

Article

Mineralogical and Geochemical Characterization of the Sta. Cruz Nickel Laterite Deposit, Zambales, Philippines

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Abstract: In this study, we present mineralogical and geochemical characterization of samples systematically collected from a nickel laterite profile at the Sta. Cruz nickel laterite deposit, Zambales, Philippines. Wavelength-dispersive X-ray fluorescence spectroscopy (WDSXRF), mass-balance element mobility calculations, transmitted and reflected light microscopy, and previously reported results from coupled X-ray diffraction (XRD) and Rietveld refinement analyses reveal that the laterite profile investigated is composed of two main horizons—the limonite and saprolite zones—separated by a thin transitional zone. Based primarily on the mineral assemblage and major element chemistry, the main zones are further subdivided into subzones: upper limonite, lower limonite, transitional zone, upper saprolite, and lower saprolite. Garnierite veins were observed cutting the upper and lower saprolite subzones. Investigation of the structure of goethite within the limonite zone via Rietveld refinement shows that the crystallinity of goethite decreases with increasing Ni content and increasing crystallite size. This suggests that upwards through the limonite zone, as goethite ages, its crystallinity increases, which possibly results in the removal of Ni from its crystal structure and eventual remobilization to the lower laterite zones.

Keywords: nickel laterites; lateritization; serpentinization; weathering; goethite ageing



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1. Introduction

Tectonic emplacement of variably serpentinized ultramafic host rock on land and subsequent chemical weathering under humid tropical to subtropical conditions results in the formation of nickel laterite deposits [1–7]. Nickel laterites typically occur as weathering mantle over ophiolite complexes, as well as komatiites and layered complexes in Archean to Phanerozoic stable cratonic platforms [2,5]. Nickel laterite deposits have a characteristic profile (from the bottom to the top): (1) bedrock consisting of partially altered ultramafics; (2) a silicate or saprolite zone characterized by Mg-silicates, such as serpentine and garnierite; and (3) an oxide or limonite zone, predominantly composed of iron oxyhydroxides, principally goethite, hematite, and maghemite [1–6]. Garnierite is a general term for a distinctively green, neoformed, fined-grained, and poorly crystalline mixture of one or more Mg-Ni phyllosilicates including serpentine, talc, chlorite, smectite, and/or sepiolite [8–13]. The term “garnierite” has been used as a field term to describe this mineral assemblage in the absence of a more detailed mineral identification. Garnierites have been classified into two groups: (a) 1:1 phyllosilicate or serpentine group and (b) 2:1 phyllosilicate group (e.g., talc, kerolite, chlorite, and sepiolite) [10,13]. They are Ni-rich and typically occur as

veins along joints and shear zones, as matrix within breccias, and as coatings on saprolite blocks [4,5,14–17].

An earlier study [18] emphasizes the primary role of “goethite ageing” with the downward decrease in the bulk Ni content within the limonite of lateritic ores from New Caledonia. Goethite ageing refers to the upward increase in crystallinity of goethite within the limonite zone resulting from the expulsion of Ni from the crystal structure of goethite. Nickel is then either leached from the limonite or is sorbed on the surface of goethite crystals. This is supported by previous works [19,20] that observed a decrease in the crystallinity of goethite with increasing depth. These results suggest that as the nickel laterite profile evolves, goethite crystallinity increases, and nickel content decreases upward through the profile. Goethite ageing is therefore an important aspect of the evolution of the nickel laterite profile.

Here, we investigate samples collected from a nickel laterite profile from the Zambales Ophiolite, Philippines. We describe the mineralogy and geochemistry of the outcrop and confirm previous work on goethite ageing [18–20]. We show that small changes in the structure of goethite within the limonite zone is related to its nickel content and to the overall evolution of the laterite profile.

1.1. Zambales Ophiolite Complex

The Zambales ophiolite complex (ZOC), located in Zambales, Philippines (Figure 1a), is a generally north–south trending, east dipping complete ophiolite suite comprised of a succession of volcanic rocks, dike-sill complexes, ultramafic and mafic cumulates, residual harzburgite, and lherzolites [21–24]. The ZOC is subdivided into three massifs from north to south: the Masinloc, Cabangan, and San Antonio massifs, with each massif separated by west-northwest fault boundaries [25,26]. The Masinloc massif is made up of two blocks: the Acoje block in the north and the Coto block in the south. The Acoje block and the San Antonio massif are compositionally similar, having an island arc tholeiite (IAT) affinity, whereas the Coto block and the Cabangan massif have a signature transitional from a mid-ocean ridge basalt to island arc (MORB-IA) [22,26]. The ZOC has been dated Eocene based on the fossil assemblage of the overlying Aksitero formation [27,28]. Direct radiometric dating of various units from the ZOC concurs with the Late Eocene age of the Aksitero formation and yielded a Middle Eocene age for the ophiolite [29,30]. Schweller et al. [31] suggest an early Miocene eastward tilting and erosion of the ZOC, likely related to the subduction initiation along the ancestral Manila Trench. The Eocene age of the ophiolite implies that it is 10–15 Ma years older than the South China Sea (SCS) crust [32], suggesting that it cannot originate from the SCS [29].

1.2. Sta. Cruz Nickel Laterite Deposit

The Sta. Cruz nickel laterite deposit formed from the weathering of the ultramafic massif of the ZOC Acoje block (Figure 1). The selected nickel laterite profile is located in the municipality of Santa Cruz, northern Zambales. The deposit exhibits a typical laterite zonation, consisting of an upper limonite layer, which is underlain by the saprolite layer and bedrock. Nickel mineralization in the deposit is associated with the low-Ni, high-Fe limonite zone and the more extensive low-Fe, high-Ni saprolite zone [33]. The underlying bedrock is harzburgite with sporadic dunite lenses and minor chromitite. The harzburgite is partly serpentinized, with olivine replaced by serpentine pseudomorphs, but the grain shape has been retained. Orthopyroxene, on the other hand, is partly replaced by talc and chlorite [22].

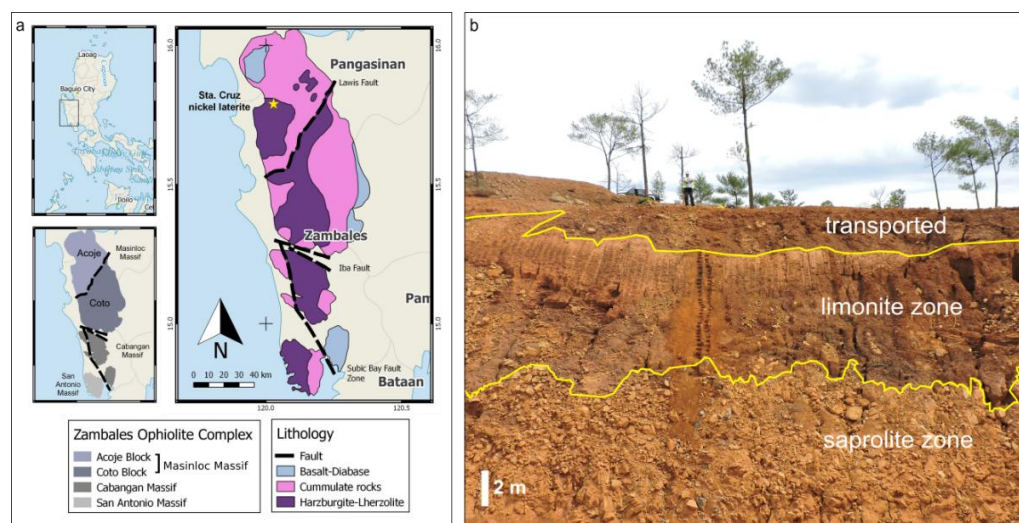


Figure 1. (a) Location of the study area. The Zambales Ophiolite Complex is in west Central Luzon, Philippines. It is subdivided into three massifs—the Masinloc, Cabangan, and San Antonio Massifs—separated by west–northwest fault boundaries. The Masinloc massif is subdivided into the Acoje and Coto blocks. Yellow star indicates the location of the Sta. Cruz nickel laterite deposit. (b) Photo of the nickel laterite profile investigated. The saprolite zone is overlain by the limonite zone. The topmost unit is a mechanically transported layer and is therefore not sampled for this study. Modified from Aquino et al. [34].

The nickel laterite profile investigated (Figure 1b) is approximately 12 m high and composed of two main units—an upper limonite zone (~7 m) and a lower saprolite zone (~5 m)—as well as a thin transitional zone (~10 cm), each characterized by a distinct set of physical, mineralogical, and geochemical properties. The detailed mineralogy of this outcrop can be found elsewhere [34,35] and is summarized in Figure 2.

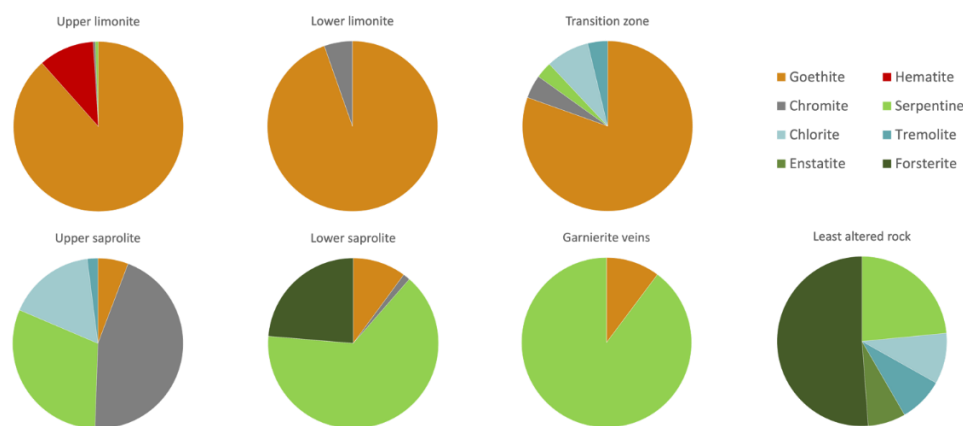


Figure 2. The laterite profile is subdivided into five subzones based on the mineralogy. The topmost zone is the upper limonite subzone, dominated by goethite with minor hematite, and is underlain by the lower limonite subzone composed of goethite and minor chromite. The transition to the saprolite is marked by the first appearance of silicate minerals and a decrease in goethite abundance. The saprolite zone is marked by the dominance of Mg-silicates and a decrease in the abundance of goethite. The upper saprolite subzone is comprised mostly of serpentine, with minor chlorite and tremolite. The lower saprolite subzone is distinguished by the presence of relict olivine. The sample taken at a depth of 10.5 m represents the least altered rock in the profile. This sample is moderately serpentinized (~40%) and has significant primary minerals. Lastly, garnierite veins are composed of about 90 wt% serpentine and 10 wt% goethite. Note that abundant chromite of primary origin was observed in the upper saprolite zone. Data are obtained from Aquino et al. [34].

