

The geology, geochemistry, and mineralogy of the Moa Bay Ni laterite mining district, Cuba

Diego Domínguez-Carretero^{1*}, Joaquín A. Proenza^{1,2}, Cristina Villanova-de-Benavent¹, Thomas Aiglsperger³, Esperança Tauler¹, Arturo Rojas-Purón⁴, Nathalia Duque¹, José-María González-Jiménez⁵, Antonio García-Casco^{5,6}, Salvador Galí¹

¹Departament de Mineralogia, Petrologia i Geologia Aplicada, Facultat de Ciències de la Terra, Universitat de Barcelona (UB), Martí i Franquès s/n, 08028 Barcelona, Spain

²Institut de Nanociència i Nanotecnologia, IN2UB Facultat de Química, Universitat de Barcelona, Spain

³Department of Civil Engineering and Natural Resources, Division of Geosciences and Environmental Engineering, Luleå University of Technology, Luleå, Sweden

⁴Departamento de Geología, Universidad de Moa, Las Coloradas, s/n, Moa, Holguín, Cuba

⁵Instituto Andaluz de Ciencias de la Tierra, CSIC-Universidad de Granada, Av. de las Palmeras 4, Armilla, 18100 Granada, Spain

⁶Departamento de Mineralogía y Petrología, Universidad de Granada, Facultad de Ciencias, Granada, Fuentenueva s/n, 18002 Granada, Spain

*Corresponding author: email, ddominguezcarretero@ub.edu

1
2
3
4
5
6
7
8
9
10
11
12
13

Abstract

The Moa Bay lateritic Ni-Co mining district (eastern Cuba) has total mineral resources of 198.54 Mt at 1.07% Ni and 0.12% Co. Laterite profiles from this district are characterized by their oxide-dominated ore zones. Laterite profiles from the Yagrumaje Norte, Punta Gorda and Yamanigüey deposits contain average Ni and Co concentrations in the oxide zone of 0.88 and 0.12%. Goethite is the most abundant mineral in the oxide zone and the most important Ni-Co-Sc bearing mineral, with median NiO, CoO and Sc contents of 0.78 wt.%, 0.07 wt.% and 58 ppm, respectively and up to 2.77 wt.%, 0.26 wt.% and 117 ppm. Maghemite is also widely present (average of 5% and up to 19% modal proportion) and represents an important but largely ignored Ni- and Co-bearing ore phase, with median NiO and CoO concentrations of 2.11 wt.% and 0.25 wt.%, respectively, and maximum values of 13.9 wt.% and 1.84 wt.% each. Nickel and Co substitute for ferric iron in the structure of maghemite. Mn-oxyhydroxides (lithiophorite, and lithiophorite-asbolane intermediate), which are also significant Ni-Co bearing phases, have median NiO and CoO contents of 10.6 wt.% and 6.41 wt.% respectively. Some Mn oxyhydroxides, which formed after replacing goethite, also contain significant amounts of Sc (up to 94 ppm).

Although most deposits in the Moa Bay lateritic district are classified as oxide-type, Yamanigüey (average Ni grade of 1.98%) is characterized by well-developed saprolite horizons, with secondary serpentine (serpentine II) and garnierite being the main Ni-bearing phases.

Introduction

Nickel laterites are supergene deposits formed by the weathering of ultramafic rocks in warm, humid climates, predominantly developed in tropical areas within 26 degrees from the equator (Golightly, 1981, 2010; Elias, 2002; Freyssinet et al., 2005; Marsh et al., 2013). These deposits contain exploitable resources of the critical metal Ni (IEA, 2021; European Commission, 2023; USGS, 2023) that is widely used in the steel, electric vehicle (EV), electroplating, catalyst, and chemical industries (Mudd and Jowitt, 2022). Nickel laterites account for 60% of worldwide nickel resources and production worldwide (Butt and Cluzel, 2013; USGS, 2021a). A steady decline in Ni-bearing sulfide deposits and the estimated increasing demand for Ni in the future make laterite deposits crucial as exploration and exploitation targets (Marsh et al., 2013; Mudd and Jowitt, 2022). Cobalt, used in rechargeable battery cathodes, is often exploited as a by-product of Ni-laterites and is also listed as a critical metal by several international agencies (IEA, 2021; European Commission, 2023; USGS, 2023). Nickel laterite deposits, together with magmatic Ni-Cu-PGE deposits, contain the second largest Co reserves in the world, second only to the sediment-hosted Cu-Co deposits of central Africa (USGS, 2021b). Occasionally, economic concentrations of other critical metals, such as Sc, used to produce alloys and solid oxide fuel cells, and platinum group elements (PGE: Os, Ir, Ru, Rh, Pt, Pd), employed, for example, in catalytic converters by the car industry, can be economically extracted as by-products in Ni-(Co) laterites (Butt and Cluzel, 2013; Aiglsperger et al., 2016; Zhou et al., 2022).

Ni laterite deposits have been classified into three broad categories: hydrous Mg silicate-type, oxide-type, and clay-type (Brand et al., 1998). The main Ni-(Co)-bearing minerals are goethite and Mg-Ni phyllosilicates (Freyssinet et al., 2005), but ore mineral complexity and heterogeneity pose difficulties in their mining and processing. The lack of precise knowledge regarding the distribution of Ni and/or Co among different mineral phases within the laterite profile, and how these metals are contained within the ore minerals (solid solution, adsorption, as nanoparticles) makes the metallurgical processes energy extensive and, often, inefficient (Elias, 2002; Hernández et al., 2006; Marsh et al., 2013). Consequently, up to 20% Ni and up to 60% Co is not extracted during processing and ends up in the mine tailings (Elias, 2002; Hernández et al., 2006).

Cuba has historically been an important producer of Ni and Co from lateritic deposits since the beginning of the 1940s, when the first nickel plant was constructed in

Nicaró (Nelson et al., 2011). Currently, Cuban laterite deposits contain 5.5 Mt of nickel (5.9% of the world's Ni reserves) and 500,000 t of cobalt (7% of the world's Co reserves) (USGS, 2021a, b). These deposits produced 49,000 t of Ni (USGS, 2021a) and 3,600 t of Co during 2020 (USGS, 2021b). Eastern Cuba is one of the largest Ni laterite mining provinces in the world, with approximately 100 km² of nickel laterites (Linchenat and Shirakova, 1964; Lavaut, 1998; Lewis et al., 2006). This laterite province hosts several important mining districts, such as Nicaró, Pinares de Mayarí, and Moa Bay, the latter being considered the best-known example of an oxide type nickel laterite deposit (Gleeson et al., 2003).

Despite the past and present-day economic importance of Cuban laterites in producing Ni and Co, most geological information on the laterite deposits of the island has been published in Cuban (e.g., Lavaut, 1998; Rojas-Purón and Turro-Breffé, 2003) and Russian journals (e.g., Voskrenskaya, 1987); relatively little information has been published in other journals (e.g., Aiglsperger et al., 2016; Villanova-de-Benavent et al., 2017; Domènech et al., 2017).

This contribution evaluates the geochemistry of Ni-laterite profiles from three different deposits in the Moa Bay mining district (Yagrumaje Norte, Punta Gorda and Yamanigüey). The mineralogy of the Ni- and Co-bearing mineral phases was determined using X-ray diffraction, scanning electron microscopy, Raman spectrometry, electron microprobe, and focused ion beam coupled with high-resolution transmission electron microscopy, to determine the mineralogical and the geochemical evolution of the deposits. This has been done to potentially improve ore treatment and extraction of Ni and (Co) in Ni-laterite deposits elsewhere.

Regional Geology

Cuba hosts the largest ophiolite belt in the Caribbean region, cropping out discontinuously for over 1000 km in a general E-W trend across the island (Fig. 1a). The Cuban Ophiolitic Belt (COB) consists of variable-sized mafic and ultramafic bodies, spatially associated with blocks subjected to high pressures within serpentinite-matrix subduction mélanges (Iturralde-Vinent, 1996; García-Casco et al., 2006; Lewis et al., 2006; Iturralde-Vinent et al., 2016). The COB represents slices of oceanic lithosphere obducted onto the North American continental paleo-margin in Late Cretaceous to Late Eocene times, during the collision of the Caribbean volcanic arc with

Jurassic-Cretaceous passive margins of the continental Maya block and the Bahamas platform (Garcia-Casco et al., 2008; Iturralde-Vinent et al., 2016; Butjosa et al., 2024).

The largest exposures of ophiolitic rocks across the COB are found in eastern Cuba (Fig. 1b), within the so-called Mayarí-Baracoa Ophiolite Belt (MBOB). The MBOB is divided into the Mayarí-Cristal (western) and the Moa-Baracoa (eastern) massifs, both of which formed during the Cretaceous (90-138 Ma; Rojas-Agramonte et al., 2016; Rui et al., 2022). The Mayarí-Cristal massif is a 5 km-thick, highly serpentized, harzburgite tectonite that contains Cr-rich chromitite bodies (Proenza et al., 1999; Gervilla et al., 2005). Several generations of websterite and gabbro dikes of island arc tholeiite (IAT) affinity crosscut the serpentized peridotites (Marchesi et al., 2006). The ultramafic rocks were thrust over a crustal unit consisting of gabbros, microgabbros, and abundant diabase dikes (Proenza et al., 1999; Marchesi et al., 2006, 2007). The easternmost part of the Mayarí-Cristal massif (Sagua de Tánamo region) is composed of highly serpentized mantle tectonites that host either Al- or Cr-rich chromitite ore bodies (Proenza et al., 1999; Gervilla et al., 2005; González-Jiménez et al., 2011). The mantle tectonites were thrust over low-Ti island arc tholeiites (LOTI) of boninitic affinity (Proenza et al., 2006, 2018). The Moa-Baracoa massif, on the other hand, is composed of a 2.2 km-thick, mantle tectonite consisting of harzburgite with subordinate dunite, and a well-preserved Moho Transition Zone (MTZ: dunite, wehrlite, plagioclase and clinopyroxene-bearing peridotites, sills and dikes of gabbro). The Moa-Baracoa massif contains several Al-rich chromitite ore bodies that are systematically restricted to the uppermost part of the MTZ, close to the layered gabbros (about 500 m thick) (Proenza et al., 1999). U-Pb ages of zircon and baddeleyite grains from gabbro dikes and sills intruding the MTZ of the Moa-Baracoa ophiolitic massif, which are interpreted to date the time of crystallization and ophiolite formation, range from 138 ± 5.9 to 124 ± 1 Ma (Rojas-Agramonte et al., 2016; Proenza et al., 2018; Pujol-Solà et al., 2020; Rui et al., 2022). Layered and isotropic gabbros and pillow basalts with a general back-arc geochemical affinity are tectonically overlain by the mantle sequence (Proenza et al., 1999, 2006, Marchesi et al., 2006, 2007).

