels present in the sepiolite structure along the *c* axis truncate the horizontal layers of NiO_6 octahedra lowering the overall local Ni coordination in Ni-bearing sepiolite (Post *et al.*, 2007). According to its symmetry the sepiolite structure has 4 Ni atoms in Wyckoff positions with two Ni positions coordinated with another 6 second shell atoms, one Ni position coordinated with 5 second shell atoms and one last Ni position coordinated with 3 second shell atoms. The overall accounts for an averaged 5 second shell atoms for each Ni position in sepiolite (Post *et al.*, 2007). Because of the lower symmetry in the talc structure the Ni atoms in Wyckoff positions in talc are 2 and according to its crystalline structure both are coordinated by another 6 second shell atoms (Gruner, 1934). Thus the differences observed in the $FT(\chi(k))$ second peak from type V garnierite when compared to types II, III, and IV are in agreement with ideal second shell coordination for Ni being smaller in sepiolite than in talc.

However there are some systematic differences from the expected ideal Ni-Ni second shell coordination number and the obtained values by means of Ni K-edge EXAFS. According to the synchrotron measurements the second Ni-Ni shell coordination number is systematically lower from garnierite samples when compared to talc and sepiolite theoretical values. These differences are not observed on the measured first Ni-O coordination shells which remain close to the theory. The agreement with the experimental and theoretical coordination values for the Ni-O shells and the discrepancy with the experimental and theoretical coordination values for the Ni-Ni shells are indicative of a disordered material and discards other explanations affecting the $FT(\chi(k))$ peaks such as overabsorption.

The present results demonstrate that the Ni-K EXAFS are sensitive to the local environments of primary hydrothermal phyllosilicates (serpentine) constituting the saprolite and the secondary phyllosilicates (serpentine, kerolite-pimelite and sepiolite) constituting the garnierites. However, it does not seem to be sensitive to the whole five different types of garnierite present in Falcondo defined by (Villanova-de-Benavent *et al.*, 2014). In terms of the Ni crystallochemistry these five types of garnierites can be classified in three groups: The primary hydrothermal serpentine, the Fe-Ni-bearing serpentine, the kerolite-pimelite (types I, II, III and IV garnierites) and the sepiolite-falcondoite (type V).

5. Conclusions

The data obtained by means of OM, EMPA μ XAS, μ XANES and μ EXAFS presented in this paper, provide the first insights on garnierite development during the maturation process of the Falcondo Ni-laterite deposits. The obtained results indicate an evolution of the laterite profile departing from the original compositions with low Ni contents and high Fe and Mg contents corresponding to the hydrothermal serpentines present in the saprolite fragments towards an enrichment of Ni and loss of Fe and Mg and followed by subsequent increase of the Si content during the development of garnierites. These combined processes associated to the progressive saprolite disappearance and garnierite precipitation episodes during the weathering–uplift–erosion cycles in that took place in Falcondo explain the five different garnierite types defined by Villanova-de-Benavent *et al.* (2014).

The described Ni crystallochemistry in this paper is consistent with the proposed dissolution, mobilization and precipitation processes of Ni involved in the weathering of saprolite and the development of garnierites. In the present work it is demonstrated that the Ni local environment changed from the primary hydrothermal serpentine with Ni forming a solid solution with Mg (homogeneous solid solution) to a clustered Ni within the serpentine, kerolite-pimelite and sepiolite-falcondoite series present on type I, II, III, IV and V garnierites (heterogeneous solid solution) with the specificity of a partly depleted second coordination shell within the sepiolite-falcondoite series that constitute the type V garnierites.

For the first time the relationship between mineral texture and Ni mobilization and accumulation in serpentines and garnierites from Falcondo Ni-laterite deposit has been elucidated. The observed mineral textures and the obtained chemical compositions demonstrated that the Ni constituting the type II, III, IV and V garnierites is provided mostly by the percolating fluids from the top of the laterite profile and that the Ni and the additional Fe that constitute type I garnierites are provided during the weathering process of the saprolite fragments that is taking place within the Falcondo Ni-laterite profile.

ACKNOWLEDGEMENTS

This research has been partially supported by the Spanish projects CGL2009-10924 and CGL2012-36263, the Catalan project SGR 2009-444, and a PhD grant to Cristina Villanova-de-Benavent sponsored by the Ministerio de Educación (Spain). The beamtime provided by the Advanced light source and the help and hospitality extended by the staff at Falcondo Glencore-Xtrata mine, especially by Francisco Longo, are also gratefully acknowledged. The authors want also to thank Professor J. F. Lewis.