2. Materials and Methods

Soil samples from the limonite and transitional zones and rock samples from the saprolite zone were collected from the nickel laterite outcrop described above (Figure 1b). The topmost 2 m of the outcrop are composed of mechanically transported materials and were not sampled for this study. Depths presented in Tables 1 and 2 and discussed throughout this paper are measured with respect to the top of the upper limonite zone. A total of 33 soil samples were collected at an interval of 20 cm, while 13 rock samples were collected at an interval of 50 cm. Samples collected near the transition zone between the limonite and saprolite zones (i.e., from 6.4 to 6.5 m) were collected at an interval of 10 cm.

2.1. Petrographic Analysis

Eight polished thin sections of the saprolite samples and the least altered rock were prepared at the Energy Research and Testing Laboratory at the Philippine Department of Energy (Taguig City, Philippines). Chromite-rich samples (>70 wt%) from the upper saprolite zone were not selected for microscopy. The samples were observed under transmitted and reflected light using a TrueVision petrographic microscope and an Olympus BX53P polarizing microscope equipped with DP74 camera at the University of the Philippines, National Institute of Geological Sciences (Quezon City, Philippines).

2.2. X-ray Diffraction Analysis

A total of 46 soil and rock samples were prepared for X-ray diffraction analyses. The samples were pulverized to ~200 mesh (<0.075 mm) using an agate mortar and pestle and were subsequently oven-dried at 105 °C for 24 h. The powdered samples were then packed on a cylindrical top-filled sample holder. The diffractograms of the samples were determined using a Bragg–Brentano Shimadzu XRD-7000 X-ray Diffractometer with CuK α radiation at the University of the Philippines, National Institute of Geological Sciences. The samples were analyzed using a step size of 1° per min at a 3° to 90° scan range and voltage of 30 kV. The mineral phases were then identified using the PDF4+ Minerals Database by the International Center for Diffraction Data (ICDD), as well as the Materials Data, Inc. MINERAL database [36]. Mineralogical phases were quantified via Rietveld refinement of the diffractograms using the program Siroquant, version 3.0 [34]. Furthermore, the crystallinity of the goethite phase was evaluated by observing the change in the full width at half maximum (FWHM) of the goethite (110) peak. The FWHM was calculated via the Debye–Scherrer equation [37]:

$$D = \frac{k\lambda}{\beta \cos \theta} \quad (1)$$

where k is a dimensionless shape factor, λ is the wavelength of the X-ray source (1.5418 Å for CuK α), D is the crystallite size of goethite phase as obtained from Rietveld refinement, θ is the peak position of the (110) peak in radians (0.1844), and β is the FWHM.

2.3. Whole Rock Analyses and Loss on Ignition

The samples were pulverized and dried at 105 °C for a minimum of 6 h and then cooled in a desiccator. Fused beads for each sample were then prepared using an AFM—ModuTemp automated fusion machine. The major and minor element concentrations of the samples were analyzed using a PANalytical Axios PW4400 X-ray fluorescence wavelength dispersive spectrometer. Preparation of fused beads, XRF, and loss on ignition (LOI) analyses were performed at Intertek Testing Services Philippines, Inc. (Muntinlupa City, Philippines).

2.4. Mass Balance Calculations

Mass balance calculations were performed following the isocon method [38,39]. Briefly, this method involves the evaluation of the relative changes in the concentration of an altered rock with respect to the parent rock. This is done by plotting the chemical composition of

the altered rock (C^A) against the composition of the parent rock (C^O). The isocon is a line defined by one or more immobile species and the origin and has the following equation:

$$C^A = \left(\frac{M^O}{M^A} \right) C^O. \quad (2)$$

Isocons were calculated using Fe and Ti as the immobile components, as has been done in similar deposits [40,41]. The relative mass changes of a component can be evaluated as follows:

- Relative mass gain—species plotting above the isocon
- Relative mass loss—species plotting below the isocon.

Additionally, the slope of the isocon gives information on the overall change in the mass relative to the protolith (M^O/M^A).

2.5. Ultramafic Index of Alteration

For each sample, an ultramafic index of alteration (UMIA) was calculated [41]. This chemical alteration index, which is a modified version of the mafic index of alteration (MIA) [42], as well as other previously used chemical alteration indices [43,44], quantifies the chemical changes that occurred during the chemical weathering process. The UMIA is defined as:

$$UMIA = 100 \times \left[\left(Al_2O_3 + Fe_2O_{3(T)} \right) / \left(SiO_2 + MgO + Al_2O_3 + Fe_2O_{3(T)} \right) \right] \quad (3)$$

where molar ratios of the respective major elements are used. The following UMIA values are expected for each of the laterite zones: unweathered peridotite bedrock, ~3; saprolite, 4–8; limonite, 60–90 [41]. No UMIA values were previously reported for samples taken from the transition zone.

3. Results

3.1. Petrography

Samples from the limonite and transition zones are extremely weathered, with no primary minerals or textures observed in hand specimen (Table 1). The saprolite samples are also heavily weathered and altered in hand specimen and thin section (Figures 3–5). Primary minerals, such as olivine and orthopyroxene, are sparse in most samples except for the least weathered sample, N-1050 (Figure 6). These primary minerals are altered mostly to serpentine (~60–85%), although poorly crystalline Fe oxides (~5–15%) and magnetite (trace) are also present. All samples contain small amounts (<5%) of chromite, except for samples N-690 and N-1000. N-690 is adjacent to a chromitite layer located at depths between 6.8 m and 7.0 m and thus contains a significant amount of chromite (~20%, Table 2). N-1000 contains visible chromite bands (Figure 3f) in hand specimen.

Table 1. Macroscopic description of samples from the limonite and transition zones.

Depth (m)	Zone ¹	Munsell Color	Descriptive	Short Description
0	UL	7.5YR 5/8	dark brown	mostly very fine soil (<1 mm) to coarse fragments (>10 mm) of Fe oxides
0.8	UL	5YR 4/8	reddish brown	mostly very fine to fine soil (<1 mm) to medium fragments (<5 mm) of Fe oxides; slightly darker red color probably due to presence of small amounts of hematite
1.6	UL	5YR 4/8	reddish brown	fine to medium (1–5 mm) grained fragments of Fe oxides; slightly darker red color probably due to presence of small amounts of hematite

Table 1. Cont.

Depth (m)	Zone ¹	Munsell Color	Descriptive	Short Description
2.4	UL	5YR 4/8	reddish brown	mostly very fine soil (<1 mm) to coarse fragments (>10 mm) of Fe oxides; slightly darker red color probably due to presence of small amounts of hematite
3.2	LL	5YR 4/8	reddish brown	mostly medium to coarse grained (5–10 mm) fragments of Fe oxides; slightly darker red color probably due to presence of small amounts of hematite
4.0	LL	7.5YR 5/8	dark brown	fine soil (~1 mm) to medium fragments (<5 mm) of Fe oxides
4.8	LL	7.5YR 5/8	dark brown	fine soil (~1 mm) to coarse fragments (>10 mm) of Fe oxides
5.6	LL	7.5YR 5/8	dark brown	mostly medium to coarse grained (5–10 mm) fragments of Fe oxides
6.4	T	7.5YR 5/8	dark brown	poorly sorted mixture of mostly very coarse grained (>30 mm) and medium grained (1–5 mm) Fe oxide-rich rock fragments

¹ UL = upper limonite, LL = lower limonite, T = transition zone.

Four types of serpentine, distinguished by their occurrence and association with secondary magnetite, were observed in the saprolite of the Sta. Cruz nickel laterite deposit. Type 1 serpentine (Figures 4–6) occurs immediately adjacent to partially or completely dissolved relict olivine grains. It is characteristically magnetite-free, or, when present, magnetite occurs only in minor amounts. Moreover, type 1 serpentine is pale green and slightly pleochroic under plane-polarized light and exhibits up to first-order yellow interference colors in crossed-polarized light. Type 1 serpentine is further subdivided into types 1a and 1b serpentine. Type 1a has a thickness of not more than 30 μm , and it occurs in the least altered rock along fractures and grain boundaries in olivine and pyroxene. Type 1b occurs in the saprolite, exhibits a mesh texture around olivine fragment, and is approximately 50 to 150 μm thick. Type 2 serpentine, on the other hand, occurs as roughly parallel serpentine veins cross-cutting type 1 serpentine and is characteristically magnetite and Fe-oxide stain free. They typically occur in the lower saprolite (e.g., N-900; Figure 5). They are colorless in plane-polarized light and exhibit almost black interference colors in crossed-polarized light. Type 3 serpentine, like type 2, occurs as veins and is typically observed in the upper saprolite. It is often associated with moderate to abundant secondary magnetite, which is usually within the core of the serpentine vein (e.g., N-650; Figure 4). In plane-polarized light, type 3 serpentine is colorless to pale greenish yellow and has low relief in crossed-polarized light. It exhibits very low interference colors of up to first-order gray to white. Lastly, garnierite serpentine veins (type 4) are light green to pale green, vein-type serpentine observed to crosscut the saprolite zone (Figure 3). In thin section, type 4 serpentine is light yellowish brown in plane-polarized transmitted light and has a bright yellowish green interference color in crossed-polarized light (Figure 5).