Geology of the Moa Bay District

The Moa Bay Ni laterites formed by weathering of serpentized ultramafic rocks (mainly harzburgite) of the Moa-Baracoa massif (Fig. 1b) (Linchenat and Shirakova, 1964; Lavaut, 1998; Lewis et al., 2006; Proenza et al., 2007; Nelson et al., 2011; Elias

et al., 2019). Laterization took place from the Miocene to the present-day (Lewis et al., 2006). According to the latest NI 43-101 technical report (Foret et al., 2023), the Moa Bay district, composed of 11 ore deposits (Fig. 2), has total mineral resources (measured, indicated, and inferred) of 198.54 Mt at a grade of 1.07% Ni and 0.12% Co. From 1959 through 2022, the Moa Bay district produced a total of 1.217 Mt of Ni and 0.055 Mt of Co, and in 2022 they produced together produced 32,268 t of nickel and 3,368 t of cobalt (Sherritt International Corporation, 2022, Foret et al., 2023). It must be noted that these numbers reflect only the resources and production from the deposits exploited by Sherritt International Corporation, which has a license to exploit the Yamanigüey, Yagrumaje Norte, Yagrumaje Sur, Moa Oriental, Moa Occidental, La Delta, Cantarrana and Santa Teresita deposits (Fig. 2). The rest of the district is under exploitation by a Cuban state company that, to the best of the authors' knowledge, does not publish the reserves and production data of their deposits. This company owns the Punta Gorda, Camarioca Norte and Camarioca Sur deposits (Fig.2). The Moa Bay deposits are classified as oxide-type because Ni and Co are mostly extracted from Fe oxyhydroxides located in the upper parts of the lateritic profiles, however, some deposits also show important Ni concentrations in their saprolitic horizons. The laterites have an average thickness of 10 m, although they can reach up to 50 m (Lavaut, 1998). They are subdivided into horizons (the terminology used by the Cuban geologists and miners, also reported by Golightly (2010), is written in brackets), which from top to bottom are: 1) ferricrete (*Ocre inestructural con perdigones*); 2) red oxide zone (*Ocre inestructural sin perdigones*); 3) yellow oxide zone (*Ocre estructural final*); 4) saprolite; and 5) bedrock.

Yagrumaje Norte

Yagrumaje Norte has proven and probable reserves of 2.6 Mt at 1.06 % Ni and 0.13 % Co (Elias et al., 2019). The studied profile has a thickness of 24.5 m with a top, fine-grained oxide zone of ~20 m where the original textures of the protolith have not been preserved. The color of the oxide zone is reddish in the upper ~4 m due to the ubiquitous presence of hematite and becomes yellowish below that depth as goethite content increases (Fig. 3). In the yellow oxide zone, Mn oxyhydroxide disseminations occur at 10 and 16 m below the surface. The saprolite horizon starts at ~23 m depth and is characterized by fine-grained minerals and the preservation of primary textures of the peridotite protolith.

Yamanigüey

Yamanigüey has proven and probable reserves of 0.9 Mt at 1.33 % Ni and 0.12 % Co (Elias et al., 2019), and is the shortest of the three studied profiles, with a thickness of 8.5 m. In contrast to the Yagrumaje Norte and Punta Gorda profiles, this profile has a thicker saprolite horizon relative to the oxide zone (Fig. 4). The upper ~3.5 m consist of a thin red oxide zone, enriched in hematite, that grades to a slightly thicker yellow oxide zone more enriched in goethite. This oxide zone contains quartz veins and Mn oxyhydroxides disseminations. At ~3.5 m, the saprolite horizon occurs, showing pale-green colors and preserving most of the original textures for ~5 m. The serpentinized protolith (harzburgite) occurs at a depth of 8.5 m.

Punta Gorda

Punta Gorda has reserves of 2.6 Mt at 1.25% Ni and 0.10% Co (Cuador-Gil, 2005). The studied profile, previously investigated by Aiglsperger et al. (2016), has a thickness of ~45 m and, from top to bottom, shows a thin ferricrete cover (~1 m) that tops a thick oxide zone of ~38 m. The latter is subdivided into a thin red oxide zone enriched in hematite, and an extensive yellow oxide zone enriched in goethite. The oxide zone also contains Mn oxyhydroxides disseminations at a depth of 12.5 m. The ~5 m thick saprolite horizon above the bedrock appears at a depth of 38 m and is pale green to yellowish in color and preserves the protolith textures.

Sample Selection and Analytical Techniques

Three diamond-drill cores (Fig. 2), each representative of one of the three studied deposits, were selected to investigate the mineralogy and geochemistry of the different lateritic deposits. The selected drill holes were chosen because they represent the different horizons observed in the field for every deposit (see Appendix 1 for the detailed core logging description of each deposit). Geochemical and mineralogical characterization was carried out on 47 samples (taken at intervals of between 0.5 to 2 m) from the three drill cores (Fig. 2): Yagrumaje Norte (18 samples), Yamanigüey (20 samples) and Punta Gorda (9 samples).

Whole rock geochemical analyses

Major, minor and trace elements were determined at Activation Laboratories Ltd. (Actlabs, Ontario, Canada) by means of X-ray fluorescence (4C Laterite – Fusion XRF package) and ion coupled plasma mass spectrometry (ICP-MS; 4Litho package), respectively (Appendix 2). The geochemistry of Punta Gorda samples was previously studied by Aiglsperger et al. (2016) while the variance of the geochemistry was evaluated here using principal component analysis (PCA) of multielement geochemical data. The PCA was carried out using the 47 samples studied here in addition to 137 samples of other Caribbean laterite deposits (see Appendix 3: Cuba, Tauler et al., 2023; Colombia, Gleeson et al., 2004 and Tobón et al., 2020; Dominican Republic, Aiglsperger et al., 2016; Venezuela, Domènech et al., 2022). The PCA was performed using IoGas software version 7.4.2 by Imdex Limited. For the interpretation of the outcomes of PCA, we relied exclusively on components contributing at least 10 % of the variance of the dataset.

X-ray diffraction analysis

Random powder X-ray diffraction (XRD) analyses were obtained at Centres Científics i Tecnològics of the Universitat de Barcelona (CCiT-UB), in a PANalytical X'Pert PRO MPD Alpha1 powder diffractometer in Bragg–Brentano $\theta/2\theta$ geometry of 240 mm of radius, nickel filtered Cu K α 1 radiation ($\lambda = 1.5406 \text{ \AA}$), 45 kV and 40 mA (Appendix 4). The samples were scanned from 4 to 100° (2 θ) with a step size of 0.017° and measuring time of 150 s per step, using an X'Celerator detector (active length = 2.122°). Mineral identification was facilitated by X'Pert Highscore search-match software using the powder diffraction database of the International Centre for Diffraction Data to estimate the proportion of the various mineral phases; the quantitative Rietveld analysis method (Young, 1993) with the software Topas V4.2 was used. X-ray diffraction analyses on samples from Punta Gorda were previously obtained by Domènech et al. (2017).

Scanning electron microscopy

The electron microscopy study was carried out on carbon-coated polished thin sections and polished sections using a Quanta FEI XTE 325/D8395 scanning electron microscope (SEM) equipped with an INCA Energy 250 coupled with an energy dispersive spectrometry (EDS) microanalysis system and a JEOL JSM-7100 field-emission SEM at the CCiT-UB. Operating conditions were 20 kV and 5 nA.

Raman spectroscopy

Raman spectra were obtained on selected polished sections using a HORIBA Jobin Yvon LabRam HR 800 dispersive spectrometer equipped with an Olympus BXFM optical microscope at the CCiT-UB. The analyses were performed using a 532 nm laser, a 100x objective, a 10% filter, and consisted of 5 accumulations of 30 seconds each. The results were processed using the LabSpec® software.

Electron microprobe (EMP) analyses

Electron microprobe (EMP) analyses on oxyhydroxides (goethite, maghemite, Mn oxyhydroxides) and silicates (serpentine and garnierite) were conducted at CCiT-UB with a JEOL JXA-8230 equipment with four wavelength-dispersive (WDS) spectrometers and one energy dispersive system (EDS) (Appendix 5). The analytical conditions were 15–20 kV accelerating voltage, 10–20 nA beam current, 1–2 µm beam diameter, and 10–20 s counting time (peak and background) per element. Measurements and calibrations were performed using the following natural and synthetic standards: hematite (Fe), rutile (Ti), periclase (Mg), rhodonite (Mn), Al₂O₃ (Al), Cr₂O₃ (Cr), diopside (Si), NiO (Ni), wollastonite (Ca), orthoclase (K), metallic cobalt (Co) and sphalerite (Zn).

A special EMP procedure was designed for measuring Sc in goethite, maghemite, Mn oxyhydroxides and hematite from the Punta Gorda and Yamanigüey deposits. Scandium was measured first with four WDS spectrometers and one EDS spectrometer for 12 minutes of counting time (peak and background), followed by the analysis of Si, Al, Cr, Mg, Ti, Co, Ni, Fe and Mn with counting times of 10–20 s (peak and background), for a 20 kV accelerating voltage and 15 nA beam current with a probe size of 5 µm. The standards used were the same as for the procedure used for major elements in oxyhydroxides and silicates, plus metallic scandium to calibrate Sc. The detection limit for Sc for these analyses is 15 ppm. Maghemite and hematite Sc measurements were all below the limit of detection.

The structural formulae of serpentine group minerals were calculated on the basis of 7 oxygens, and that of garnierites on the basis of 7 or 11 oxygens, depending on the predominance of serpentine or kerolite-pimelite (talc) in the mixture. The talc fraction or X_{talc} in the mixture was calculated using the method of Villanova-de-Benavent et al. (2022). Iron in primary hydrothermal serpentine (“serpentine I”) was calculated as Fe²⁺,

and in secondary weathering serpentine (“serpentine II”) and in garnierites as Fe³⁺ (Roqué-Rosell et al., 2017; Villanova-de-Benavent et al., 2017).

Focused ion beam (FIB)

One electron transparent thin-foil sample was analyzed using a dual beam FEI Thermo-Fisher Scientific Helios 650 focused ion beam scanning electron microscope (FIB-SEM) at the Laboratorio de Microscopías Avanzadas (LMA) at the Instituto de Nanociencia de Aragón (INA) – University of Zaragoza, Spain. The selected area of interest was first covered by a thin strip (~ 300 nm) of carbon by focused electron beam deposition (FEBID), followed by a second strip of Pt (~ 1 µm). These two strips acted as protectors during the extraction process of the thin foils. The bulk material was first removed on both sides of the lamella by a rough Ga⁺ ion milling at 30 kV with 2.5 nA current and the subsequent polishing at 30 kV with 0.23 nA current. The final polishing step was completed by milling the samples at 5 kV with 68 pA current until electron transparency was achieved. An Everhart-Thornley SE detector was used to monitor the electron transparency of the sample. Once the electron transparency was obtained, the thin-foil sample was rapidly polished at 6 kV using a low current of 10 pA to reduce amorphization until a final thin-foil thickness of ~100 nm was achieved. After that, the sample was undercut at 30 kV with a 2.5 nA current, lifted-out and transferred to a TEM grid using an OmniProbe nanomanipulator with a tungsten tip. Finally, ion-beam assisted Pt deposition was performed to weld the thin-foil samples to the tungsten tip, and subsequently to the TEM grid.