797

798 **REFERENCES**

799

800 Andreani M., Muñoz M., Marcaillou C., Delacour A.(2013). μ XANES study of iron redox state in
801 serpentine during oceanic serpentinization. *Lithos.* 178, 70-83,

802 Brindley G.W., Hang P.T. (1973). The nature of garnierite: I. Structure, chemical compositions and
803 color characteristics. *Clay Clay Miner.* 21, 27-40.

804

805 Brindley G.W. (1978). The structure and chemistry of hydrous nickel containing silicate and
806 aluminate minerals. *Bull. BRGM* sec. II, 3 233-245.

807

808 Dublet G., Juillot F., Morin G., Fritsch E., Fandeur D., Ona-Nguema G., Brown G.E.Jr. (2012). Ni
809 speciation in a New Caledonian lateritic regolith: A quantitative X-ray absorption spectroscopy
810 investigation. *Geochim. Cosmochim. Acta* 95, 119-133.

811

812 Dzemua G. L., Gleeson S. A., Schofield P. F. (2013). Mineralogical characterization of the
813 Nkamouna Co-Mn laterite ore, southeast Cameroon. *Miner. Deposita* 48, 155-171.

814

815 Elias M., Donaldson M.J., Giorgetta N. (1981). Geology, mineralogy, and chemistry of lateritic
816 nickel-cobalt deposits near Kalgoorlie, Western Australia. *Econ. Geol.* 76, 1775–1783.

817

818 Fan R., Gerson A.R. (2011). Nickel geochemistry of a Philippine laterite examined by bulk and
819 microprobe synchrotron analyses. *Geochim. Cosmochim. Acta* 75, 6400-6415.

820

821 Faust G.T. (1966). The hydrous nickel–magnesium silicates — the garnierite group. *Am. Mineral.*
822 51, 33–36.

823

824 Freyssinet Ph., Butt C.R.M., Morris R.C. (2005). Ore-forming processes related to lateritic
825 weathering. *Econ. Geol. 100th Anniversary Vol.*, 681-722.

826

827 Fu W., Yang J.W., Yang M.L., Pang B.C., Liu X.J., Niu H.J., Huang X.R. (2014). Mineralogical and
828 geochemical characteristics of a serpentinite-derived laterite profile from East Sulawesi, Indonesia:
829 Implications for the lateritization process and Ni supergene enrichment in the tropical rainforest. *J.*
830 *Asian Earth Sci.* 93, 74-88.

831

832 Galí S., Soler J.M., Proenza J.A., Lewis J.F., Cama J., Tauler E. (2012). Ni-enrichment and stability of
833 Al-free garnierite solid-solutions: a thermodynamic approach. *Clay. Clay Miner.* 60, 121-135.

834

835 Galois L., Calas G., Brown Jr. G. E. (1995). Intracrystalline distribution of Ni in San Carlos olivine:
836 An EXAFS study. *Am. Mineral.* 80, 1089-1092.