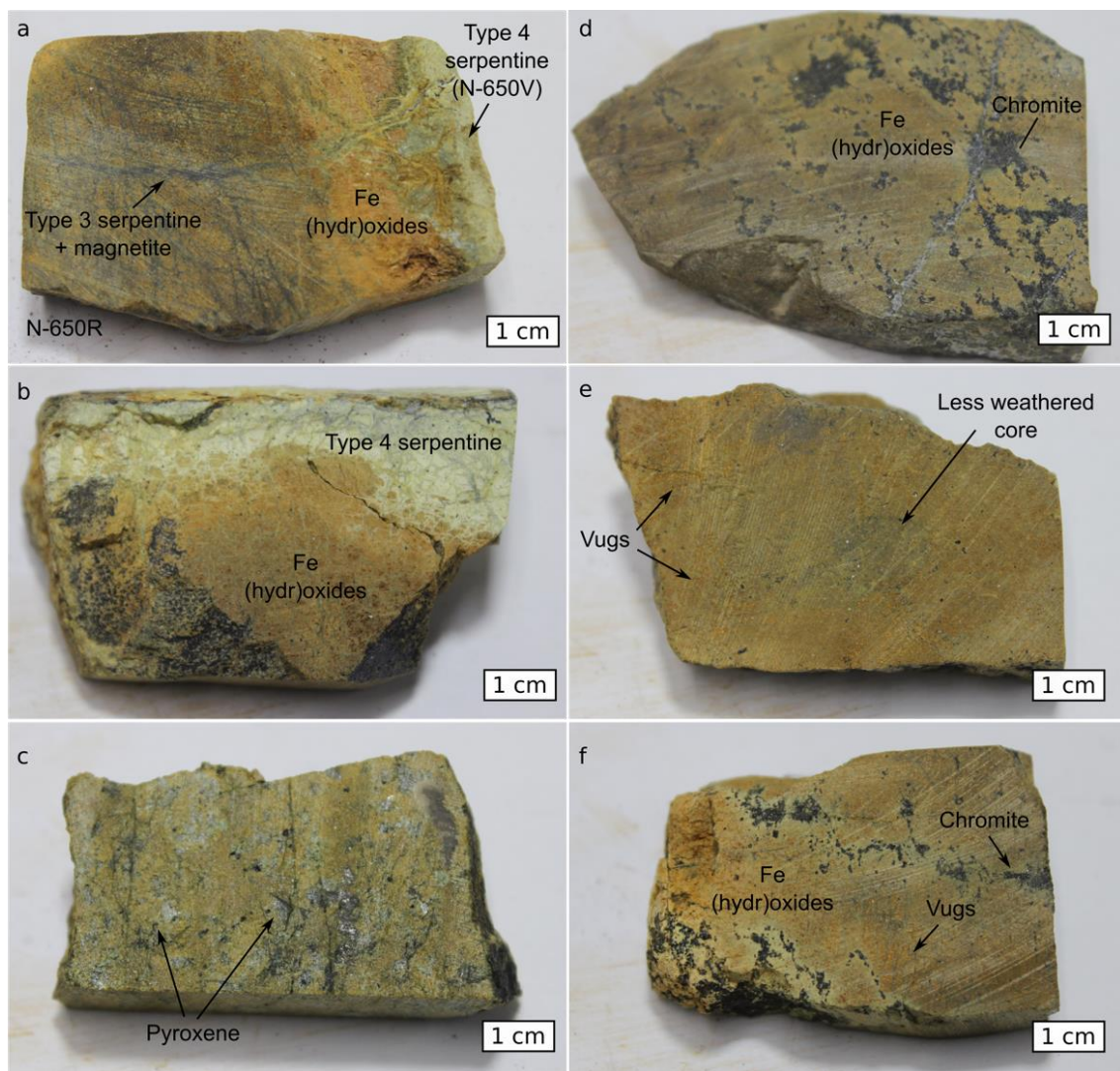


Figure 3. Saprolite samples in hand specimen. (a) Sample N-650R showing black serpentine–magnetite veins (type 3) being altered into light-green serpentine (type 4, N-650V). (b) Sample N-1100, heavily altered saprolite sample with a garnierite vein (type 4). Note that the serpentine vein emanates from what appears to be boundaries of relict grains. (c) Sample N-1050, least altered saprolite sample showing pyroxene crystals about 2–3 mm in size. (d) Sample N-690, containing unaltered chromite disseminated in a matrix of strongly weathered Fe (hydr)oxides. (e) Sample N-850, heavily weathered sample with a less altered core. Small dissolution vugs later filled by Fe hydr(oxides) are also present. (f) Sample N-1000, showing unaltered disseminated chromite in an Fe hydr(oxide) weathered matrix. Dissolution vugs are also present.

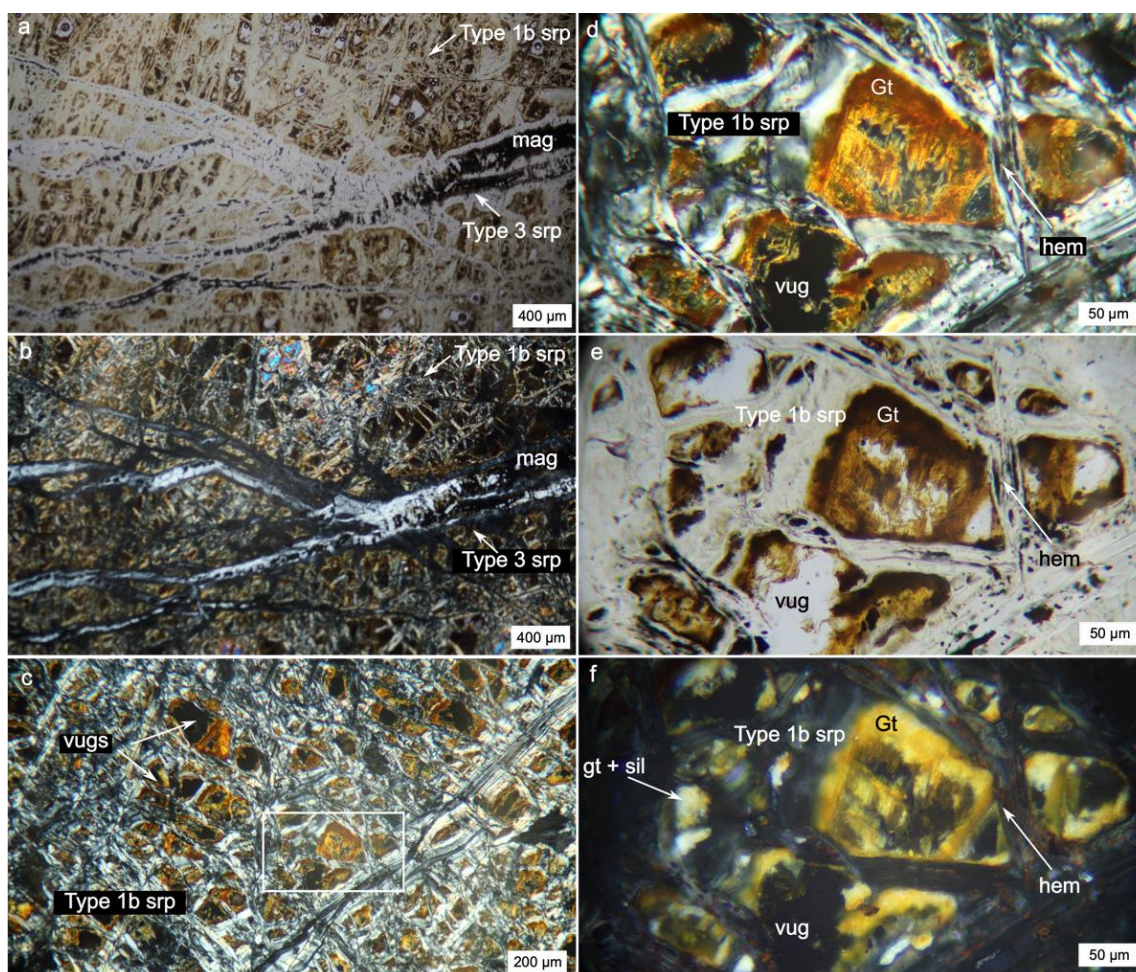


Figure 4. Upper saprolite sample N-650R in thin section. (a) Sample N-650R is a heavily serpentinized rock with almost no primary olivine remaining. Type 1b (mesh-type) serpentine (srp) surrounding partially or completely dissolved olivine, crosscut by type 3 (vein-type, magnetite-rich) serpentine in plane-polarized transmitted light. (b) Same as (a) in crossed-polarized transmitted light. (c) Occurrence of poorly crystalline Fe-oxides (gt), as well as minor amorphous silica (sil), as precipitates within dissolution vugs after olivine, in crossed-polarized transmitted light. (d) Detail of white box in (c), showing a dissolution vug filled with Fe-oxides. Surrounding mesh serpentine (type 1b) contains minor hematite (hem), likely from oxidation of magnetite. (e) Same as (c) in plane-polarized transmitted light. (f) Same as (c) in crossed-polarized reflected light, showing bright orange internal reflections of poorly crystalline Fe-oxides, red internal reflections of hematite, and white internal reflections of amorphous silica.