High resolution transmission electron microscopy (HRTEM)

A FEI Titan G2 TEM equipped with a Field Emission Gun (FEG) was used to analyze the thin-foil at the Centro de Instrumentación Científica of the University of Granada, Spain. The FEI Titan G2 microscope is equipped with four energy dispersive spectrometers (EDX) X-ray detectors (FEI microanalysis Super X) and a high-angle annular dark-field (HAADF) detector. The FEI Titan G2 microscope has a spherical aberration correction at the objective lens. Selected mineral areas of interest sampled within the thin-foil were imaged on the FEI Titan G2 microscope using a combination of HAADF imaging, to obtain Z high contrast images, and HRTEM imaging, to characterize the texture of the grains and to properly define the ordering of the mineral aggregates. All the images were treated using the Digital Micrograph® software

Version 1.71.38, while maps were processed with the VELOX® software package. The FEI Titan G2 was operated at 300 kV and HRTEM images were acquired using a Gatan CCD Camera. Elemental maps were also processed using the VELOX® software.

Results

Profile petrography and mineralogy of the lateritic horizons

The studied profiles from Yagrumaje Norte, Yamanigüey and Punta Gorda are very similar in terms of the petrography and the mineral distribution of their different horizons (Figs. 3-6).

The oxide zone of all deposits (Figs. 3-5; Domènech et al., 2017) is dominated by goethite, followed by hematite and maghemite, and minor proportions of Mn oxyhydroxides, gibbsite, Cr-spinel, magnetite, and silicates. Goethite is ubiquitous throughout the oxide zone and its content increases in the intermediate and lower levels of this horizon (up to 93 % modal proportions; Fig. 5). Goethite is usually found as fine-grained aggregates making up most of the matrix of the oxide zone (Fig. 6a-b). However, they may also occur as botryoidal aggregates (Fig. 6a), as fibrous, elongated crystals (Fig. 6b), or as pseudomorphs of the primary bedrock minerals (e.g., olivine). Hematite is more common towards the uppermost levels of the oxide zone (10-89 % modal proportions; Fig. 5) and usually forms fine-grained aggregates that replaced goethite. Maghemite is particularly abundant towards the lower levels of the oxide zone (modal proportions between 10-19 %; Fig. 5), and found either as isolated, euhedral, octahedral grains up to 50 µm in size (Supplementary Figure 1), or as sets of various euhedral, ~10 µm sized grains surrounded by elongated goethite grains in a “baguette-like” texture (Fig. 6c-d). The margins of maghemite grains are locally oxidized to hematite. Mn oxyhydroxides replace goethite or occur as individual colloform aggregate grains (Fig. 6e-f). Weathered Cr-spinel grains, crosscut by numerous dissolution cracks that resemble a wormy texture (Supplementary Figure 2), martitized subhedral magnetite grains (Supplementary Figure 1), gibbsite, quartz and small amounts of silicates (enstatite, chlorite and serpentine) are also present in the oxide zone.

In the saprolite horizons, serpentine (in combination with fine-grained smectite and talc [*kerolite*]) is the most abundant mineral (modal proportions > 80 %; Fig. 5), and is present as a colorless primary serpentine (Ni-poor, hereafter “serpentine I”) or as a yellowish secondary serpentine (Ni-rich, hereafter “serpentine II”; Fig. 6g-h).

Serpentine preserves the mesh texture of the primary bedrock, and also occurs as pseudomorphs of residual olivine and pyroxene. Small amounts of magnetite, Cr-spinel, and low quantities of forsterite and enstatite (< 10 % modal proportions), remnants of the original ultramafic protolith mineralogy, are also found in all the different saprolitic horizons. Additionally, in the Yamanigüey profile, multiple generations of micrometer-thick garnierite veins crosscut the saprolite matrix (Fig. 6g). In some veins, Mn oxyhydroxide fibrous aggregates (Fig. 6h) partially replace garnierite.

The bedrock has only been observed in the Yamanigüey and Punta Gorda profiles, where it preserves up to 35 % modal proportions of primary, anhydrous silicates (forsterite, enstatite and rarer clinopyroxene). However, most of their grains are generally completely replaced and/or surrounded by colorless serpentine and, to a lesser degree, magnetite. The bedrock preserves its original mesh texture resulting from the pseudomorphic replacement of olivine and orthopyroxene (now “bastite”) by serpentine. Accessory, subhedral Cr-spinel, partially altered at the rims by chlorite, is also found in these rocks.

Geochemistry

At Yagrumaje Norte, dominated by a thick oxide zone, Fe₂O₃ (median values of 63 wt.%) and Al₂O₃ (median values of 11 wt.%) are very high throughout most of the profile (Fig. 3). Median concentrations of MgO and SiO₂ are 0.7 and 4.8 wt.%, respectively, in the oxide zone, whereas they both show an abrupt increase in their contents at the transition between the oxide zone and the saprolite horizon, yielding median values of 27.0 and 32.9 wt.%, respectively. The oxide zone and the saprolite horizon have similar Ni concentrations, reaching up to 1.30 and 1.27 wt.%, respectively. The concentration of Co is higher in the oxide zone, up to 0.19 wt.%, especially where MnO is also significantly concentrated (up to 1.57 wt.%, and median value of 0.63 wt.%). Scandium is also more enriched in the oxide zone (up to 96 ppm, with median values of 72 ppm) than in the saprolite horizon (up to 33 ppm).

The upper part of the Yamanigüey profile (Fig. 4) has a ~3 m thick oxide zone dominated by Fe₂O₃ (median value of 66.9 wt.%) and Al₂O₃ (median value of 7.68 wt.%). MgO and SiO₂ concentrations rise in the saprolite horizon, with median values of 33.3 wt.% and 40.5 wt.%, respectively. Nickel is higher in the saprolite horizon (up to 2.84 wt.% and median values of 1.96 wt.%). However, Ni concentrations in the oxide

zone are also high, with median values of 1.18 wt.%, and reach a maximum of 1.67 wt.%. Cobalt (up to 0.43 wt.% and median values of 0.15 wt.%) and MnO (up to 2.31 wt.% and median values of 1.12 wt.%) are higher in the oxide zone too, due to the presence of disseminated Mn oxyhydroxides. The concentration of Sc in the oxide zone (up to 92 ppm, with median values of 79 ppm) is also higher than in the saprolitic horizon (up to 18 ppm).

The Punta Gorda profile mostly consists of an oxide zone dominated by high concentrations of Fe₂O₃ (median value of 68.7 wt.%), followed by Al₂O₃ (median value of 9.16 wt.%). MgO and SiO₂ median values in the saprolite horizon are 35.7 wt.% and 39.4 wt.%, respectively. The highest Ni concentrations occur in the upper parts of the saprolite horizon, with contents of up to 1.79 wt.%, however, the oxide zone has higher median values of Ni (1.33 wt.%), compared to those of the saprolite horizon (0.41 wt.%). Cobalt (up to 0.47 wt.% and median value of 0.12 wt.%) and MnO (up to 4.24 wt.% and median value of 1.02 wt.%) are also higher in the oxide zone especially at the levels with abundant Mn-oxyhydroxides. The oxide zone also contains the highest concentrations of Sc (up to 98 ppm, with median values of 85 ppm) compared to the saprolite horizon (up to 17 ppm).

Mineral Compositions

Oxide zone (goethite, maghemite, Mn-oxyhydroxides)

- Goethite

Nickel is higher in goethite grains from Punta Gorda (NiO concentrations up to 2.77 wt.%, and median values of 1.18 wt.%) than in those from Yagrumaje Norte (up to 1.89 wt.%, and median values of 0.54 wt.%) and Yamanigüey (up to 1.87 wt.%, and median values of 0.68 wt.%) (Fig. 7). Cobalt contents are similar in the three studied deposits. Goethite grains from Punta Gorda have CoO concentrations up to 2615 ppm and median values of 735 ppm. Goethite from Yagrumaje Norte has CoO contents up to 2560 ppm, with a median value of 741 ppm. Goethite in the Yamanigüey deposit have CoO concentrations of up to 1720, with a median value of 753 ppm. Goethite from Yagrumaje Norte have higher and more variable SiO₂ (up to 17.1 wt.%) and Al₂O₃ contents (up to 17.9 wt.%) compared to those from Punta Gorda (SiO₂ up to 3.58 wt.% and Al₂O₃ up to 11.1 wt.%) and Yamanigüey (SiO₂ up to 11.8 wt.% and Al₂O₃ up to

11.4 wt.%). Scandium concentrations in goethite range from 23 ppm to 117 ppm, with median values of 58 ppm.

- Maghemite

Nickel contents in maghemite are higher in Yagrumaje Norte samples (NiO up to 13.9 wt.%, and median values of 2.99 wt.%) than in those from Punta Gorda (NiO up to 10.1 wt.%, and median values of 1.60 wt.%) and Yamanigüey (NiO up to 1.25 wt.%, and median values of 0.49 wt.%) (Fig. 8). Similarly, Co is also higher in maghemite from Yagrumaje Norte (CoO up to 1.84 wt.%, and median values of 0.74 wt.%) compared to that from Punta Gorda (CoO up to 0.58 wt.%, and median values of 0.19 wt.%) and Yamanigüey (CoO up to 0.16 wt.%, and median values of 0.10 wt.%). SiO₂ and MnO median contents in maghemite vary from 0.5 to 1 wt.% (Fig. 8a). Nickel, and to a lesser extent Co, show negative correlations with Fe³⁺ content (R² of 0.66 and 0.51, respectively). Ni in maghemite is heterogeneously distributed within the grains, either in the isolated, euhedral grains or the ones with baguette-like textures (Fig. 9b-f). Conversely, Co is more homogeneously distributed among the grains (Fig. 9c-g).

A nanoscale study performed in one grain of maghemite precludes the presence of Ni- and/or Co-bearing nanoparticles as the responsible for the high Ni and Co contents of maghemite, thus confirming that these metals are found within the maghemite crystal structure (Fig. 10). Moreover, the Ni content of maghemite does not significantly modify its cell parameter. The measured d₃₁₁ spacing is 2.516 Å in the Ni-enriched zone (Fig. 10g), and 2.518 Å in the Ni-depleted zone (Fig. 10f). Mn oxyhydroxides

Most Mn oxyhydroxides found within the three studied deposits occur in the oxide zone and display a wide range of MnO (10.3-53.1 wt.%; median value of 35.8 wt.%), FeO (0.22-45.2 wt.%; median value of 4.24 wt.%), NiO (1.68-21.7 wt.%; median value of 13.5 wt.%), Al₂O₃ (2.66-20.9 wt.%; median value of 6.85 wt.%) and CoO contents (1.50-12.8 wt.%; median value of 7.46 wt.%) (Fig. 11a). Besides, the analyzed grains have low concentrations of K₂O (median values of 0.72 wt.%), MgO (median value of 0.49 wt.%) and SiO₂ (median values of 0.47 wt.%). The Sc content in Mn oxyhydroxides with low MnO contents (median value of 15.3 wt.%), and intermediate to high Al₂O₃ and FeO contents (median values of 9.95 wt.% and 12.5 wt.%, respectively) that are replacing goethite grains, ranges from 57 to 94 ppm.