837

838 Gleeson S.A., Butt C.R., Elias M. (2003). Nickel laterites: a review. *SEG Newsl.* 54, 11-18.

839

840 Kuck P.H. (2013). Nickel. *USGS Mineral Commodity Summaries*, 108-109.

841

842 Golightly J.P. (1979). Geology of Soroako nickeliferous laterite deposits. *Int. Laterite*

- Symposium 3, 38-55.
- Golightly J.P. (1981). Nickeliferous laterite deposits. *Econ. Geol. 75th Anniversary Vol.*, 710-735.
- Golightly J.P. (2010). Progress in understanding the evolution of nickel laterites. *Econ. Geol. Spec. Publ.* 15, 451-485.
- Gruner J.W. (1934). The crystal structure of talc and pyrophyllite. *Zeitschrift fur Kristallographie.* 88, 412-419.
- Manceau A., Calas G., Decarreau A. (1985). Nickel-bearing clay minerals: I. Optical spectroscopic study of nickel crystal chemistry. *Clay Miner.* 20, 367-387.
- Manceau A., Calas G. (1986). Nickel-bearing clay minerals: II. Intracrystalline distribution of Nickel: An X-ray absorption study. *Clay Miner.* 21, 341-360.
- Manceau A., Calas G. (1985). Heterogeneous distribution of nickel in hydrous silicates from New Caledonia ore deposits. *Am. Mineral.* 70, 549-558.
- Marcus M.A., MacDowell A.A., Celestre R., Manceau A., Miller T., Padmore H.A., Sulett R.E. (2004). Beamline 10.3.2 at ALS: a hard X-ray microprobe for environmental and materials sciences. *J. Synchrotron Radiat.* 11, 239-247.
- Mosselmans J.F.W., Quinn P.D., Roque-Rosell J., Atkinson K.D., Dent A.J., Cavill S.I., Hodson M.E., Kirk C.A., Schofield P.F. (2008). The first environmental science experiments on the new microfocus spectroscopy beamline at diamond. *Mineral. Mag.* 72, 197-200
- Mosselmans J.F.W., Quinn P.D., Dent A.J., Cavill S.A., Diaz Moreno S., Peach A., Leicester P.J., Keylock S.J., Gregory S.R., Atkinson K.D., Roque Rosell J. (2009). I18 — the microfocus spectroscopy beamline at the Diamond light source. *J. Synchrotron Radiat.* 16, 818-824.
- Mudd G.M. (2010). Global trends and environmental issues in nickel mining: sulfides versus laterites. *Ore Geol. Rev.* 38, 9-26.
- Post J.E., Bish D.L., Heaney P.J. (2007). Synchrotron powder X-ray diffraction study of the structure and dehydration behavior of sepiolite. *Am. Mineral.* 92, 91-97.
- Ravel B., Newville M., (2005). ATHENA, ARTEMIS, HEPHAESTUS: data analysis for X-ray absorption spectroscopy using IFEFFIT. *J. Synchrotron Radiat.* 12, 537-541.
- Ressler T., Wong J., Roos J., Smith I.L. (2000). Quantitative Speciation of Mn-Bearing Particulates Emitted from Autos Burning (Methylcyclopentadienyl) manganese Tricarbonyl-Added Gasolines Using XANES Spectroscopy. *Environ. Sci. Technol.* 34, 950-958.
- Roqué-Rosell J., Mosselmans J. F. W., Proenza J. A., Labrador M., Gali S., Atkinson K. D., Quinn P. D. (2010). Sorption of Ni by "lithiophorite-asbolane" intermediates in Moa Bay lateritic deposits, eastern Cuba. *Chem. Geol.* 275, 9-18.

891 Springer G. (1974). Compositional and structural variations in garnierites. *Can. Mineral.* 12, 381-
892 388.

893

894 Sutton S.R., Bajt S., Delaney J., Schulze D., Tokunaga T. (1995). Synchrotron x-ray fluorescence
895 microprobe: Quantification and mapping of mixed valence state samples using micro-XANES. *Rev.*
896 *Sci. Inst.* 66, 1464-1467.

897

898 Tauler E., Proenza J.A., Galí S., Lewis J.F., Labrador M., García-Romero E., Suárez M., Longo F.,
899 Bloise G. (2009). Ni-sepiolite–falcondoite in garnierite mineralization from the Falcondo Ni-laterite
900 deposit, Dominican Republic. *Clay Miner.* 44, 435-454.

901

902 Villanova-de-Benavent C., Proenza J.A., Galí S., García-Casco A., Tauler E., Lewis J.F., Longo F.
903 (2014). Garnierites and garnierites: Textures, mineralogy and geochemistry of garnierites in the
904 Falcondo Ni-laterite deposit, Dominican Republic. *Ore Geol. Rev.* 58, 91-109.

905

906 Whitney D.L., Evans B.W. (2010). Abbreviations for names of rock-forming minerals. *Am. Miner.*
907 95, 185-187.

Table 1. Compositions of the analyzed points obtained by EMPA in %.wt. The obtained compositions have been used to classify the samples into the five garnierite types described by (Villanova-de-Benavent *et al.*, 2014).

Table 2. These are the fittings displaying the reference spectra used as standards selected from (Villanova-de-Benavent *et al.*, 2014) and the amounts of the selected references that provide the best fit for each Fe-K XANES as a weighted sum. The normalized sum—squared residual from each Fe-K XANES fit are displayed.

Table 3. Fitting values for Ni K-edge μ EXAFS on LC101A, LC100B and GAR2C. $R(\text{\AA})$ corresponds to the interatomic distances, N number of neighboring atoms, σ^2 the Debye-Waller factor, e_0 (eV) is the difference between the defined threshold energy and the experimentally determined threshold energy, R-factor is the fit coefficient and RedChi2 correspond to the goodness of fit. Errors on R and N values are usually considered around $\pm 20\%$ and $\pm 5\%$, respectively.

Table 4. Fitting values for Ni K-edge μ EXAFS on GAR6C. $R(\text{\AA})$ corresponds to the interatomic distances, N number of neighboring atoms, σ^2 the Debye-Waller factor, e_0 (eV) is the difference between the defined threshold energy and the experimentally determined threshold energy, R-factor is the fit coefficient and RedChi2 correspond to the goodness of fit. Errors on R and N values are usually considered around $\pm 20\%$ and $\pm 5\%$, respectively.