3.1.1. Petrography of Upper Saprolite Samples

Samples from the upper saprolite (e.g., N-650R; Figure 4) are strongly weathered and altered to serpentine (up to 85%). Most of the primary minerals are altered to serpentine, 15% poorly crystalline goethite (poorly crystalline iron oxide), and about 3% magnetite. Primary minerals, including about 5% olivine, 2% tremolite, and trace amounts of orthopyroxene, are sparse. Olivine crystals, where present, are about 40 to 200 μm in size with average size of about 100 μm , whereas orthopyroxene minerals are about 200 to 1400 μm in size. Dissolution cavities occur within sites of relict primary minerals (Figure 4). In sample N-660, the size of the cavities is approximately 50 to 300 μm , which is similar in size to the cavities and relict olivine minerals observed in sample N-650R. These cavities are often filled partially or completely with secondary, poorly crystalline goethite $\pm$ amorphous silica (Figure 4c–f). Serpentine occurs both as vein-type serpentine (type 3), as well as

mesh-type serpentine (type 1b) around completely or partially dissolved olivine crystals (Figure 4c).

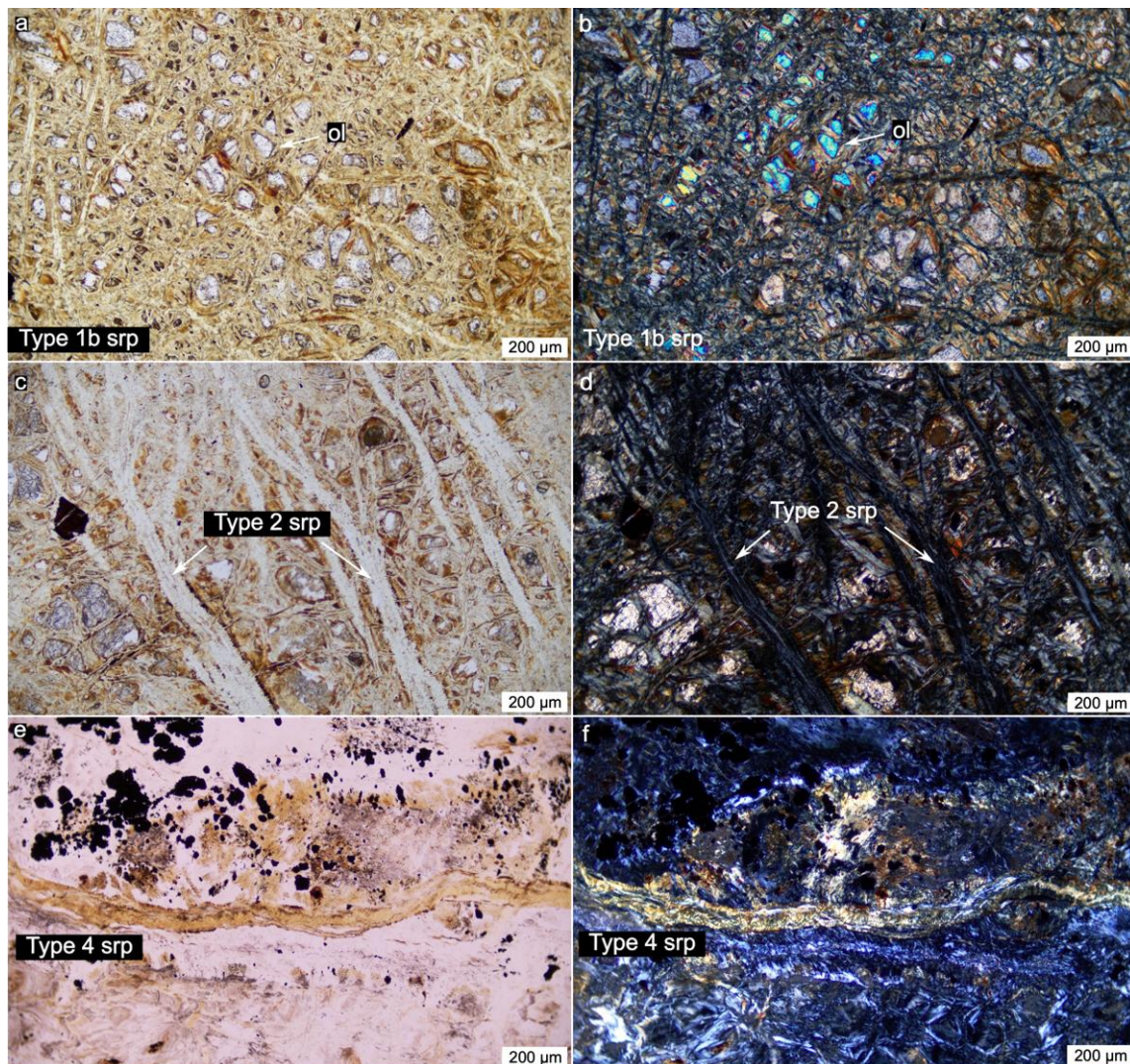


Figure 5. Thin section of samples from the lower saprolite. (a) Sample N-750 is strongly serpentinized and contains a significant amount of primary olivine fragments in optical continuity. Note the brown discoloration on some of the type 1b serpentines, likely due to the presence of Fe-oxide. (b) Same as (a) in crossed-polarized transmitted light. (c) N-900 showing roughly parallel serpentine veins (type 2 serpentine) free from Fe-oxide discoloration. Further shown are partially dissolved relict olivine grains. (d) Same as (c) in crossed-polarized transmitted light. (e) Photomicrograph of type 4 serpentine crosscutting the lower saprolite in plane-polarized transmitted light. (f) Same as (e) in crossed-polarized transmitted light.

3.1.2. Petrography of Lower Saprolite Samples

Samples from the lower saprolite zone (Figure 5) are less altered to serpentine (~60%) than the upper saprolite samples. Primary minerals, mostly olivine, are more abundant (up to 30%) and occur as 2–4 mm-sized groups of optically continuous crystals, with each individual fragment about 30 to 300 µm in size. Minor minerals include chromite (5%), as well as amorphous Fe oxides and trace amounts of magnetite. In sample N-750, serpentine occurs both as vein-type and mesh-type (type 1b), with the vein-type serpentine associated with fillings of magnetite (type 3). Samples taken from the deeper sections (e.g., N-900) are observed to contain both mesh-type (type 1b) and magnetite-free, subparallel

serpentine veins (type 2) (Figure 5c,d). Throughout the lower saprolite, olivine crystals show dissolution features and, in places, are observed to be directly altered to brown Fe-oxides (Figure 5). Poorly crystalline goethite imparts a generally brown tinge in the lower saprolite samples as a result of either direct replacement of partially dissolved olivine (i.e., as discoloration in minerals) or infills within dissolution cavities.

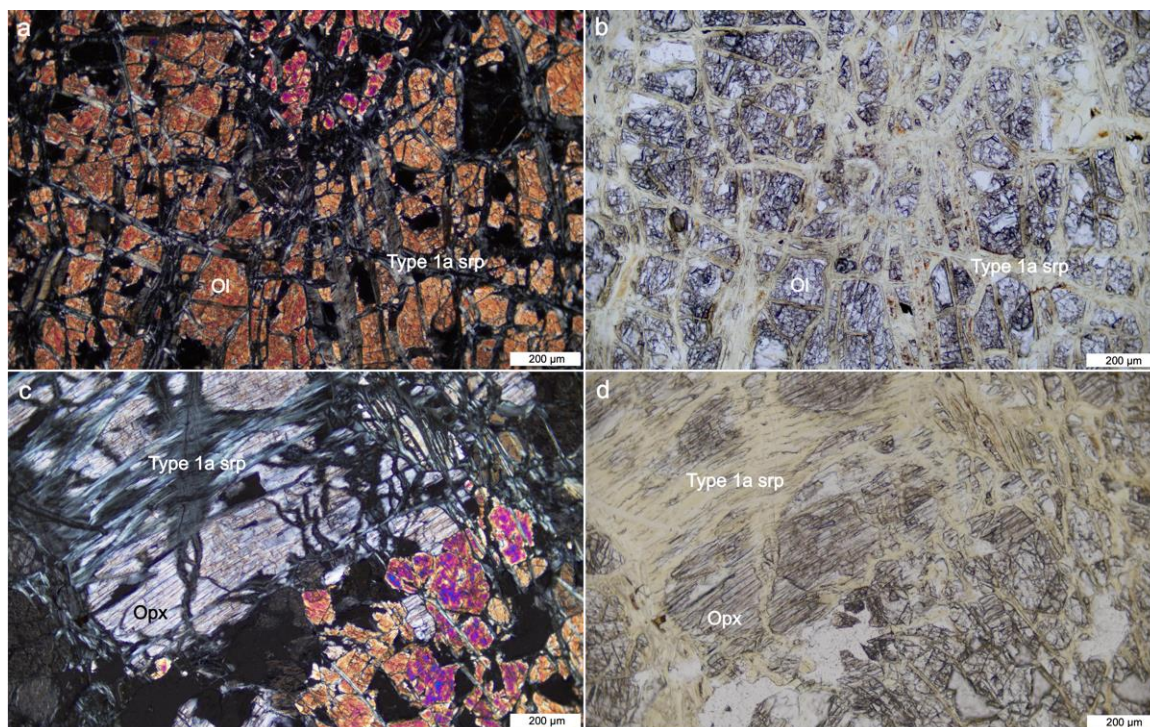


Figure 6. Photomicrographs of the least altered rock in the profile investigated. (a) Olivine (Ol) cut by crosscutting serpentine (type 1a) in transmitted plane-polarized light and (b) in crossed-polarized light. (c) Pyroxene (Opx) is also partially serpentinized parallel to its cleavage planes, in transmitted plane-polarized light. (d) Same as (c) in crossed-polarized transmitted light.

3.1.3. Petrography of the Least Altered Rock

Sample N-1050 represents the least altered rock in the profile (Figure 6). The sample is moderately serpentinized and contains about 40% serpentine but is also composed of abundant primary minerals including about 50% olivine, 10% pyroxene, and trace amounts of chromite. Olivine is fragmented and is cut by crosscutting vein-type type 1a serpentine approximately 20–30 µm thick, forming isolated fragments about 100 to 200 µm in size in optically continuous groups of about 2 to 4 mm. The olivine surface is rough and dissolved, as clearly seen in plane-polarized transmitted light. Dissolution cavities are also present locally in the sample and have not yet been filled with any secondary material. Unlike in other samples, olivine crystals are colorless with minimal alteration to Fe-oxides. The serpentine veins are also colorless and do not seem to have Fe-oxide staining. Pyroxene minerals are preserved in this sample and occur as large crystals more than 4 mm in size, often cut by serpentine (type 1a) parallel to cleavage traces (Figure 6).