Saprolite horizon (serpentine, garnierite, Mn oxyhydroxides)

448 - Serpentine

449 Serpentine I (hydrothermal, primary) from Yamanigüey yields up to 0.48 wt.% NiO and
450 3.55-16.05 wt.% FeO, with an average structural formula of
451 $(\text{Mg}_{2.582}\text{Fe}_{0.360}\text{Al}_{0.021}\text{Ni}_{0.011})(\text{Si}_{1.986}\text{Al}_{0.014})\text{O}_5(\text{OH})_4$. In contrast, serpentine II contains
452 0.55-3.70 wt.% NiO and 4.39-34.51 wt.% Fe_2O_3 , with an average structural formula of
453 $(\text{Mg}_{2.371}\text{Fe}_{0.384}\text{Ni}_{0.063})(\text{Si}_{1.968}\text{Al}_{0.026})\text{O}_5(\text{OH})_4$. In Punta Gorda, serpentine I contains ~0.4
454 wt.% NiO (Proenza et al., 2007), whereas serpentine II contains 0.97-2.67 wt.% NiO
455 and 3.29-14.05 wt.% Fe_2O_3 , with an average structural formula of
456 $(\text{Mg}_{2.724}\text{Fe}_{0.194}\text{Ni}_{0.069})(\text{Si}_{1.826}\text{Al}_{0.042}\text{Fe}_{0.132})\text{O}_5(\text{OH})_4$. In Yagrumaje Norte, only
457 serpentine I was analyzed, yielding 0.4-0.6 wt.% NiO, similar to olivine from the
458 bedrock (Proenza et al., 2007). When compared to other Ni-laterite saprolites
459 worldwide, serpentine II from Moa Bay has similar Ni contents, but both serpentine I
460 and II from Yamanigüey have the highest Fe contents (Fig. 12).

461 - Garnierite

462 The garnierite from Yamanigüey consists of mixtures of serpentine and kerolite-
463 pimelite. While most of the analyses display compositions near the kerolite-pimelite end
464 member, a few analyses fall closer to serpentine (Fig. 13g). Those closer to the kerolite-
465 pimelite end-member contain 39.79-52.53 wt.% SiO_2 , < 0.59 wt.% Al_2O_3 , 4.84-22.06
466 wt.% MgO, 10.92-32.49 wt.% NiO and 0.26-11.00 wt.% Fe_2O_3 , with a mean structural
467 formula of $(\text{Ni}_{1.839}\text{Mg}_{1.213}\text{Fe}^{3+}_{0.071}\text{Mn}_{0.003})(\text{Si}_{3.866}\text{Al}_{0.003})\text{O}_{10}(\text{OH})$. The serpentine-
468 dominant ones contain 40.15-45.32 wt.% SiO_2 , 0.01-0.44 wt.% Al_2O_3 , 12.52-23.77
469 wt.% MgO, 13.21-31.53 wt.% NiO and 0.74-9.24 wt.% Fe_2O_3 , with a mean structural
470 formula of $(\text{Ni}_{1.333}\text{Mg}_{1.071}\text{Fe}^{3+}_{0.060}\text{Mn}_{0.002})(\text{Si}_{2.255}\text{Al}_{0.004})\text{O}_5(\text{OH})_4$. Hence, there is a wide
471 variation in terms of X_{talc} and Ni content, comparable to garnierite from the Falcondo
472 Ni-laterite district in the Dominican Republic (Fig. 13g; Villanova-de-Benavent et al.,
473 2014). It is worth noting that the composition of garnierite varies across the same vein,
474 for example, Fig. 13a-d shows that a more Ni enriched kerolite-pimelite dominated
475 garnierite precipitated first as thin films parallel to the vein walls, followed by an
476 intergrowth of a similar garnierite, with a fish-like texture, and a more Ni-poor, Fe-rich,
477 serpentine-dominated garnierite matrix.

478 - Mn oxyhydroxides

Mn oxyhydroxides from the saprolite horizon of Yamanigüey (Fig. 11a) have high MnO concentrations (34.6-54.1 wt.%; median value of 51.6 wt.%) and moderate MgO (6.83-13.2 wt.%; median value of 7.94 wt.%), NiO (5.25-7.46 wt.%; median value of 6.20 wt.%), SiO₂ (3.99-21.2 wt.%; median value of 6.32 wt.%), and FeO concentrations (1.35-6.38 wt.%; median value of 1.73 wt.%). The Mn oxyhydroxides from the saprolitic horizon have lower CoO (up to 0.44 wt.%) and negligible Al₂O₃ contents (below the detection limit) with respect to those of the oxide zone.

Discussion

Geochemical distribution along the studied profiles

From bottom to top, the three studied profiles (Figs. 3-4, and Fig. 5 of Aiglsperger et al., 2016) evolve from the MgO- and SiO₂-rich saprolite horizon to the Fe₂O₃- and Al₂O₃-rich yellow and red oxide zones. The concentrations of MgO and SiO₂ show a marked drop at the interface between the saprolite and the oxide horizon, which has been described in many lateritic profiles worldwide as the Mg-discontinuity (i.e. Freyssinet et al., 2005; Butt and Cluzel, 2013), due to the disappearance of Mg silicates. The trend of Mg and Si depletion and Fe, and Al enrichment towards the surface is well observed in the Fe₂O₃+Al₂O₃-MgO-SiO₂ ternary diagram (Fig. 14), which shows the weathering trend from the MgO-, SiO₂-rich bedrock (ultramafic rock), with low ultramafic index of alteration (UMIA) values (≤ 10), to the saprolite zone samples, with intermediate UMIA values (11-26), and ultimately to the Fe₂O₃-Al₂O₃-rich oxide zone with high UMIA values (≥ 85). This weathering trend from low to high UMIA values is consistent with trends observed in laterite profiles from other lateritic mining districts (Fig. 14).

The results of a PCA carried out using the whole rock geochemistry of the studied samples and including samples from other lateritic mining districts from the Caribbean region, show that the first two components (PC1-PC2) comply with the 10% cut-off value of the explained variance and together account for almost 75% of the total variance of our dataset (Fig. 15a). PC1 (54.92% of variance) produces two antithetic sets of elements, MgO-SiO₂ and Fe₂O₃-Al₂O₃-Sc, which have negative and positive values respectively, reflecting their opposite trends (Fig. 15b). These antithetic values are seen as two clusters of samples along the PC1 axis, with negative and positive values in the samples from the bedrock + saprolite and oxide zones, respectively (Fig. 15b).

The opposite behavior between $\text{Fe}_2\text{O}_3\text{-Al}_2\text{O}_3$ and MgO-SiO_2 (Figs. 14 and 15) reflects the mineralogy of the different horizons within the lateritic profile. The bedrock and the saprolite zone consist mostly of Mg silicates (olivine and orthopyroxene, and serpentine, respectively), whereas the oxide zones are composed largely of Fe- and Al-oxyhydroxides. During laterization, Mg silicates are dissolved progressively, and Mg and Si were leached and transported downwards, whereas Fe^{2+} was oxidized to Fe^{3+} and fixed as insoluble Fe-oxyhydroxides, that may also accumulate large amounts of insoluble Al^{3+} (Freyssinet et al., 2005; Roqué-Rosell et al., 2010; Golightly, 2010; Villanova-de-Benavent et al., 2017).

In the studied profiles, Ni is slightly more enriched in the saprolite horizons (median content of 1.43 wt.%) than in the oxide zones (median content of 0.75 wt.%). This behavior is illustrated in Figure 15b where Ni is almost perpendicular to PC1, indicating that it can be significant in both the saprolite and oxide zones. Nickel enrichment started with the weathering of olivine, the main Ni-bearing mineral of the ultramafic bedrock. The released Ni was subsequently retained mostly in goethite, either adsorbed or substituting Fe^{3+} in its structure (Freyssinet et al., 2005; Roqué-Rosell et al., 2010; Dublet et al., 2015; Domènech et al., 2017). It is noted that Ni is also incorporated in maghemite and Mn oxyhydroxides in the oxide zone. Further weathering caused goethite to dissolve and reprecipitate, releasing Ni that is incorporated in serpentine II or in garnierite in the saprolite zone (Freyssinet et al., 2005; Villanova-de-Benavent et al., 2014, 2017).

Cobalt is more enriched in the oxide zones (median values of 0.1 wt.%) compared to the saprolite zones (median values of 117 ppm). Despite this, Co behavior deviates from the PC1 axis and the multi-elemental cluster made by $\text{Fe}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-Sc}$ (Fig. 15b). In this case, Co is highly correlated with MnO ($R^2 = 0.92$). This is because Mn oxyhydroxides are enriched in Co, with CoO median contents of 7.46 wt.%, compared to the CoO median contents of 2700 and 600 ppm of maghemite and goethite respectively. This enrichment in Co of Mn oxyhydroxides in the oxide zone is very common in lateritic profiles worldwide (i.e. Llorca, 1993; Lambiv-Dzemua et al., 2013; Domènech et al., 2022).

Scandium is more enriched in the oxide zone (median content of 77 ppm) than in the saprolite zones (median content of 13 ppm). Scandium plots parallel to the PC1 axis forming a well-defined set of elements with Fe_2O_3 and Al_2O_3 (Fig. 15b). Scandium and

Fe₂O₃ have an excellent positive correlation ($R^2 = 0.97$; Supplementary Figure 3), most likely because Sc is largely associated with goethite, which is the main Sc-bearing mineral in lateritic deposits (Levard et al., 2018, Chassé et al., 2017, 2019).

Ni- and Co-bearing mineral phases in the oxide zone

Nickel and cobalt in goethite have been typically interpreted as either structural, by their cationic exchange with Fe³⁺ (i.e. Manceau et al., 2000; Carvalho-e-Silva et al., 2003; Dublet et al., 2017), or as adsorbed cations on the surface of goethite (i.e. Myagkiy et al., 2017; Domènech et al., 2017; Putzolu et al., 2018). Goethite grains show no correlation between Fe³⁺ and Ni or Co (Fig. 7b-c), suggesting that Ni and Co do not significantly substitute for Fe³⁺ in the structure. In addition, charge balance calculations indicate how the median content of Ni and Co entering the goethite crystal structure is only around 5 %. Consequently, the remaining 95 % of Ni and Co must be adsorbed. The capacity of a mineral to adsorb cations is mainly controlled by its surface area and its surface charge values (Zhao et al., 2021). Goethite has a relatively high surface area that allows the adsorption of metals such as Ni, Co, Pb, Sb, Cr or Cd (Cornell and Schwertmann, 2003; Das and Hendry, 2011). Furthermore, goethite surface charge values also favor adsorption under a wide range of pH conditions (Gaboriaud and Ehrhardt, 2003). In the oxide zone at Moa Bay, goethite either forms as coarse grains or as fine-grained aggregates that constitute most of the oxide zone matrix. The latter are the ones of most interest because of their smaller size, with their corresponding higher specific surface area, would make them more prone to adsorb higher concentrations of Ni and Co.