Table 5. Fitting values for Ni K-edge μ EXAFS on FALC3. $R(\text{\AA})$ corresponds to the interatomic distances, N number of neighboring atoms, σ^2 the Debye-Waller factor, e_0 (eV) is the difference between the defined threshold energy and the experimentally determined threshold energy, R-factor is the fit coefficient and RedChi2 correspond to the goodness of fit. Errors on R and N values are usually considered around $\pm 20\%$ and $\pm 5\%$, respectively.

Table 1.

Sample Type	LC-101a saprolite	LC-101a saprolite	LC-101a saprolite	LC-101a saprolite	LC-101a type I	LC-101a type I	LC-101a type I	LC-101a type I	LC-100Bb saprolite	LC-100Bb saprolite	LC-100Bb type II	LC-100Bb type II	LC-100Bb type II	GAR-3 saprolite
SiO ₂	42.7	41.6	37.4	41.4	40.7	42.5	44.8	42.1	43.1	40.8	41.0	40.2	43.1	41.45
TiO ₂	-	0.03	0.06	-	-	-	-	0.02	-	0.03	-	-	-	-
Al ₂ O ₃	0.11	2.92	0.2	3.13	0.02	0.01	0.05	0.01	1.32	2.94	1.40	1.06	1.11	0.18
Cr ₂ O ₃	-	0.93	0.09	1.11	0.12	0.03	0.04	-	0.02	-	0.02	-	0.02	0.04
V ₂ O ₃	-	-	-	-	-	-	-	-	-	-	0.05	0.02	0.02	-
Fe ₂ O ₃	3.90	4.65	10.60	3.36	8.91	2.66	4.91	3.05	1.92	4.92	0.66	0.46	0.60	7.54
MnO	0.01	0.03	0.06	-	0.01	0.05	0.03	-	0.04	0.08	0.01	0.05	0.03	6.78
ZnO	-	-	-	-	-	-	-	-	-	-	0.01	-	-	0.05
MgO	36.8	35.3	30.8	36.7	33.4	39.6	27.6	40.4	34.7	30.1	17.7	17.6	19.1	38.29
NiO	2.38	1.5	4.43	1.44	5.33	1.19	8.92	1.51	5.23	6.14	25.2	24.5	21.6	0.8
CoO	-	0.02	0.02	0.02	0.03	-	-	0.02	-	-	-	-	-	-
CaO	0.04	-	0.03	0.01	0.07	0.01	0.09	0.01	-	-	0.1	0.07	0.06	-
Na ₂ O	-	-	-	-	-	-	-	-	-	-	-	-	-	-
K ₂ O	0.01	0.02	-	-	0.04	-	0.06	0.01	-	-	-	-	-	-
Sum Ox%	86.0	87.0	83.7	87.1	88.6	86.0	86.6	87.1	86.4	85.0	86.1	83.9	85.7	95.1
O (Str Form)	7	7	7	7	7	7	7	7	7	7	7	7	7	7
Si	2.035	1.912	1.809	2.042	1.955	2.008	2.181	1.976	2.036	1.956	2.173	2.178	2.237	1.869
Ti	0	0.001	0.002	0	0	0	0	0.001	0	0.001	0	0	0	0
Al	0.006	0.158	0.011	0.049	0.001	0.001	0.003	0.001	0.073	0.166	0.087	0.068	0.068	0.010
Cr	0	0.034	0.003	0.002	0.005	0.001	0.002	0	0.001	0	0.001	0	0.001	0.001
V	0	0	0	0	0	0	0	0	0	0	0.002	0.001	0.001	0
Fe ³⁺	0.140	0.161	0.385	0.088	0.322	0.095	0.180	0.108	0.068	0.178	0.026	0.019	0.023	0.256
Mn	0	0.001	0.002	0.001	0	0.002	0.001	0	0.002	0.003	0	0.002	0.001	0.002
Zn	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Mg	2.62	2.43	2.22	2.54	2.39	2.79	2.01	2.83	2.44	2.15	1.40	1.42	1.48	2.57
Ni	0.091	0.056	0.172	0.170	0.206	0.045	0.349	0.057	0.199	0.237	1.08	1.07	0.904	0.029
Co	0	0.001	0.001	0	0.001	0	0	0.001	0	0	0	0	0	0
Ca	0.002	0	0.002	0	0.004	0.001	0.005	0.001	0	0	0.006	0.004	0.003	0
Na	0	0	0	0	0	0	0	0	0	0	0	0	0	0
K	0.001	0.001	0	0	0.002	0	0.004	0.001	0	0	0	0	0	0
Σcations	4.89	4.75	4.60	4.89	4.88	4.94	4.73	4.97	4.82	4.69	4.77	4.76	4.72	4.74
XTlc (*)	-	-	-	-	0.008	0.113	0.293	0.009	-	-	0.359	0.365	0.439	-