3.2. Goethite Crystallinity and Crystallite Size Measurements

Crystallite size measurements of the goethite phase obtained from Rietveld refinement of the limonite layer reveal a generally decreasing trend with depth (Figure 7a, Table A1). Goethite crystallite sizes, which initially increase from 115 to 139 Å in the topmost upper limonite, show a pronounced decreasing trend from 139 to 112 Å in the upper limonite (i.e., depths of 0.8 to 3.2 m). Towards the mid-lower limonite, at depths of 3.6 to 4.8 m, the

crystallite sizes slightly increase in value to 127 Å before decreasing again to 117 Å towards the bottom of the lower limonite. In the transition zone, the value increases again to 124 Å.

The calculated full width at half maximum (FWHM) values from the measured crystallite sizes are shown in Figure 7b and Table A1. As expected from the Debye–Scherrer equation (Equation (1)) [37], the crystallite size and the FWHM have an inverse relationship. Thus, a generally increasing trend with depth in the FWHM values is observed for the studied limonite samples. FWHM values first decrease slightly from a value of 1.09 degrees at the uppermost limonite layer (0 m) to 0.91 degrees at 0.8 m and then generally increase to a maximum of 1.11 degrees at a depth of 3.2 m. The FWHM values decrease slightly again to 0.99 degrees at 4.8 m and decrease again up to 1.07 towards the bottom of the lower limonite at a depth of 6.0 m.

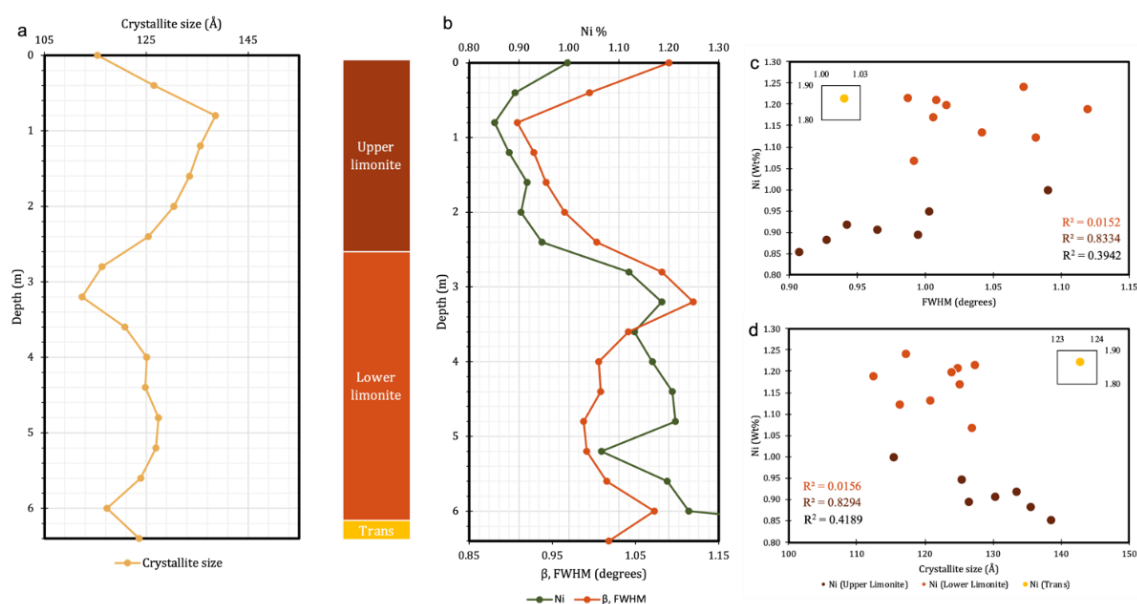


Figure 7. (a) Variations in crystallite size of goethite in the limonite and transition zones with depth, as calculated via Rietveld refinement. (b) Bulk Ni content and calculated full width at half maximum values of goethite in the limonite and transition zones with depth. (c) Relationship of bulk Ni content and full width at half maximum (FWHM) of goethite and (d) bulk Ni content and crystallite size of goethite in the limonite and transition zones. Further shown are the R² values of the samples from the upper limonite (red), lower limonite (orange), and whole limonite (black) zones.

3.3. Bulk Major and Minor Geochemistry

3.3.1. Limonite Zone

The limonite zone contains elevated Fe₂O₃ (up to 75.4 wt%) and Al₂O₃ (up to 14.4 wt%) and relatively low MgO (average: 1.5 wt%) and SiO₂ (average: 4.5 wt%) concentrations (Table 2, Figure 8a). Within the limonite, Fe content slightly decreases upwards. Interestingly, the Al₂O₃ content of the upper limonite zone is generally higher compared to the lower limonite zone. Within the limonite, the MgO content slightly increases downwards from an average value of 1.2 wt% in the upper limonite to 1.7 wt% in the lower limonite. Contrary to the behavior of MgO values, SiO₂ content shows a decreasing trend downwards within the limonite, with an average value of 6.6 wt% in the upper limonite to 2.9 wt% in the lower limonite. Significant concentrations of Ni, Mn, and Co are noted in the limonite zone of the investigated profile (Figure 8b). Within the limonite, NiO content ranges from 1.1 to 1.6 wt% and generally increases with depth. Average values for MnO and Co are 0.91 and 0.10 wt%, respectively. Both MnO and Co show a slightly increasing trend in the limonite zone with depth. MnO values are enriched up to 1.09 wt% at the lower limonite while Co values are enriched up to 0.16 wt% near the transition zone to the saprolite.

3.3.2. Transition Zone, Saprolite Zone, and Garnierite Veins

Fe_2O_3 shows a sharp decrease in concentration towards the transition and saprolite zones (average of 43.2 wt% and 12.5 wt%, respectively; Figure 8a). Al_2O_3 content in the transition zone is 6.2 wt%, which decreases further to an average of 3.1 wt% in the saprolite zone. From the limonite zone, MgO and SiO_2 increase to values of 12.6 wt% and 16.5 wt%, respectively, in the transition zone and to values of 31.6 wt% and 32.7 wt%, respectively, in the saprolite zone. NiO content is generally more elevated in the saprolite than in the limonite, with values of up to 3.0 wt% (Figure 8b). MnO and Co values are generally not as significant within the saprolite as in the limonite zone, with average values of 0.21 wt% for MnO and 0.02 wt% for Co .

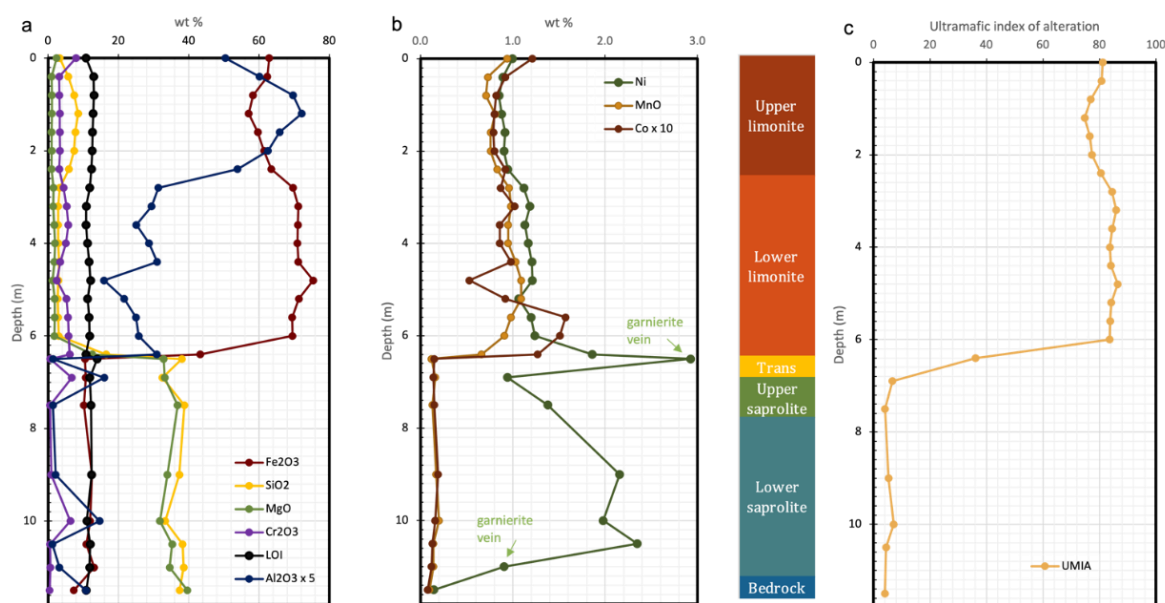


Figure 8. (a) Major and (b) minor element geochemistry of the studied profile and the corresponding laterite horizons. (c) Calculated ultramafic index of alteration (UMIA) [41]. Note the relatively high Ni contents of the upper garnierite vein.

Overall, the two garnierite veins have slightly higher SiO_2 , MgO , and NiO and lower Fe_2O_3 , Al_2O_3 , and MnO than the average saprolite (Table 2). Interestingly, the serpentine vein sampled at a higher depth has a higher NiO content than the vein sampled below the lower saprolite. LOI values do not show any significant difference between each laterite horizon, with values ranging from 10.8 to 14.0 wt% within the profile.

3.4. Ultramafic Index of Alteration

The ultramafic index of alteration (UMIA) values calculated for the Sta. Cruz nickel laterite profile (Table 2, Figure 8c) are generally consistent with expected values [41]. UMIA values in the limonite zone range from 74.7 to 86.5. The upper limonite has slightly lower UMIA values than the lower limonite. Towards the transition zone, the UMIA values decrease to 36.1, before decreasing significantly to values less than 8 in the saprolite. There is no significant trend in the UMIA values between the upper and lower saprolite or the garnierite veins.