At Moa Bay, the fine-grained goethite from the matrix appears darker in BSE images compared to the coarser grained goethite grains (Fig. 6a-b). This contrast in BSE brightness between coarse- and fine-grained goethite is very common in many oxide zones of laterite deposits worldwide (see for example Fig. 6d in Putzolu et al., 2018; Fig. 10h in Ito et al., 2021). Coarse grains have total oxides close to the 89 wt.% of ideal goethite (Cornell and Schwertmann, 2003). However, the analysis of fine-grained goethite using EMP implies that the electron beam (diameter ~ 1 µm) measures the volume combination of different sub-micrometric goethite grains and the porosity found in-between. As the porosity, most likely filled with volatiles (i.e. water, organic matter), cannot be quantified by EMP, the sum of oxides in the measured fine-grained goethite grains yields lower values. This decrease in the total oxides is mostly accounted for by

Fe₂O₃ (Fig. 16a), nevertheless, Ni and Co contents in goethite are independent of the total oxides and have very similar concentrations in fine- and coarse-grained goethite (Fig. 16b-c). Consequently, for the same NiO and CoO concentrations, the NiO/ Fe₂O₃ (Fig. 16d-f) and CoO/ Fe₂O₃ (Fig. 16e) ratios are higher in the goethite with lower total oxide values. This means that the fine-grained goethite from the matrix is relatively more enriched in Ni and Co compared to the coarse-grained goethite.

Goethite is affected by a series of reactions thorough time (known as goethite aging or maturing) that steadily reduce its surface area and the number of contained micro or nanopores resulting in an increase of crystallinity and desorption of Ni and Co (Das and Hendry, 2011). At the deposit scale, Dublet et al. (2015) and Domènech et al. (2017) observed how more mature goethite grains from the upper levels of a lateritic profile contain less Ni than less evolved grains from deeper levels. At Moa Bay, this process occurs at the hand-specimen scale, where larger, more crystalline goethite grains have relatively less Ni and Co (lower NiO/Fe₂O₃ and CoO/Fe₂O₃ ratios) compared to the less mature, more porous, goethite grains of the matrix that have higher Ni and Co adsorption potential (higher NiO/Fe₂O₃ and CoO/Fe₂O₃ ratios; Fig. 16f). Consequently, the coexistence of coarse- and fine-grained goethite grains reflects the complex, multi-episodic evolution and nature of laterite deposits.

Goethite is also the main Sc-bearing mineral phase in the Moa Bay district, with median contents of 58 ppm, and maximum measured contents of 117 ppm, as it is in many other laterite deposits worldwide (Chassé et al., 2017, 2019; Teitler et al., 2022; Santoro et al., 2022). However, the median Sc content of the analyzed goethite grains is lower than the median Sc content of the oxide zones (77 ppm), suggesting that either Sc in goethite has been underestimated by our analyses, or that there may be other mineral phases within the oxide zone capable of hosting Sc. How Sc is found in goethite has been a topic of recent discussion with authors claiming that almost all Sc is incorporated within the goethite structure, with Sc behaving as an almost ideal solid solution with Fe³⁺ (Levard et al., 2018), while others show that part of the Sc can be adsorbed onto its surface (Chassé et al., 2017; 2019). An underestimation of the Sc measured in goethite might have been a product of analyzing only large grains of goethite with less porosity and less sorption capacity. However, this is not the case here as both fine- and coarse-grained goethite grains (lower and higher oxide totals, respectively) were measured (see Appendix 5). Therefore, the most feasible option to explain the Sc underestimation is

that Sc is also hosted by other minerals. Hematite, the second most abundant mineral in the oxide zone, yields Sc values below the detection limit of 15 ppm, despite hematite being an important Sc-bearing mineral in other laterite deposits (Chassé et al., 2017). Maghemite, also abundant in the studied profiles, has also been ruled out, as its Sc contents are below the detection limit. However, some Mn oxyhydroxides replacing goethite have Sc contents ranging from 57 to 94 ppm. This likely indicates that Sc, originally hosted by goethite, has been transferred to the Mn oxyhydroxides. The presence of Sc in some Mn oxyhydroxide grains reveals that part of the Sc budget in the oxide zones of Moa Bay occurs in minerals other than goethite.

The Mn oxyhydroxides from the oxide zones are classified as lithiophorite, or lithiophorite-asbolane intermediates, in contrast to the minor Ni-asbolane found in the saprolite zone (Fig. 11b-c). Mn oxyhydroxides represent a significant ore mineral for Ni and Co in the oxide zone (up to 21.7 wt.% NiO and 7.46 wt.% CoO). The most abundant Mn oxyhydroxides in terms of Ni and Co are those enriched in Mn, moderately enriched in Al, and depleted in Fe (Fig. 11b-c). The enrichment of Ni and Co in Mn oxyhydroxides is caused by the strong negative surface charges that these minerals have at pH values commonly observed in soils (McKenzie, 1989). Hence, cations, such as Ni and Co are easily adsorbed onto the surface of Mn oxyhydroxides. Furthermore, with time, Co can become permanently fixed in the structure of Mn oxyhydroxides (Lambiv-Dzemua et al., 2013).

The Al present in the Al-bearing Mn oxyhydroxides (lithiophorite and lithiophorite-asbolane intermediates), and other Al-bearing minerals (gibbsite, Al-rich goethite) is derived from the weathering of plagioclase-, clinopyroxene- and Cr-spinel-bearing peridotites and/or gabbro sills and dikes, all abundant within the mantle transition zone section of eastern Cuba (Marchesi et al., 2006). Lithiophorite and lithiophorite-asbolane intermediates are the final products of the breakdown of less stable, Al-poor Mn oxyhydroxides, such as birnessite, hollandite, or cryptomelane (Dowding and Fey, 2007; Lambiv-Dzemua et al., 2013; Putzolu et al., 2018), which are yet to be identified in the Moa Bay deposits. In addition, lithiophorite and lithiophorite-asbolane intermediates form under well-drained, oxygenated and moderately acidic (pH ~ 6) conditions (Llorca, 1993; Lambiv-Dzemua et al., 2013). This makes them good reliable markers of the position of a previous water table in the lateritic profile (Domènech et al., 2022).

In the oxide zone from the Moa Bay district, maghemite is an abundant ore mineral (average modal proportions of 5% and up to ~20 %; Fig. 5), with NiO and CoO concentrations of 13.9 and 1.84 wt.%, respectively. The negative correlation between Ni and Co with Fe^{3+} (Fig. 8 b-c) suggests that Ni and Co substitute for ferric iron and that they fill maghemite lattice vacancies.

Despite maghemite occurring in the oxide zone of different laterite deposits (i.e. Indonesia, Santoro et al., 2022; Dominican Republic, Aiglsperger et al., 2015, Tauler et al., 2017; Australia, Elias, 1981; Oman, Al-Khirbash, 2015; Colombia, Gleeson et al., 2004), its potential as an ore mineral for hosting notable concentrations of Ni and Co has not been taken into consideration. This is partially due to the difficulty in differentiating maghemite from magnetite, as both minerals have euhedral octahedral morphologies, both are mainly composed of Fe, and the conventional analytical techniques generally do not distinguish Fe^{2+} from Fe^{3+} (see Appendix 6 for a thorough, step-by-step maghemite reconnaissance, and differentiation from magnetite). In laterite deposits where maghemite is present, due to its high magnetic susceptibility (Mullins, 1977), maghemite concentrates can be produced using magnets. Furthermore, Ni and Co are efficiently liberated from maghemite (recovery rates of 98 and 88%, respectively; Liu et al., 2010) using high-pressure acid leaching (HPAL), a metallurgical process commonly used to process oxide ores from lateritic deposits.

Maghemite formation has traditionally been attributed to: 1) oxidation of magnetite (e.g., Liu et al., 2004); 2) dehydroxylation of lepidocrocite (e.g., Cudennec and Lecerf, 2005); 3) heating of goethite in the presence of organic matter (e.g., Schwertmann and Taylor, 1989); and 4) a transient phase in the transformation of ferrihydrite to hematite (Barrón and Torrent, 2002; Torrent et al., 2006; Liu et al., 2008; Bilardello et al., 2020). The oxidation of magnetite has been the preferred option for maghemite genesis (Domènech et al., 2017; Santoro et al., 2022). However, this cannot be the case for the studied maghemite because the analyzed magnetite is depleted in Ni and Co (Supplementary Figure 1), which does not match the high concentrations of these elements in maghemite. Moreover, partial oxidation of the studied magnetite grains produces hematite (martitization) instead of maghemite (Supplementary Figure 1a). The dehydroxylation of lepidocrocite ($\gamma\text{-FeOOH}$) to form maghemite has also been ruled out because the Fe-hydroxides here are goethite-like ($\alpha\text{-FeOOH}$) as identified by XRD (Fig. 5) and micro-Raman spectroscopy (Fig. 9d-h). In addition, lepidocrocite is generally

found in more temperate climates (Till et al., 2014). The formation of maghemite via thermal transformations of goethite in the presence of organic matter could explain some of the maghemite grains found in the upper levels of the studied profiles. Though the temperature needed for this process could eventually be provided by vegetation fires above the lateritic soil, the thermal aureole of these fires cannot penetrate deep enough to explain the genesis of the maghemite grains found in the deeper parts of the oxide zone (Barrón and Torrent, 2002).

Ferrihydrite constitutes a poorly ordered and thermodynamically unstable hydrous iron oxide that slowly recrystallizes into goethite and/or hematite (Schwertmann and Cornell, 2000). The transformation of some ferrihydrite into hematite (Torrent et al., 2006) takes place in soils that remain moist, but not saturated in water, and warm (20-30°C). In the ferrihydrite to hematite reaction, maghemite forms as an intermediate phase (Barrón and Torrent, 2002; Torrent et al., 2006; Liu et al., 2008; Bilardello et al., 2020). The kinetics of the ferrihydrite → maghemite → hematite reaction is highly dependent on temperature and rainfall (Barrón and Torrent, 2002; Torrent et al., 2006). According to these authors, the time needed to fully transform ferrihydrite to hematite takes millions of years at 25°C. Furthermore, in areas where the rainfall is abundant and dry seasons are short, like in Cuba, the kinetics of the first part of the reaction ferrihydrite → maghemite is fast, whereas the kinetics of the second part (maghemite → hematite) is very slow, thus favoring the formation of abundant maghemite in the profiles (Barrón and Torrent, 2002; Torrent et al., 2006). Consequently, maghemite may form as a transient mineral phase in the ferrihydrite to hematite reaction and remain stable in the lateritic profiles due to the slow kinetics of the maghemite → hematite reaction. However, in the upper parts of the oxide zone, maghemite is scarce and hematite is abundant (Fig. 5) because: 1) water easily evaporates favoring drying conditions that accelerate the kinetics of the maghemite → hematite reaction; and 2) the upper parts of the profile are the oldest in the profile and ferrihydrite has had more time to fully transform into hematite.