Table 1 (Continued)

Sample Type	GAR-3 saprolite	GAR-3 type III	GAR-3 type III	GAR-3 type III	GAR-3 type III	GAR-6 type IV	GAR-6 type IV	GAR-6 type IV	GAR-6 type IV	FALC-3 sep-falc	FALC-3 sep-falc	FALC-3 sep-falc	FALC-3 sep-falc
SiO ₂	45.1	43.1	44.8	39.4	39.5	45.6	46.6	51.0	47.3	52.3	47.6	49.6	49.60
TiO ₂	0.02	0.03	-	-	0.02	-	0.03	0.01	0.01	-	-	-	0.03
Al ₂ O ₃	0.06	0.09	0.03	-	0.02	0.08	0.15	0.14	0.13	0.53	0.33	0.31	0.50
Cr ₂ O ₃	-	0.03	0.05	0.04	0.04	0.02	0.02	0.03	-	0.02	-	0.00	0.02
V ₂ O ₃	-	-	-	-	-	-	-	0.04	-	-	-	-	-
Fe ₂ O ₃	1.923	0.834	0.20	0.067	0.122	0.011	0.067	-	-	0.089	0.044	0.089	0.033
MnO	1.73	-	-	0.00	-	0.02	-	-	-	0.01	0.06	0.02	0.02
ZnO	0.02	-	-	-	-	0.05	0.06	-	-	-	-	-	-
MgO	40.8	11.5	11.0	7.57	6.88	7.99	9.42	14.7	8.7	14.9	9.5	10.8	10.64
NiO	0.32	29.1	33.2	37.6	41.1	31.8	29.9	24.3	31.4	12.3	26.8	23.4	18.26
CoO	-	-	-	-	-	-	-	-	-	-	-	-	-
CaO	-	-	-	-	-	0.04	0.09	0.04	0.06	-	-	-	-
Na ₂ O	-	0.04	-	0.01	-	-	-	-	-	-	0.06	0.04	0.03
K ₂ O	-	-	0.02	0.02	-	-	-	-	-	-	0.06	0.10	-
Sum Ox%	89.9	84.7	89.3	84.7	87.7	85.6	86.3	90.2	87.5	80.0	84.5	84.3	79.13
O (Str Form)	7	7	7	7	7	11	11	11	11	32	32	32	32
Si	2.04	2.36	2.36	2.29	2.26	3.89	3.89	3.90	3.91	12.2	11.6	11.8	12.1
Ti	0.001	0.001	0	0	0.001	0	0.002	0.001	0.001	0	0	0	0.006
Al	0.003	0.006	0.002	0	0.001	0.008	0.015	0.013	0.013	0.145	0.094	0.087	0.144
Cr	0	0.001	0.002	0.002	0.002	0.001	0.001	0.002	0	0.004	0	0	0.004
V	0	0	0	0	0	0	0	0.002	0	0	0	0	0
Fe ³⁺	0.065	0.034	0.008	0.003	0.005	0.001	0.004	0	0	0.016	0.008	0.016	0.006
Mn	0.001	0	0	0	0	0.001	0	0	0	0.002	0.012	0.004	0.004
Zn	0	0	0	0	0	0.003	0.004	0	0	0	0	0	0
Mg	2.75	0.94	0.86	0.66	0.59	1.02	1.17	1.67	1.07	5.15	3.42	3.82	3.88
Ni	0.012	1.28	1.41	1.76	1.89	2.18	2.01	1.49	2.09	2.29	5.24	4.46	3.59
Co	0	0	0	0	0	0	0	0	0	0	0	0	0
Ca	0	0	0	0	0	0.004	0.008	0.003	0.005	0	0	0	0
Na	0	0.004	0	0.001	0	0	0	0	0	0	0.028	0.018	0.014
K	0	0	0.001	0.001	0	0	0	0	0	0	0.019	0.030	0
Σcations	4.86	4.62	4.62	4.71	4.74	7.10	7.10	7.09	7.08	19.75	20.40	20.21	19.79
XTlc (*)	-	0.575	0.557	0.424	0.369	0.829	0.838	0.860	0.866	1.48	1.02	1.14	1.466

Table 2.