Figure 9 shows plots of the Sta. Cruz nickel laterite samples in molar ternary AF-S-M ($\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3 - \text{SiO}_2 - \text{MgO}$) and A-SM-F ($\text{Al}_2\text{O}_3 - \text{SiO}_2 + \text{MgO} - \text{Fe}_2\text{O}_3$) diagrams, including their corresponding UMIA values. Both diagrams show weathering of an initially Mg- and Si-rich peridotite bedrock towards an Al- and Fe-rich limonite. There is a clear separation of the upper and lower limonite samples in both diagrams, indicating that the upper limonite contains relatively more Al and Si compared to the lower limonite.

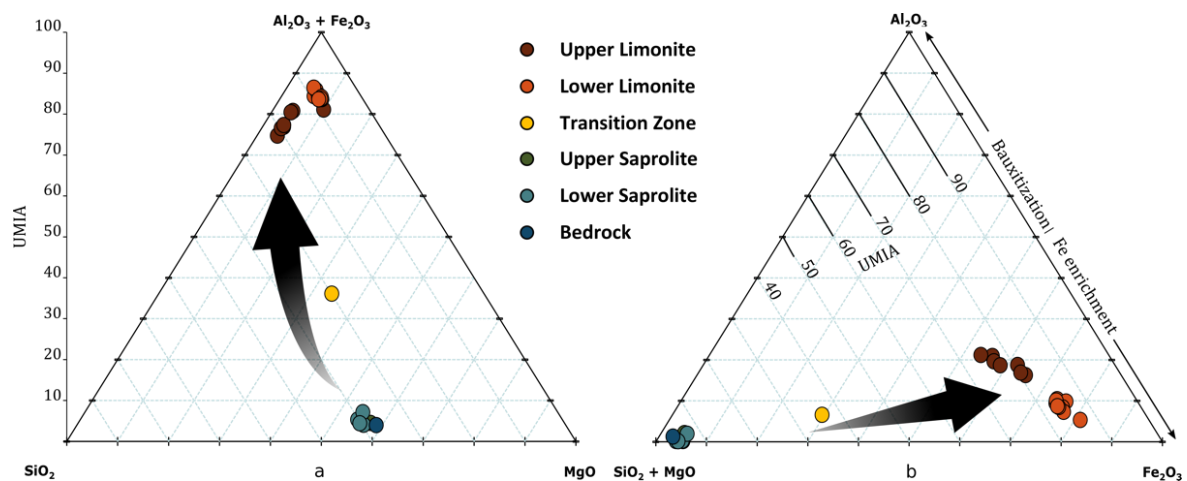


Figure 9. Chemical evolution of the laterite profile during weathering as shown by (a) molar ternary $\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$ - SiO_2 - MgO (AF-S-M) and (b) molar ternary Al_2O_3 - $\text{SiO}_2 + \text{MgO}$ - Fe_2O_3 (A-SM-F) diagrams. Both diagrams show weathering of an initially Mg- and Si-rich peridotite bedrock towards an Al- and Fe-rich limonite while (b) highlights that Fe-enrichment is predominant over bauxitization in the Sta. Cruz nickel laterite. Further shown is the ultramafic index of alteration (UMIA) [41].

3.5. Relative Mass Changes

Relative mass changes (Figure 10, Table A2) calculated for the studied outcrop are similar to those observed in other laterite deposits [40,45]. The limonite zone is characterized by an almost complete removal of SiO_2 (i.e., up to 99% relative mass loss) and MgO (up to 100% mass loss). Ni is also leached by up to about 50% in the limonite, with the amount of depletion decreasing with depth. Co and MnO, on the other hand, are associated with mass gains in the limonite. Co mass gains increase in the lower limonite towards the transition zone. A similar behavior is observed for Mn but to a lesser degree.

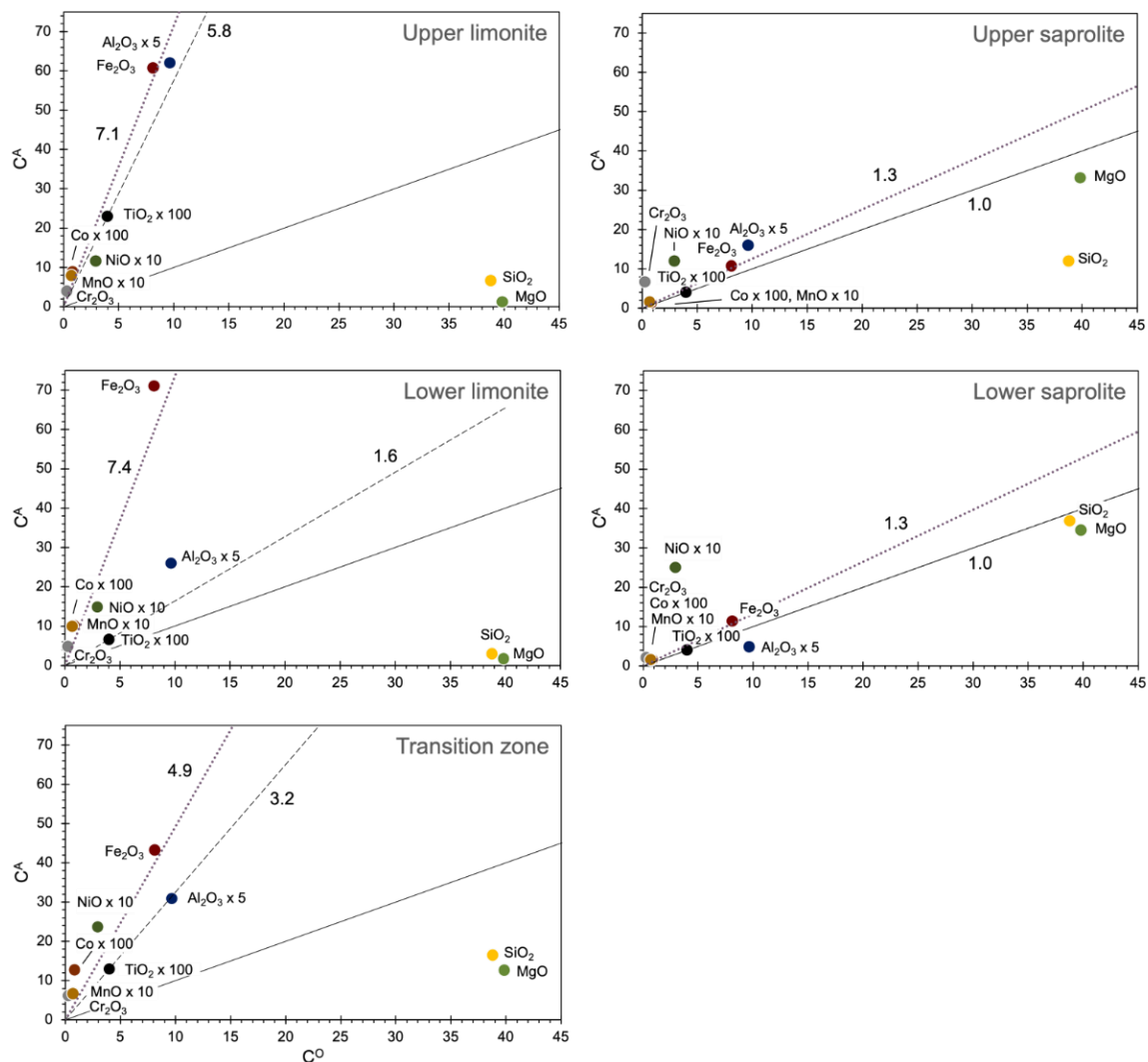


Figure 10. Isocon diagrams for each laterite zone in the outcrop investigated. Altered compositions (C^A) are the average composition of the samples from each zone. The composition of the parent rock (C^O) is the average composition of two peridotite samples collected near the study area (Table 2). Dashed line is the isocon defined by the immobile species Ti and the origin, while dotted line is the best-fit isocon defined by Fe, Ti, and the origin. Solid line represents $M^O/M^A = 1$. The numbers are the slope of the isocon or M^O/M^A . Species plotting along the isocon did not change their mass during transformation, species plotting above the isocon experienced mass gains, whereas species plotting below the isocon experienced mass loss during transformation.

The transition zone is characterized by a slight decrease in the associated SiO_2 and MgO mass loss. Ni starts to experience a slight mass gain (+64%), while Co mass gains are the highest around this zone. Towards the saprolite zone, MgO and SiO_2 mass losses decrease to an average of -34% and -33% , respectively. The saprolite zone is also characterized by mass gains of NiO, MnO, and Co, with the NiO mass gains reaching more than +600%. Interestingly, the least altered rock (N-1050) is associated with significant Ni mass gain of +668%.

Table 2. Bulk geochemistry and ultramafic index of alteration (UMIA) of samples from the Sta. Cruz nickel laterite. All compositions are in wt%.