Ni-bearing mineral phases in the saprolite horizon

In the Yamanigüey deposit, both serpentine I and II have high Fe contents, while Ni contents are similar to those reported in other localities (Fig. 12). Serpentine I ($\Sigma_{\text{tetrahedral}} = 2.000\text{-}2.111$ a.p.f.u., and $\Sigma_{\text{octahedral}} = 2.765\text{-}3.073$ a.p.f.u.) is, in general, more stoichiometric than serpentine II ($\Sigma_{\text{tetrahedral}} = 2.000\text{-}2.162$ a.p.f.u., and

$\Sigma_{\text{octahedral}} = 2.244\text{--}2.261$ a.p.f.u.). Golightly and Arancibia (1979) and Orberger et al. (1990) related this non-stoichiometry to the substitution of Mg by Fe^{3+} in the octahedral position during weathering. The fact that Fe enters the octahedral position is observed in the negative correlation between Mg and Fe+Ni (Fig. 12c). However, it must be noted that high Fe contents, also in serpentine I, indicate that (a) the serpentine was already enriched in Fe prior to weathering, (b) Fe enters the structure of serpentine faster than Ni (opposite to the hydrous Mg silicate-type Loma Caribe Ni-laterite profile, Villanova-de-Benavent et al., 2017), or (c) a combination of both. Regarding garnierite, the variation in composition in terms of Ni and X_{talc} in the same vein (Fig. 13d-g) points to marked changes in the saturation conditions of the percolating aqueous solution, as noted by Villanova-de-Benavent et al. (2014, 2022). Overall, the mineralogy, textures, and chemical composition of Ni-bearing phyllosilicates in the saprolite horizon of an oxide-type Ni-laterite profile do not differ much from those of typical hydrous Mg silicate-type deposits (Figs. 13-14), and therefore should also be considered attractive exploration targets.

Conclusions

Deposits from the Moa Bay lateritic mining district have ore-grade Ni-(Co) mineralization in both oxide (average Ni and Co of 0.88 % and 0.12 %, respectively) and saprolite horizons (average Ni of 1.98 %). In the oxide zone, goethite represents the most abundant ore mineral, with Ni and Co being adsorbed onto its surface. Goethite grain size plays an important role in adsorbing Ni and Co, as the smaller the grains, the more Ni and Co they adsorb. Goethite is also the main Sc-bearing mineral from the oxide zone, with a median Sc content of 58 ppm. Most likely, Sc in goethite is found as a combination of i) incorporated Sc substituting Fe^{3+} in the goethite structure, and ii) adsorbed Sc onto the goethite surface. Maghemite is found in the oxide zones from the three studied deposits, with average modal proportions of 5 %. Maghemite, despite being described in many other laterite deposits, has been commonly overlooked as a potential ore mineral in laterite literature. In the Moa Bay district, maghemite represents an important ore phase with NiO and CoO contents of 14 and 2 wt.%, respectively. A detailed nanoscale study performed on maghemite indicates that Ni and Co enter the maghemite crystal structure by substituting for the ferric iron, and filling some of the maghemite lattice vacancies. This study also precludes that the Ni and Co enrichment in maghemite is related to the presence of Ni- and/or Co-bearing nanoparticles.

Identification of maghemite in oxide zones from other laterite deposits might help to enhance their Ni-Co recovery rates. Mn oxyhydroxides from the oxide zone, classified as lithiophorite and lithiophorite-asbolane intermediates, are found as abundant disseminations at specific levels of the oxide zone, likely indicating the location of previous water table levels in the profile. These Mn oxyhydroxides contain very high Ni and Co contents (median 10.6 wt.% NiO and 6.41 wt.% CoO). Some of these Mn oxyhydroxides replaced goethite and contain significant Sc contents.

In the Moa Bay district, there are also very well developed saprolitic horizons, especially in the Yamanigüey deposit. In these horizons, Ni-rich, serpentine-II represents the main Ni-bearing phase, due to its high modal proportions (> 80 %) and median NiO contents (1.57 wt.%). Additionally, the saprolite horizon at Yamanigüey is crosscut by several generations of garnierite veins, with remarkable NiO contents (10.9 to 32.5 wt.%).

Acknowledgements

This research was financially supported by Spanish grant PID 2019-105625RB-C21 funded by MCIN/AEI/10.13039/501100011033. and by a “Ayudas predoctorales 2020” number PRE 2020-092140 PhD grant to DD-C by the Spanish Ministry of Science and Innovation. Additional funding was provided by the Spanish grant NANOMET PID2022-138768OB-I00 funded by the MCIN/AEI/10.13039/501100011033 and by “ERDF A way of making Europe” by the European Union. This paper has been produced within the framework of the MinResET (Mineral Resources for the Energy Transition) research group (2021-SGR-00239, Agència de Gestió d'Ajuts Universitaris i de Recerca de Catalunya). We are indebted to Xavier Llovet (CCiTUB, Universitat de Barcelona) for his help with the EMP analyses. Laura Casado (Laboratorio de Microscopías Avanzadas, University of Zaragoza) and María del Mar Abad (CIC, University of Granada) are acknowledged for her assistance with FIB and HRTEM, respectively. We are grateful to associate editor Dr. Paul Spry, and the reviewers Dr. Matthieu Chassé (Sorbonne University) and Dr. Adrian Martinez-Vargas (Agnico Eagle) for their constructive suggestions that helped to improve the quality of the manuscript. Editor Dr. Lawrence Meinert is greatly appreciated for professional editorial handling of the manuscript.

775 **References**

- 776 - Aiglsperger, T., Proenza, J.A., Lewis, J.F., Labrador, M., Svotjka, M., Rojas-
777 Purón, A., Longo, F., and Durisová, J., 2016, Critical metals (REE, Sc, PGE) in
778 Ni laterites from Cuba and the Dominican Republic: *Ore Geology Reviews*, v.
779 73, p. 127-147.
- 780 - Aiglsperger, T., Proenza, J.A., Zaccarini, F., Lewis, J.F., Garuti, G., Labrador,
781 M., and Longo, F., 2015, Platinum group minerals (PGM) in the Falcondo Ni
782 laterite deposit, Loma Caribe peridotite (Dominican Republic): *Mineralium*
783 *Deposita*, v. 50, p. 105-123.
- 784 - Al-Khirbash, S.A., 2015, Genesis and mineralogical classification of Ni-laterites
785 Oman Mountains: *Ore Geology Reviews*, v. 65, p. 199-212.
- 786 - Barrón, V., and Torrent, J., 2002, Evidence for a simple pathway to maghemite
787 in Earth and Mars soils: *Geochimica et Cosmochimica Acta*, v. 66, p. 2801-
788 2806.
- 789 - Bilardello, D., Banerjee, S.K., Volk, M.W.R., Soltis, J.A., and Lee Penn, R.,
790 2020: Simulation of natural iron oxide alteration in soil: conversion of synthetic
791 ferrihydrite to hematite without artificial dopants, observed with magnetic
792 methods: *Geochemistry, Geophysics, Geosystems*, v. 20, article
793 e2020GC009037.
- 794 - Brand, N.W., Butt, C.R.M., and Elias, M., 1998, Nickel laterites: Classification
795 and features: *AGSO Journal of Australian Geology and Geophysics*, v. 17, p.
796 81-88.
- 797 - Butjosa, L., Cambeses, A., Proenza, J.A., Agostini, S., Iturralde-Vinent, M.
798 Bernal-Rodríguez, L., and Garcia-Casco, A., 2024, Relict abyssal mantle in a
799 Caribbean forearc ophiolite (Villa Clara, central Cuba): petrogenetic and
800 geodynamic implications: *International Geology Reviews*, v. 66, p. 196-227.
- 801 - Butt, C.R.M., and Cluzel, D., 2013, Nickel laterite ore deposits: Weathered
802 serpentinites: *Elements*, v. 9, p. 123-128.
- 803 - Carvalho-e-Silva, M.L., Ramos, A.Y., Tolentino, H.C.N., Enzweiler, J., Netto,
804 S.M., and Alves, M.D.C.M., 2003, Incorporation of Ni into natural goethite: An
805 investigation by X-ray absorption spectroscopy: *American Mineralogist*, v. 88,
806 p. 876-882.
- 807 - Chassé, M., Griffin, W.L., O'Reilly, S.Y., and Calas, G., 2017, Scandium
808 speciation in a world-class lateritic deposit: *Geochemical Perspectives Letters*, v.
809 3, p. 105-114.
- 810 - Chassé, M., Griffin, W.L., O'Reilly, S.Y., and Calas, G., 2019, Australian
811 laterites reveal mechanisms governing scandium dynamics in the critical zone:
812 *Geochimica et Cosmochimica Acta*, v. 260, p. 292-310.
- 813 - Cornell, R.M., and Schwertmann, U., 2003, *The Iron Oxides: Structure,*
814 *properties, reactions, occurrences, and uses:* Berlin, Wiley-VCH, 664 p.
- 815 - Cuador-Gil, J.Q., 2005, Estudios de estimación y simulación geoestadística para
816 la caracterización de parámetros geológico - industriales en el yacimiento
817 laterítico Punta Gorda: *Minería y Geología*, v. 21, p. 1-49.

- Cudennec, Y., and Lecerf, A., 2005, Topotactic transformations of goethite and lepidocrocite into hematite and maghemite: *Solid State Sciences*, v. 7, p. 520-529.
- Das, S., and Hendry, M.J., 2011, Changes of crystal morphology of aged goethite over a range of pH (2–13) at 100 °C: *Applied Clay Science*, v. 51, p. 192-197.
- Domènech, C., Galí, S., Villanova-de-Benavent, C., Soler, J.M., and Proenza, J.A., 2017, Reactive transport model of the formation of oxide-type Ni-laterite profiles (Punta Gorda, Moa Bay, Cuba): *Mineralium Deposita*, v. 52, p. 993-1010.
- Domènech, C., Villanova-de-Benavent, C., Proenza, J.A., Tauler, E., Lara, L., Galí, S., Soler, J.M., Campeny, M., and Ibáñez-Insa, J., 2022, Co–Mn mineralisations in the Ni Laterite Deposits of Loma Caribe (Dominican Republic) and Loma de Hierro (Venezuela): *Minerals*, v. 12, article 927.
- Dowding, C.E., and Fey, M.V., 2007, Morphological, chemical and mineralogical properties of some manganese-rich oxisols derived from dolomite in Mpumalanga province, South Africa: *Geoderma*, v. 141, p. 23-33.
- Dublet, G., Juillot, F., Brest, J., Noël, V., Fritsch, E., Proux, O., Olivi, L., Ploquin, F., and Morin, G., 2017, Vertical changes of the Co and Mn speciation along a lateritic regolith developed on peridotites (New Caledonia): *Geochimica et Cosmochimica Acta*, v. 217, p. 1-15.
- Dublet, G., Juillot, F., Morin, G., Fritsch, E., Fandeur, D., and Brown Jr., G.E., 2015, Goethite aging explains Ni depletion in upper units of ultramafic lateritic ores from New Caledonia: *Geochimica et Cosmochimica Acta*, v. 160, p. 1-15.
- Elias, M., 2002, Nickel laterite deposits — geological overview, resources and exploitation, in Cooke, D.R., and Pongratz, J., eds., *Giant Ore Deposits: Characteristics, genesis and explorations*, CODES Special Publication. Centre for Ore Deposit Research, University of Tasmania, p. 205–220.
- Elias, M., Donaldson, M.J., and Giorgetta, N.E., 1981, Geology, mineralogy, and chemistry of lateritic nickel-cobalt deposits near Kalgoorlie, Western Australia: *Economic Geology*, v. 76, p. 1775-1783.
- Elias, M., O’Callaghan, P., Martínez, A., and Buban, K., 2019, NI 43-101 Technical Report. Moa Nickel Project Cuba: CSA Global Report N° R117.2019, 127 p.
- European Commission, 2023, Study on the Critical Raw Materials for the EU (Final Report): European Commission, Brussels, p. 1–158.
- Foret, B., Breed, M.F., Jacobs, C., and Reid, B., 2023, NI 43-101 Technical Report for the mineral resource and mineral reserve estimate on the Moa Project, Province of Holguin, Cuba: Micon International Co Limited, 234 p.
- Freyssinet, P., Butt, C.R.M., Morris, R.C., and Piantone, P., 2005, Ore-forming processes related to lateritic weathering: *Economic Geology 100th Anniversary Volume*, p. 681–722.
- Gaboriaud, F., and Ehrhardt, J.J., 2003, Effects of different crystal faces on the surface charge of colloidal goethite (α -FeOOH) particles: an experimental and modeling study: *Geochimica et Cosmochimica Acta*, v. 67, p. 967–983.