Sample	LC101A_1	LC101A_2	LC101A_3	LC100B_1	LC100B_2	GAR2C_2
Type	saprolite	saprolite	Type I	saprolite	saprolite	saprolite
Forsterite(%)	20	-	-	-	-	-
Magnetite (%)	33	10	-	14	-	-
Serpentine(%)	48	66	77	59	36	31
Maghemite(%)	-	24	23	18	35	51
Goethite(%)	-	-	-	10	30	18
Norm. Sum. Sq. Res.	1.59E-04	1.86E-04	3.06E-04	2.57E-04	3.38E-04	2.76E-4

Table 3.

LC101A_1	Ni-O	Ni-Mg	Ni-Ni	Ni-Si	e0	R-factor	RedChi2
R(Å)	2.08	3	-	3.3	1.23	3.3E-2	9.22
N	4.6	4.6	-	3.1			
Ss2	0.004	0.01	-	0.004			
LC101A_2	Ni-O	Ni-Mg	Ni-Ni	Ni-Si	e0	R-factor	RedChi2
R(Å)	2.06	3.06	3.06	3.3	-3.46	2E-2	8.12
N	4.2	3.1	2.9	2.8			
Ss2	0.003	0.011	0.011	0.003			
LC101A_3	Ni-O	Ni-Mg	Ni-Ni	Ni-Si	e0	R-factor	RedChi2
R(Å)	2.06	-	3.04	3.17	-3.28	4.1E-3	6.09
N	5.2	-	5.2	3.8			
Ss2	0.006	-	0.007	0.007			
LC100B_1	Ni-O	Ni-Mg	Ni-Ni	Ni-Si	e0	R-factor	RedChi2
R(Å)	2.06	3.08	3.08	3.17	-3.46	2E-2	8.12
N	5.8	0.3	5.7	3.9			
Ss2	0.007	0.009	0.009	0.007			
LC100B_2	Ni-O	Ni-Mg	Ni-Ni	Ni-Si	e0	R-factor	RedChi2
R(Å)	2.06	-	3.08	3.21	-3.39	1E-3	8.28
N	4.8	-	5.22	4.24			
Ss2	0.006	-	0.006	0.006			
GAR2C_1	Ni-O	Ni-Mg	Ni-Ni	Ni-Si	e0	R-factor	RedChi2
R(Å)	2.06	-	3.08	3.24	-2.45	1E-3	3.98
N	4.8	-	3.72	2.04			
Ss2	0.006	-	0.006	0.007			

Table 4.

GAR6C_1	Ni-O	Ni-Ni	Ni-Si	e0	R-factor	RedChi2
R(Å)	2.06	3.08	3.24	-0.05	2E-2	7.47
N	5.12	5.05	3.2			
Ss2	0.005	0.006	0.007			
GAR6C_2	Ni-O	Ni-Ni	Ni-Si	e0	R-factor	RedChi2
R(Å)	2.06	3.08	3.24	-3.46	2E-2	8.12
N	5.04	4.68	3.36			
Ss2	0.006	0.005	0.007			
GAR6C_3	Ni-O	Ni-Ni	Ni-Si	e0	R-factor	RedChi2
R(Å)	2.06	3.08	3.25	-3.28	4.1E-3	6.09
N	4.68	4.68	3.36			
Ss2	0.005	0.004	0.008			
GAR6C_4	Ni-O	Ni-Ni	Ni-Si	e0	R-factor	RedChi2
R(Å)	2.06	3.08	3.24	-4.63	1E-3	1.27
N	5.04	4.68	3.4			
Ss2	0.006	0.005	0.007			
GAR6C_5	Ni-O	Ni-Ni	Ni-Si	e0	R-factor	RedChi2
R(Å)	2.05	3.07	3.21	-3.39	1E-3	8.28
N	4.56	4.99	3.99			
Ss2	0.005	0.006	0.009			
GAR6C_6	Ni-O	Ni-Ni	Ni-Si	e0	R-factor	RedChi2
R(Å)	2.06	3.07	3.23	-2.45	1E-3	3.98
N	4.56	4.08	3.88			
Ss2	0.005	0.006	0.008			

Table 5.