Sample	Horizon ¹	Depth (m)	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	Cr ₂ O ₃	MnO	NiO	Co	MgO	CaO	BaO	Na ₂ O	K ₂ O	P ₂ O ₅	SO ₃	LOI	Total	UMIA
N-000	UL	0.0	3.28	0.12	10.08	62.91	7.91	0.94	1.27	0.12	2.42	<0.01	<0.005	<0.01	<0.01	0.01	0.29	10.78	100.0	81.1
N-040	UL	0.4	5.75	0.21	12.03	62.34	3.14	0.73	1.14	0.09	1.02	<0.01	<0.005	0.02	<0.01	0.02	0.39	12.96	99.7	80.8
N-080	UL	0.8	7.43	0.29	13.94	58.27	3.23	0.71	1.08	0.08	1.09	<0.01	<0.005	0.02	0.01	0.02	0.34	13.03	99.5	76.9
N-120	UL	1.2	8.53	0.31	14.42	57.04	3.33	0.81	1.12	0.08	1.07	<0.01	<0.005	<0.01	0.02	0.02	0.30	12.84	99.8	74.7
N-160	UL	1.6	7.74	0.26	13.17	59.67	3.33	0.76	1.17	0.08	1.01	<0.01	<0.005	0.01	0.01	0.02	0.30	12.65	100.1	76.6
N-200	UL	2.0	7.38	0.24	12.51	61.43	3.38	0.76	1.15	0.08	1.04	<0.01	<0.005	<0.01	<0.01	0.01	0.30	12.57	100.8	77.3
N-240	UL	2.4	5.92	0.18	10.78	63.52	3.16	0.83	1.20	0.09	0.95	<0.01	<0.005	0.02	<0.01	0.01	0.24	12.34	99.2	80.5
N-280	LL	2.8	3.27	0.08	6.27	69.67	4.38	0.96	1.43	0.09	1.51	<0.01	0.02	0.02	<0.01	0.01	0.18	11.86	99.7	84.4
N-320	LL	3.2	2.85	0.06	5.88	71.17	5.26	0.98	1.51	0.10	1.42	<0.01	0.01	0.01	<0.01	0.01	0.17	10.84	100.2	85.9
N-360	LL	3.6	2.84	0.06	5.02	71.05	5.76	0.95	1.44	0.09	1.75	<0.01	0.01	0.02	<0.01	0.01	0.15	10.81	99.9	84.5
N-400	LL	4.0	2.90	0.06	5.74	70.90	5.06	0.95	1.49	0.09	1.99	<0.01	<0.005	0.01	<0.01	0.01	0.16	11.19	100.5	83.7
N-440	LL	4.4	3.09	0.07	6.20	71.19	3.49	1.03	1.54	0.10	1.80	<0.01	<0.005	0.02	<0.01	0.01	0.17	11.66	100.3	84.1
N-480	LL	4.8	2.89	0.04	3.18	75.38	2.47	1.09	1.54	0.05	1.24	<0.01	0.06	0.03	<0.01	0.01	0.14	12.07	100.1	86.5
N-520	LL	5.2	2.76	0.06	4.33	71.31	5.24	1.09	1.36	0.09	1.86	<0.01	0.03	0.02	<0.01	0.01	0.12	11.25	99.4	84.2
N-560	LL	5.6	2.86	0.08	5.00	69.43	5.70	0.98	1.52	0.16	1.86	<0.01	<0.005	0.02	<0.01	0.01	0.13	11.65	99.2	83.8
N-600	LL	6.0	3.05	0.08	5.15	69.53	5.85	0.91	1.58	0.15	1.79	0.01	<0.005	<0.01	<0.01	0.01	0.14	11.82	99.9	83.6
N-640	T	6.4	16.48	0.13	6.18	43.23	6.16	0.66	2.37	0.13	12.57	0.65	<0.005	0.04	<0.01	0.01	0.06	10.77	99.3	36.1
N-650	V	6.5	38.04	<0.01	0.29	10.47	0.63	0.12	3.72	0.02	32.87	<0.01	<0.005	<0.01	<0.01	<0.001	0.02	13.98	100.1	
N-690	US	6.9	32.52	<0.01	3.19	10.68	6.73	0.16	1.20	0.01	33.16	<0.01	0.01	0.19	<0.01	<0.001	<0.001	11.87	99.7	6.7
N-750	LS	7.5	38.74	<0.01	0.28	10.16	0.57	0.13	1.75	0.02	36.85	0.02	<0.005	0.01	<0.01	<0.001	0.01	12.20	100.7	4.1
N-900	LS	9.0	37.34	<0.01	0.43	12.51	0.90	0.17	2.75	0.02	33.94	0.01	<0.005	<0.01	<0.01	<0.001	0.01	12.36	100.4	5.3
N-1000	LS	10.0	33.31	0.04	2.93	11.96	6.33	0.20	2.52	0.02	31.83	<0.01	<0.005	<0.01	<0.01	<0.001	0.01	11.01	100.1	7.2
N-1050	LS	10.5	38.27	<0.01	0.25	10.88	0.54	0.14	2.99	0.01	35.29	0.01	<0.005	<0.01	<0.01	<0.001	0.01	11.98	100.4	4.5
N-1100	V	11.0	38.55	0.01	0.64	13.08	0.65	0.14	1.15	0.01	34.60	<0.01	<0.005	<0.01	<0.01	<0.001	0.01	11.82	100.7	
PH-S-15A	BR		37.42	0.04	2.16	7.29	0.19	0.08	0.19	0.01	39.61	1.99	0.01	<0.01	0.01	0.01		10.89	99.9	4.0
PH-S-15B	BR		40.13	0.04	1.70	8.93	0.36	0.06	0.40	0.01	40.05	1.49	<0.01	<0.01	0.01	0.01		7.73	100.5	4.2

¹ UL = upper limonite, LL = lower limonite, T = transition zone, V = vein, US = upper saprolite, LS = lower saprolite, BR = bedrock.

4. Discussion

4.1. Laterite Zonation

Based on mineralogy, geochemistry, and calculated UMIA, the Sta. Cruz nickel laterite deposit can be divided into two main zones—an upper limonite layer and a lower saprolite layer—separated by a transition zone. The transition zone is characterized by mineralogy and geochemistry intermediate between the limonite and saprolite layer. The limonite is further subdivided into two layers: upper and lower limonite. Similarly, the saprolite can be divided into upper and lower saprolite zones. Lastly, garnierite veins were observed cutting the upper and lower saprolite layers.

4.1.1. Limonite Zone

The limonite zone represents the most evolved layer of the laterite profile investigated, with a UMIA value of 78. It is an Fe- and Al-rich layer, completely devoid of primary minerals and made up of the mineral assemblage goethite + hematite for the upper limonite and goethite + chromite for the lower limonite. Mg and Si are almost completely leached out of this layer, with relative mass losses of almost 100%. The upper limonite contains a slightly higher amount of SiO₂ than the lower limonite, resulting in a lower UMIA for the upper limonite. This is probably due to the presence of amorphous silica, a common reaction product of weathering, along with amorphous Fe-oxides. Amorphous silica could not be detected by X-ray diffraction due to the absence of a crystalline structure. Within the limonite, MnO, NiO, and Co generally increase with depth and are enriched in the lower limonite. Bulk chemistry of the samples reveals a significant amount of Al₂O₃ of more than 10 wt%, although Al-bearing minerals, such as gibbsite, were not observed in the limonite zone. Goethite with 18% Al substitution best fits the X-ray diffractogram of samples from the upper limonite [35]. Therefore, in the absence of mineral chemistry data, it is inferred here that Al is hosted in the limonite by goethite. We hypothesize that Ni within the limonite is hosted primarily by goethite, with the nickel contents observed to be directly proportional to the FWHM of the goethite (110) peak and inversely proportional to the goethite crystallite size (Figure 7). A stronger correlation ($R^2 = 0.83$) is observed in the upper limonite than in the lower limonite ($R^2 = 0.016$) for both FWHM and crystallite size. One possibility is that Ni is not exclusively hosted by goethite in the lower limonite zone. For example, Mn oxyhydroxides, which are often reported in lower oxide zones of Ni laterites [5,46], including two other deposits from the Philippines [47,48], can host Ni. In particular, significant amounts of Ni (up to 15.6 wt%) have been reported to be associated with Mn oxyhydroxides from the Intex deposit in Mindoro, Philippines [48]. Mn oxyhydroxides are difficult to detect with the methods performed in this paper, but the slight increase in Mn and Co concentrations towards the lower limonite may hint at their presence in the Sta. Cruz laterite. Because phases other than goethite may host Ni, a weaker correlation between the bulk Ni contents and both goethite crystallite size and FWHM of the goethite (110) peak is observed. The stronger correlation between bulk Ni and goethite crystallinity in the upper limonite support our hypothesis that goethite is the main host of Ni.

4.1.2. Transition Zone

The transition zone (~6.5 m) is a thin layer between the saprolite and limonite zone and is characterized by an abrupt mineralogical, textural, and geochemical transition from the limonite into the saprolite layer. This layer is comprised of the mineral assemblage goethite + lizardite + chlorite + tremolite + chromite. Goethite is the dominant mineral in the limonite zone, whereas lizardite, together with minor amounts of chlorite and tremolite, is characteristic of the saprolite zone. The change in the mineral assemblage in the transition zone is reflected in the geochemistry: abrupt increase in Mg and SiO₂ corresponds to the first appearance of Mg-silicates and a decrease in the Fe₂O₃ associated with a decrease in abundance of goethite. The transition zone has a UMIA of 36, a value in between the

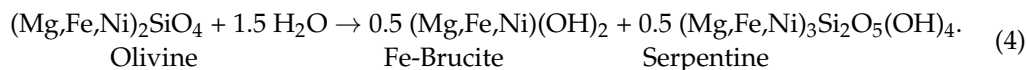
expected value of at least 60 for the limonite zone and the expected value of 4–8 for the saprolite zone.

Ni in the transition zone is hosted predominantly by goethite, but other phases, such as serpentine and chlorite, may also host Ni. Thus, bulk Ni content cannot be used to determine the effect of Ni content on the structure of goethite in the sample from the transition zone. For both FWHM and crystallite size, the sample from the transition zone is a clear outlier in the generally observed trends.

4.1.3. Saprolite Zone

The saprolite zone is comprised mostly of serpentine and has a geochemistry dominated by MgO and SiO₂. The upper saprolite (6.6 to 6.9 m) is composed of the assemblage lizardite + chlorite + chromite + goethite ± tremolite. The lower saprolite (7.5 to 11 m) contains a significant amount of primary minerals, mostly olivine, and is made up of the mineral assemblage lizardite + olivine + goethite. Except for the topmost sample from the upper saprolite, samples from the saprolite zone have UMIA values between 4 and 7. Fe is hosted in the saprolite within serpentine, chromite, and poorly crystalline Fe-oxides, occurring as alteration of olivine and serpentine. Minor amounts of Al₂O₃ in the saprolite suggest the absence of Al-bearing minerals, although small amounts of Al may substitute for Si in the serpentine crystal structure [49,50]. Significant concentrations of Al were observed in saprolite samples containing chlorite.