- García-Casco, A., Iturralde-Vinent, M.A., and Pindell, J., 2008, Latest cretaceous collision/accretion between the Caribbean plate and Caribean: origin of metamorphic terranes in the Greater Antilles: *International Geology Reviews*, v. 50, p. 781–809.
- García-Casco, A., Torres-Roldán, R.L., Iturralde-Vinent, M.A., Millán, G., Núñez-Cambra, K., Lázaro, C., and Rodríguez Vega, A., 2006, High pressure metamorphism of ophiolites in Cuba: *Geologica Acta*, v. 4, p. 63–88.
- Gervilla, F., Proenza, J.A., Frei, R., González-Jiménez, J.M., Garrido, C.J., Melgarejo, J.C., Meibom, A., Díaz-Martínez, R., and Lavaut, W., 2005, Distribution of platinum-group elements and Os isotopes in chromite ores from Mayarí-Baracoa Ophiolitic Belt (eastern Cuba): *Contributions to Mineralogy and Petrology*, v. 150, p. 589–607.
- Gleeson, S.A., Butt, C.R.M., and Elias, M., 2003, Nickel laterites: A review: *SEG Newsletter*, v. 54, p. 11–18.
- Gleeson, S.A., Herrington, R.J., Durango, J., Velásquez, C.A., and Koll, G., 2004, The mineralogy and geochemistry of the Cerro Matoso S.A. Ni laterite deposit, Montelíbano, Colombia: *Economic Geology*, v. 99, p. 1197–1213.
- Golightly, J.P., 1981, Nickeliferous laterite deposits: *Economic Geology 75th Anniversary Volume*, p. 710–735.
- Golightly, J.P., 2010, Progress in understanding the evolution of nickel laterites: *Economic Geology Special Publications*, v. 15, p. 451–485.
- Golightly, J.P., and Arancibia, O.N., 1979, The chemical composition and infrared spectrum of nickel- and iron-substituted serpentine from a nickeliferous laterite profile, Soroako, Indonesia: *Canadian Mineralogist*, v.17, p. 719–728.
- González-Jiménez, J.M., Proenza, J.A., Gervilla, F., Melgarejo, J.C., Blanco-Moreno, J.A., Ruiz-Sánchez, R., and Griffin, W.L., 2011, High-Cr and high-Al chromitites from the Sagua de Tánamo district, Mayarí-Cristal ophiolitic massif (eastern Cuba): Constraints on their origin from mineralogy and geochemistry of chromian spinel and platinum-group elements: *Lithos*, v. 125, p. 101–121.
- Hernández, C. M., Banza, A., and Gock, E., 2006, Recovery of metals from Cuban nickel tailings by leaching with organic acids followed by precipitation and magnetic separation: *Journal of Hazardous Materials*, v. 139, p. 25–30.
- IEA, 2021, *The Role of Critical Minerals in Clean Energy Transitions*: Paris, International Energy Agency, 43 p.
- Ito, A., Otake, T., Maulana, A., Sanematsu, K., Sufriadin, and Sato, T., 2021, Geochemical constraints on the mobilization of Ni and critical metals in laterite deposits, Sulawesi, Indonesia: A mass-balance approach: *Resource Geology*, v. 71, p. 255–282.
- Iturralde-Vinent, M.A., 1996, Geología de las ofiolitas de Cuba, *in* Iturralde-Vinent, M.A., ed., *Ofiolitas y arcos volcánicos de Cuba*, IGCP Project 364, Special Contribution 1, p. 83–120.
- Iturralde-Vinent, M.A., García-Casco, A., Rojas-Agramonte, Y., Proenza, J.A., Murphy, J.B., and Stern, R.J., 2016, The geology of Cuba: a brief overview and synthesis: *GSA Today (Geological Society of America)*, v. 26, p. 4–10.

- 907 - Lambiv-Dzemua, G., Gleeson, S.A., and Schofield, P.F., 2013, Mineralogical
908 characterization of the Nkamouna Co–Mn laterite ore, southeast Cameroon:
909 Mineralium Deposita, v. 48, p. 155-171.
- 910 - Lavaut, W., 1998, Tendencias geológicas del intemperismo de las rocas
911 ultramáficas en Cuba oriental: Minería y Geología, v. 15, p. 9–16.
- 912 - Levard, C., Borschneck, D., Grauby, O., Rose, J., and Ambrosi, J.P., 2018,
913 Goethite, a tailor-made host for the critical metal scandium: The $\text{Fe}_x\text{Sc}_{(1-x)}\text{OOH}$
914 solid solution: Geochemical Perspectives Letters, v. 9, p. 16-20.
- 915 - Lewis, J.F., Draper, G., Proenza, J.A., Espaillat, J., and Jiménez, J., 2006,
916 Ophiolite-related ultramafic rocks (serpentinites) in the Caribbean region: a
917 review of their occurrence, composition, origin, emplacement and nickel laterite
918 soils: Geologica Acta, v. 4, p. 237–263.
- 919 - Linchenat, A., and Shirakova, I., 1964, Individual characteristics of
920 nickeliferous iron (laterite) deposits of the northeast part of Cuba (Pinares de
921 Mayari, Nicaro and Moa) [ext. abs]: International Geological Congress, 24th,
922 Montreal, Canada, 1964, Extended Abstracts, p. 172–187.
- 923 - Liu, K., Chen, Q., Hu, H., Yin, Z., and Wu, B., 2010, Pressure acid leaching of a
924 Chinese laterite ore containing mainly maghemite and magnetite:
925 Hydrometallurgy, v. 104, p. 32-38.
- 926 - Liu, Q. S., Banerjee, M. J., Jackson, C. L., Deng, Y. X., Pan, R.X., and Zhu R.X.,
927 2004, New insights into low-temperature oxidation of magnetites and thermal
928 alteration of magnetic mineralogy of the Chinese loess in air: Geophysical
929 Journal International, v. 158, p. 506-514.
- 930 - Liu, Q., Barrón, V., Torrent, J., Eeckhout, S.G., Deng, C., 2008, Magnetism of
931 intermediate hydromaghemite in the transformation of 2-line ferrihydrite into
932 hematite and its paleoenvironmental implications: Journal of Geophysical
933 Research, v. 113, article B01103.
- 934 - Llorca, S., 1993, Metallogeny of supergene cobalt mineralization, New
935 Caledonian: Australian Journal of Earth Sciences, v. 40, p. 377–385.
- 936 - Manceau, A., Schlegel, M.L., Musso, M., Sole, V.A., Gauthier, C., Petit, P.E.,
937 and Trolard, F., 2000, Crystal chemistry of trace elements in natural and
938 synthetic goethite: Geochimica et Cosmochimica Acta, v. 64, p. 3643–3661.
- 939 - Marchesi, C., Garrido, C.J., Bosch, D., Proenza, J.A., Gervilla, F., Monié, P.,
940 and Rodríguez-Vega, A., 2007, Geochemistry of Cretaceous magmatism in
941 eastern Cuba: Recycling of North American continental sediments and
942 implications for subduction polarity in the Greater Antilles Paleo-arc: Journal of
943 Petrology, v. 48, p. 1813-1840.
- 944 - Marchesi, C., Garrido, C.J., Godard, M., Proenza, J.A., Gervilla, F., and Blanco-
945 Moreno, J., 2006, Petrogenesis of highly depleted peridotites and gabbroic rocks
946 from the Mayarí-Baracoa Ophiolitic Belt (eastern Cuba): Contributions to
947 Mineralogy and Petrology, v. 151, p. 717–736.
- 948 - Marsh, E., Anderson, E., and Gray, F., 2013, Nickel-cobalt laterites: A deposit
949 model: Reston, VA, U.S. Geological Survey Scientific Investigations Report
950 2010–5070–H, 38 p.