Falc3_1	Ni-O	Ni-Ni	Ni-Si	e0	R-factor	RedChi2
R(Å)	2.06	3.09	3.23	1.69	4.8E-3	8.42
N	5.34	3.04	5.08			
Ss2	0.006	0.006	0.006			
Falc3_2	Ni-O	Ni-Ni	Ni-Si	e0	R-factor	RedChi2
R(Å)	2.07	3.07	3.26	2.34	4.6E-3	8.79
N	5.1	2.82	3.72			
Ss2	0.005	0.007	0.003			
Falc3_3	Ni-O	Ni-Ni	Ni-Si	e0	R-factor	RedChi2
R(Å)	2.06	3.07	3.24	1.17	5.1E-3	7.15
N	5.34	3.6	3.56			
Ss2	0.005	0.007	0.004			
Falc3_4	Ni-O	Ni-Ni	Ni-Si	e0	R-factor	RedChi2
R(Å)	2.06	3.07	3.26	1.88	3.6E-3	17.8
N	5.04	3.18	3.36			
Ss2	0.005	0.006	0.004			
Falc3_5	Ni-O	Ni-Ni	Ni-Si	e0	R-factor	RedChi2
R(Å)	2.05	3.08	3.25	1.54	2.7E-3	8.51
N	5.52	3.48	2.72			
Ss2	0.005	0.007	0.002			
Falc3_6	Ni-O	Ni-Ni	Ni-Si	e0	R-factor	RedChi2
R(Å)	2.06	3.08	3.2	1.43	7.2E-3	20.05
N	5.1	5.1	3.44			
Ss2	0.005	0.007	0.005			

Figure 1. Images of the samples (left) and optical photomicrographs in plane polarized light of the regions of interest (ROI) selected to perform EMPA, μ XRF and μ XAS from samples **(a)** LC101A (saprolite and type I garnierite), **(b)** LC100B (saprolite and type II garnierite), **(c)** GAR2C (saprolite and type III), **(d)** GAR6 (type IV garnierite) and **(e)** FALC3 (type V garnierite). The brown fragments of the weathered saprolite are surrounded by the green garnierite veins.

Figure 2. Ternary plots showing the compositions of the analyzed garnierites compared to the five garnierite types described by (Villanova-de-Benavent et al., 2014). The compositions of the selected samples fall into the saprolite serpentine, and the garnierite type I, II, III, IV and V fields. Abbreviations are after Whitney & Evans (2010), Tauler *et al.* (2009) and Villanova-de-Benavent *et al.* (2014), except Pec for pecoraite.

Figure 3. The μ XRF corresponding to the selected ROI on samples LC101A, LC100B, GAR2C, GAR6 and FALC3. The red channel corresponds to Fe K α , the green channel to Ni K α and the blue channel to Cr K α . The greyscale maps correspond to the chemical maps plotting the distribution of the saprolite phases identified by means of Fe K-edge μ XANES. The LC101A and LC100B maps show Fe⁺² rich veins within the Fe⁺³ rich saprolite fragments. The GAR2C shows Fe⁺³ rich saprolite fragments. The inset graph **(a)** corresponds to the integrated XRF intensities at 10keV for samples LC101A, LC100B and GAR2C.

Figure 4. Ni K α vs Fe K α scatter plots for sample LC101A in blue, LC100B in green and GAR2C in red **(a)**. LC101A has a characteristic anticorrelation of Ni and Fe which corresponds to garnierite type I surrounding the saprolite fragments **(b)**. The anticorrelation diminishes in LC100B4 and does correspond to the Ni-rich serpentine relicts present within the saprolite **(c)** and disappears in GAR2C **(d)**. The non-correlated Fe cts. corresponds to the saprolite fragments and the non-correlated Ni cts. to the garnierite matrix.

Figure 5. Fe K-edge μ XANES and the resulting fits with Gt (yellow), Mgh (red), Srp (green) and Fo (blue) **(a)** corresponds to LC101A_02 on the Ni-rich serpentine **(b)** corresponds to LC101A_01 on the saprolite fragment (c) corresponds to LC101A_3 on the type I garnierite **(d)** corresponds to LC100B_01 on the serpentine vein and **(e)** corresponds to LC100B_02 on the saprolite fragment. **(f)** corresponds to GAR2C on the saprolite fragment.

Figure 6. Ni K-edge μ EXAFS, the corresponding $FT(\chi(k))$ and the resulting fits from samples L101A, LC100B and GAR2C. Differences on the second shell peak height at 2.8-2.9 Å are clearly visible.

Figure 7. Ni K-edge μ EXAFS, the corresponding $FT(\chi(k))$ and the resulting fits from sample GAR6C. No differences on the second shell peak height at 2.8-2.9 Å are visible despite of the differences of Ni content.

Figure 8. Ni K-edge μ EXAFS, the corresponding $FT(\chi(k))$ and the resulting fits from sample FALC3. No major changes on the second shell peak height at 2.8-2.9 Å are visible.