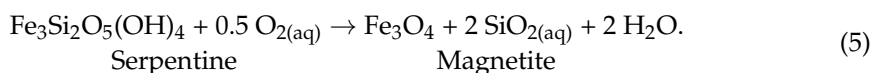
Four types of serpentine have been recognized in the saprolite zone of the deposit. Type 1a serpentine is interpreted to have formed earlier during the initial hydrothermal serpentinization of the ZOC [51–54]:



This is supported by the pseudomorphic nature of type 1a serpentine after primary minerals. Although both olivine and orthopyroxene can be altered to serpentine, olivine is more abundant and has more Ni content (0.24 to 0.36 wt%) than orthopyroxene (0.07 to 0.08 wt%) in the ZOC peridotite [22]. It follows that olivine is the main source of Ni in the deposit. Over time and with further reaction with water, serpentinization may continue, resulting in the continued formation of serpentine along olivine grain boundaries and thickening of type 1a serpentine to form type 1b serpentine, which were observed in the upper levels of the saprolite.

One major consequence of the hydration of peridotite is the associated volume increase that occurs as a rock composed of dense minerals is altered to less-dense secondary minerals [55–57]. Volume expansion associated with serpentinization has been discussed earlier [56]. More recently, a volume increase of $44 \pm 8\%$ [55] has been experimentally measured associated with serpentinization for a duration of 10 to 18 months. The associated volume expansion can both seal existing fractures in the system and induce new fractures at the same time. These tension cracks or cross-fractures [56] are formed during earlier, moderately high-temperature (>200 °C) serpentinization, although we recognize that this process may continue at lower temperatures (<100 °C) [58–64]. Relatively high Ni content in the least altered rock relative to unaltered protolith (1.15% vs. 0.29 wt% NiO), which contains only type 1 serpentine, may hint at the lower temperature formation of the serpentine, although further analyses will be needed to confirm this. Roughly parallel serpentine veins (type 2 serpentine) may later form in these cracks, likely from solutions leached [4,5,12] from the upper horizons of the profile. Type 2 serpentine have been observed to cut earlier formed type 1 serpentine in the saprolite samples (Figure 5).

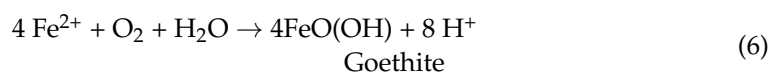
Type 3 serpentine are characteristically magnetite rich. As suggested earlier [54], magnetite may form from the oxidation of pre-existing Fe-rich serpentine via:



Thus, we interpret type 3 serpentine to have formed from oxidation of earlier-formed type 1 or type 2 serpentine. Lastly, type 4 serpentine (garnierite) were observed to either directly crosscut oxidized saprolite samples or alter pre-existing serpentine, suggesting that type 4 serpentine is formed during weathering after the formation of the saprolite zone. In addition, the upper garnierite vein contains significant amounts of Ni (up to 3.72 wt% NiO) and is similar to garnierite serpentine described in previous studies [12,48].

4.2. Goethite Ageing and Hematite Formation

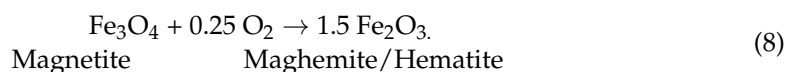
Structural investigation of the mineral goethite allows us to highlight the importance of this mineral in the development of the oxide zone of the laterite deposit. Reaction of oxidized rainwater and dissolution of primary minerals in the upper horizon result in the leaching of mobile elements such as Mg and Si downwards the profile while immobile elements, such as Fe and Al, are enriched in the limonite zone. Residually enriched Fe can be oxidized to form poorly crystalline goethite [3,5,65,66]:



Goethite initially has low crystallinity [3,18,65], which is attributed to the incorporation of elements, including Ni, that introduce structural defects in the goethite crystal structure [18]. As this stage, lateritization proceeds and goethite ages, and Ni and other impurities are expelled from the structure of goethite and subsequently leach away towards the lower horizons [7,18,65]. The expulsion of Ni from goethite results in goethite ageing or the upward increase in the crystallinity of goethite within the limonite zone as lateritization progresses [18–20]. In the Sta. Cruz deposit, goethite ageing is supported by the observed correlation between the bulk Ni content in the limonite and FWHM of the goethite (110) peak. Ni expelled during goethite ageing may contribute to the supergene Ni enrichment in the saprolite zone and in the garnierite veins. Higher up in the profile, hematite may form from the dehydroxylation of goethite according to [67]:



Petrographic investigation of saprolite samples revealed that secondary magnetite is altered to hematite, especially at higher depths (e.g., N-650, N-660; Figure 4). In the presence of oxygen, magnetite can be altered to maghemite and then to hematite [67], according to the following reaction:



Over time, the limonite zone expands as oxide-forming reactions continue to progress, deepening the limonite-saprolite zone boundary and increasing the thickness of the limonite zone. The expansion of the limonite zone is affected by a number of factors, including time, the rate of erosion, relief, and climate. A moderate to low-lying relief in a tropical climate provides the ideal conditions for laterite formation. Low to moderate relief results in a limited erosion rate allowing the preservation of the newly formed limonite zone and at the same time providing a low-lying water table. Since leaching occurs above the water table, a deep water table allows leaching of a thicker layer of rock and, consequently, an enhanced supergene Ni enrichment below the water table [1,6].

5. Conclusions

We report the mineralogy and geochemistry of a laterite profile formed from the alteration of the ultramafic rocks from the Zambales Ophiolite Complex. Combined mineralogical–geochemical analysis reveal that the Sta. Cruz nickel laterite deposit is

composed of two main zones—the limonite and saprolite zones—separated by a thin transition zone. Late-stage, Ni-rich serpentine garnierite veins are observed to crosscut the saprolite zone. The limonite zone is characterized by Mg and Si mass loss and residual enrichment of Fe, Al, and Ni. The saprolite zone, on the other hand, is associated with Mg and Si mass gains. Similar to other deposits, the limonite zone is dominated by goethite with minor hematite, while the saprolite zone is dominated by the mineral serpentine. At least four types of serpentine are characterized and distinguished based on occurrence and association with magnetite. Structural investigation of goethite within the limonite zone resulted in a negative correlation between the bulk nickel content and crystallinity of goethite and between bulk nickel content and crystallite size, emphasizing the important role that goethite plays during the formation of the limonite zone.

Author Contributions: K.A.A. conceptualized the study, collected the samples, performed the analyses, and wrote the first draft of the manuscript. C.A.A. and C.S. supervised the study. C.A.A. provided resources to conduct the study. C.A.A., C.S. and C.A.J.T. reviewed, revised, and edited the manuscript. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: Data are contained within the article or in Appendix A.

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Conflicts of Interest: The authors declare no conflict of interest.

Appendix A

Table A1. Goethite crystallite size obtained from Rietveld refinement and calculated full width at half maximum values (FWHM).

Sample	Crystallite size	FWHM
N-000	115	1.09
N-040	127	0.99
N-080	139	0.91
N-120	136	0.93
N-160	134	0.94
N-200	130	0.96
N-240	125	1.00
N-280	116	1.08
N-320	112	1.12
N-360	121	1.04
N-400	125	1.01
N-440	125	1.01
N-480	127	0.99
N-520	127	0.99
N-560	124	1.02
N-600	117	1.07
N-640	124	1.02

Table A2. Calculated relative mass changes of the samples from the Sta. Cruz laterite.

Sample	Horizon ¹	Depth (m)	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	Cr ₂ O ₃	MnO	NiO	MgO	Co	LOI
N-000	UL	0	−99	−27	8	307	90	−40	−99	101	16
N-040	UL	0.4	−98	−13	8	62	47	−46	−100	53	39
N-080	UL	0.8	−97	1	0	66	43	−48	−100	36	40
N-120	UL	1.2	−97	5	−2	71	63	−47	−100	33	38
N-160	UL	1.6	−97	−4	3	72	53	−45	−100	31	36
N-200	UL	2	−97	−9	6	74	53	−45	−100	33	35
N-240	UL	2.4	−98	−22	10	63	67	−43	−100	53	33
N-280	LL	2.8	−99	−56	17	119	88	−34	−99	40	27
N-320	LL	3.2	−99	−59	19	163	92	−30	−100	64	16
N-360	LL	3.6	−99	−65	19	188	86	−34	−99	39	16
N-400	LL	4	−99	−60	19	153	86	−31	−99	39	20
N-440	LL	4.4	−99	−56	19	74	102	−29	−99	58	25
N-480	LL	4.8	−99	−78	26	24	113	−29	−100	−15	30
N-520	LL	5.2	−99	−70	19	162	113	−37	−99	48	21
N-560	LL	5.6	−99	−65	16	185	92	−30	−99	153	25
N-600	LL	6	−99	−64	16	192	78	−27	−99	143	27
N-640	T	6.4	−91	−35	8	361	93	64	−94	206	16
N-690	US	6.9	−33	32	5	1876	84	225	−34	33	27
N-750	LS	7.5	−25	−89	−5	60	42	350	−30	35	31
N-900	LS	9	−27	−83	16	151	85	605	−36	70	33
N-1050	LS	10.5	−35	15	1	49	53	668	−33	17	29

¹ UL = upper limonite, LL = lower limonite, T = transition zone, US = upper saprolite, LS = lower saprolite. Calculated for each component using the equation $\Delta C/CO = (MA/MO)(CA/CO) - 1$ [38,39] using the Fe and Ti isocon.

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