Figure 9. Ni K-edge μ EXAFS from samples LC101A, LC100B, GAR2C and FALC3 showing the main differences on Ni local environment from primary hydrothermal serpentine (LC101A_1 and LC100B_1), Fe-bearing serpentine from type I garnierite (LC101A_3), from kerolite-pimelite from type II and III garnierites (LC100B_2 and GAR2C_1) and sepiolite-falcondoite from type V garnierites (FALC3_3).

Figure 1

Figure 2.

Figure 3.

Figure 4.

Figure 5.

Figure 6.

Figure 7.

Figure 8.

Figure 9.

Figure 1. Images of the samples (left) and optical photomicrographs in plane polarized light of the regions of interest (ROI) selected to perform EMPA, μ XRF and μ XAS from samples **(a)** LC101A (saprolite and type I garnierite), **(b)** LC100B (saprolite and type II garnierite), **(c)** GAR2C (saprolite and type III), **(d)** GAR6 (type IV garnierite) and **(e)** FALC3 (type V garnierite). The brown fragments of the weathered saprolite are surrounded by the green garnierite veins.

Figure 2. Ternary plots showing the compositions of the analyzed garnierites compared to the five garnierite types described by (Villanova-de-Benavent et al., 2014). The compositions of the selected samples fall into the saprolite serpentine, and the garnierite Type I, II, III, IV and V fields. Abbreviations are after Whitney & Evans (2010), Tauler *et al.* (2009) and Villanova-de-Benavent *et al.* (2014), except Pec for pecoraite.

Figure 3. The μ XRF elemental maps (Fe K α in red, Ni K α in green and Cr K α in blue) and the chemical-state maps (in greyscale Fe⁺² and the Fe⁺³) showing ferrous veins within ferric saprolite fragments. The labelled points on the elemental map correspond to the spots where Ni-K EXAFS have been acquired and on the chemical-state maps correspond to the spots where Fe-K XANES have been acquired. The selected spots can be grouped in hydrothermal serpentine veins (LC101A_1 and LC100B_1), saprolite fragments (LC101A_2, LC100B_3 and GAR2C_2), Type I garnierite (LC100B_2), Type II garnierite (LC100B_2), Type III garnierite (GAR2C_1), Type IV garnierite (from GAR6_1 to GAR6_6) and Type V garnierite (from FALC3_1 to FALC3_6). The inset graph **(a)** shows the integrated XRF intensities at 10keV for samples LC101A, LC100B and GAR2C.

Figure 4. Ni K α vs Fe K α scatter plots for sample LC101A in blue, LC100B in green and GAR2C in red **(a)**. LC101A has a characteristic anticorrelation of Ni and Fe which corresponds to garnierite Type I surrounding the saprolite fragments **(b)**. The anticorrelation diminishes in LC100B4 and does correspond to the Ni-rich serpentine relicts present within the saprolite **(c)** and disappears in GAR2C **(d)**. The non-correlated Fe cts. corresponds to the saprolite fragments and the non-correlated Ni cts. to the garnierite matrix.

Figure 5. Fe K-edge μ XANES and the resulting fits with goethite (yellow), maghemite (red), serpentine (green) and forsterite (blue) **(a)** corresponds to LC101A_1 on the saprolite fragment **(b)** corresponds to LC101A_2 on the Ni-rich serpentine **(c)** corresponds to LC101A_3 on the Type I garnierite **(d)** corresponds to LC100B_1 on the serpentine vein and **(e)** corresponds to LC100B_2 on the saprolite fragment. **(f)** corresponds to GAR2C_2 on the saprolite fragment.

Figure 6. Ni K-edge μ EXAFS, the corresponding $FT(\chi(k))$ and the resulting fits from samples LC101A, LC100B and GAR2C. Differences on the second shell peak height at 2.8-2.9 Å are clearly visible.

Figure 7. Ni K-edge μ EXAFS, the corresponding $FT(\chi(k))$ and the resulting fits from sample GAR6C. No differences on the second shell peak height at 2.8-2.9 Å are visible despite of the differences of Ni content.

Figure 8. Ni K-edge μ EXAFS, the corresponding $FT(\chi(k))$ and the resulting fits from sample FALC3. No major changes on the second shell peak height at 2.8-2.9 Å are visible.

Figure 9. Ni K-edge μ EXAFS from samples LC101A, LC100B, GAR2C and FALC3 showing the main differences on Ni local environment from primary Ni-poor serpentine (LC101A_1 and LC100B_1), Fe-bearing serpentine from Type I garnierite (LC101A_3), from kerolite-pimelite from Type II and

III garnierites (LC100B_2 and GAR2C_1) and sepiolite-falcondoite from Type V garnierites (FALC3_3).