- 951 - McKenzie, R.M., 1989, Manganese oxides and hydroxides, *in* Dixon, J.B., and
 952 Weed, S.B., eds., *Minerals in soil environments*, 2nd edition. Madison, SSSA, p.
 953 439–465.
- 954 - Mudd, G.M., and Jowitt, S.M., 2022, The new century for nickel resources,
 955 reserves, and mining: Reassessing the sustainability of the devil’s metal:
 956 *Economic Geology*, v. 117, p. 1961-1983.
- 957 - Mullins, C.E., 1977, Magnetic susceptibility of the soil and its significance in
 958 soil science - a review: *Journal of Soil Science*, v. 28, p. 223-246.
- 959 - Myagkiy, A., Truche, L., Cathelineau, M., and Golfier, F., 2017, Vertical
 960 changes of the Co and Mn speciation along a lateritic regolith developed on
 961 peridotites (New Caledonia): *Chemical Geology*, v. 466, p. 274-284.
- 962 - Nelson, C.E., Proenza, J.A., Lewis, J.F., and López-Kramer, J., 2011, The
 963 metallogenic evolution of the Greater Antilles: *Geologica Acta*, v. 9, p. 229–
 964 264.
- 965 - Orberger, B., Friedrich, G., and Woermann, D., 1990, The distribution of
 966 halogens and carbon in PGE-bearing ultramafics of the Acoje ophiolite block,
 967 Zambales, Philippines: *Journal of Geochemical Exploration*, v. 37, p. 147–169.
- 968 - Pelletier, B., 1996, Serpentine in nickel silicate ore from New Caledonia [ext.
 969 abs]: Nickel Conference, Kalgoorlie (Western Australia), 1996, Extended
 970 Abstracts, p. 197–205.
- 971 - Proenza, J.A., Díaz-Martínez, R., Iriondo, A., Marchesi, C., Melgarejo, J.C.,
 972 Gervilla, F., Garrido, C.J., Rodríguez-Vega, A., Lonzano-Santacruz, R., and
 973 Blanco-Moreno, J., 2006, Primitive Cretaceous island-arc volcanic rocks in
 974 eastern Cuba: the Téneme Formation: *Geologica Acta*, v. 4, p. 103–121.
- 975 - Proenza, J., Gervilla, F., Melgarejo, J.C., and Bodinier, J.L., 1999, Al- and Cr-
 976 rich chromitites from the Mayari-Baracoa ophiolitic belt (eastern Cuba);
 977 consequence of interaction between volatile-rich melts and peridotites in
 978 suprasubduction mantle: *Economic Geology*, v. 94, p. 547–566.
- 979 - Proenza, J.A., González-Jiménez, J.M., García-Casco, A., Belousova, E.,
 980 Griffin, W.L., Talavera, C., Rojas-Agramonte, Y., Aiglsperger, T., Navarro-
 981 Ciurana, D., Pujol-Solà, N., Gervilla, F., O’Reilly, S.Y., and Jacob, D.E., 2018,
 982 Cold plumes trigger contamination of oceanic mantle wedges with continental
 983 crust-derived sediments: Evidence from chromitite zircon grains of eastern
 984 Cuban ophiolites: *Geoscience Frontiers*, v. 9, p. 1921-1936.
- 985 - Proenza, J.A., Tauler, E., Melgarejo, J.C., Galí, S., Labrador, M., Marrero, N.,
 986 Pérez-Melo, A.N., Rojas Purón, A., and Blanco-Moreno, J.A., 2007,
 987 Mineralogy of oxide and hydrous silicate Ni laterite profiles in Moa Bay area,
 988 northeast Cuba [abs.]: Ninth Biennial SGA Meeting, Dublin, 2007, Proceedings
 989 of the Ninth Biennial SGA Meeting, p. 1389-1392.
- 990 - Pujol-Solà, N., Proenza, J.A., García-Casco, A., González-Jiménez, J.M.,
 991 Román-Alpiste, M.J., Garrido, C.J., Melgarejo, J.C., Gervilla, F., and Llovet, X.,
 992 2020, Fe-Ti-Zr metasomatism in the oceanic mantle due to extreme
 993 differentiation of tholeiitic melts (Moa-Baracoa ophiolite, Cuba): *Lithos*, v. 358-
 994 359, article 105420.
- 995 - Pushcharovsky, Y., 1988, Geological map of the Republic of Cuba (scale
 996 1:250000): Cuba and USSR Academy of Science.

- 997 - Putzolu, F., Balassone, G., Boni, M., Maczurad, M., Mondillo, N., Najorka, J.,
998 and Pirajno, F., 2018, Mineralogical association and Ni-Co deportment in the
999 Wingellina oxidetype laterite deposit (Western Australia): *Ore Geology*
1000 *Reviews*, v. 97, p. 21-34.
- 1001 - Rojas-Agramonte, Y., Garcia-Casco, A., Kemp, A., Kröner, A., Proenza, J.A.,
1002 Lázaro, C., and Liu, D., 2016, Recycling and transport of continental material
1003 through the mantle wedge above subduction zones: A Caribbean example: *Earth*
1004 *and Planetary Science Letters*, v. 436, p. 93-107.
- 1005 - Rojas-Purón, A., and Turro-Breffe, A.T., 2003, Composición mineralógica de
1006 las colas del proceso Caron en Moa, Holguín, Cuba: *Minería y Geología*, v. 3-4,
1007 p. 21-28.
- 1008 - Roqué-Rosell, J., Mosselmans, J.F.W., Proenza, J.A., Labrador, M., Galí, S.,
1009 Atkinson, K.D., and Quinn, P.D., 2010, Sorption of Ni by “lithiophorite–
1010 asbolane” intermediates in Moa Bay lateritic deposits, eastern Cuba: *Chemical*
1011 *Geology*, v. 275, p. 9-18.
- 1012 - Roqué-Rosell, J., Villanova-de-Benavent, C., and Proenza, J.A., 2017, The
1013 accumulation of Ni in serpentines and garnierites from the Falcondo Ni-laterite
1014 deposit (Dominican Republic) elucidated by means of μ XAS: *Geochimica et*
1015 *Cosmochimica Acta*, v. 198, p. 48–69.
- 1016 - Rui, H., Yang, J., Zheng, J., Llanes-Castro, A.I., Liu, F., Wu, Y., Wu, W.,
1017 Mariño, Y.V., and Masoud, A.E., 2022, Early Cretaceous subduction initiation
1018 of the proto-Caribbean plate: geochronological and geochemical evidence from
1019 gabbros of the Moa-Baracoa ophiolitic massif, eastern Cuba: *Lithos*, v. 418-419,
1020 article 106674.
- 1021 - Santoro, L., Putzolu, F., Mondillo, N., Boni, M., and Herrington, R., 2022, Trace
1022 element geochemistry of iron-(oxy)-hydroxides in Ni(Co)-laterites: Review, new
1023 data and implications for ore forming processes: *Ore Geology Reviews*, v. 140,
1024 article 104501.
- 1025 - Schwertmann, U., Cornell, R. M. 2000. *Iron oxides in the laboratory:*
1026 *Preparation and characterization:* Weinheim, Germany, Wiley-VCH, 188 p.
- 1027 - Schwertmann, U., and Taylor, R.M., 1989, *Iron oxides*, in Dixon, J.B., and
1028 Weedm S.B., eds. *Minerals in Soil Environments*, Madison, WI, Soil Science
1029 Society of America, p. 379-438.
- 1030 - Sherritt International Corporation, 2022. *Financial Results Report: Sherritt*
1031 *International Corporation*, 137 p.
- 1032 - Tauler, E., Galí, S., Villanova-de-Benavent, C., Chang-Rodríguez, A., Núñez-
1033 Cambra, K., Khazaradze, G., and Proenza, J.A., 2023, *Geochemistry and*
1034 *Mineralogy of the Clay-Type Ni-Laterite Deposit of San Felipe (Camagüey,*
1035 *Cuba): Minerals*, v. 13, article 1281.
- 1036 - Tauler, E., Lewis, J.F., Villanova-de-Benavent, C., Aiglsperger, T., Proenza,
1037 J.A., Domènech, C., Gallardo, T., Longo, F., and Galí, S., 2017, Discovery of
1038 Ni-smectite rich saprolite at Loma Ortega, Falcondo mining district (Dominican
1039 Republic): geochemistry and mineralogy of an unusual case of “hybrid hydrous
1040 Mg silicate – clay silicate” type Ni-laterite: *Mineralium Deposita*, v. 52, p. 1011-
1041 1030.

- 1042 - Tavchandjian, O., and Golightly, J.P., 2010, Update to the mineral resource
1043 estimates of the Fenix project, Izabal, Guatemala: (<http://www.sedar.com>;
1044 HudBay Minerals Inc., filed 31st March 2010).
- 1045 - Teitler, Y., Favier, S., Ambrosi, J.P., Sevin, B., Golfier, F., and Cathelineau, M.
1046 2022, Evaluation of Sc concentrations in Ni-Co laterites using Al as a
1047 geochemical proxy: *Minerals*, v. 12, article 615.
- 1048 - Till, J.L., Guyodo, Y., Lagroix, F., Ona-Nguema, G., and Brest, J., 2014,
1049 Magnetic comparison of abiogenic and biogenic alteration products of
1050 lepidocrocite: *Earth and Planetary Science Letters*, v. 395, p. 149-158.
- 1051 - Tobón, M., Weber, M., Proenza, J.A., Aiglsperger, T., Betancur, S., Farré-de-
1052 Pablo, J., Ramírez, C., and Pujol-Solà, N., 2020, Geochemistry of platinum-
1053 group elements (PGE) in Cerro Matoso and Planeta Rica Ni-Laterite deposits,
1054 northern Colombia: *Boletín de la Sociedad Geológica Mexicana*, v. 72, article
1055 A201219.
- 1056 - Torrent, J., Barrón, V., and Liu, Q., 2006, Magnetic enhancement is linked to
1057 and precedes hematite formation in aerobic soil: *Geophysical Research Letters*,
1058 v. 33, article L02401.
- 1059 - USGS, 2021a, United States Geological Survey, Mineral Commodity
1060 Summaries: Nickel, *in* U.S. Geological Survey, ed., United States Geological
1061 Survey, Mineral Commodity Summaries: Reston, VA, U.S. Geological Survey,
1062 p. 112-114.
- 1063 - USGS, 2021b. United States Geological Survey, Mineral Commodity
1064 Summaries: Cobalt, *in* U.S. Geological Survey, ed., United States Geological
1065 Survey, Mineral Commodity Summaries: Reston, VA, U.S. Geological Survey,
1066 p. 50-52.
- 1067 - USGS, 2023. United States Geological Survey, Mineral Commodity Summaries:
1068 Reston, VA, U.S. Geological Survey, 210 p.
- 1069 - Voskresenskaya, N. T., 1987, Ni-bearing minerals in oxide-, silicate-ores from
1070 Cuba (in Russian): *Geochemistry*, v. 2, p. 71-89.
- 1071 - Villanova-de-Benavent, C., Cama, J., Soler, J.M., Domènech, C., Galí, S., and
1072 Proenza, J.A., 2022, Dissolution kinetics of garnierites from the Falcondo Ni-
1073 Laterite deposit (Dominican Republic) under acidic conditions: *Applied*
1074 *Geochemistry*, v. 143, article 105357.
- 1075 - Villanova-de-Benavent, C., Domènech, C., Tauler, E., Galí, S., Tassara, S., and
1076 Proenza, J.A., 2017, Fe–Ni-bearing serpentines from the saprolite horizon of
1077 Caribbean Ni-laterite deposits: New insights from thermodynamic calculations:
1078 *Mineralium Deposita*, v. 52, p. 979–992.
- 1079 - Villanova-de-Benavent, C., Proenza, J.A., Galí, S., García-Casco, A., Tauler, E.,
1080 Lewis, J.F., and Longo, F., 2014, Garnierites and garnierites: Textures,
1081 mineralogy and geochemistry of garnierites in the Falcondo Ni-laterite deposit,
1082 Dominican Republic: *Ore Geology Reviews*, v. 58, p. 91-109.
- 1083 - Wilson, F.H., Orris, G., and Gray, F., 2021, Preliminary geologic map of the
1084 Greater Antilles and the Virgin Islands: U.S. Geological Survey Open-File
1085 Report 2019–1036, pamphlet 50 p., 2 sheets, scales 1:2,500,000 and 1:300,000.
- 1086 - Young, R.A., 1993, *The Rietveld Method*: Oxford, Oxford University Press, 298
1087 p.

- Zhao, Y., Wang, W., and Yi, H. 2021. Mineral Adsorbents and Characteristics, *in* Song, S., and Li, B., eds., Adsorption at Natural Minerals/Water Interfaces: New York, Springer, p. 3-24.
- Zhou, Z., Ma, B., Wang, C., Chen, Y., and Wang, L., 2022, Recovery of scandium and aluminum from limonitic laterite intermediate product: Minerals Engineering, v. 188, article 107844.

Figure captions

Figure 1: (a) Simplified geological map of the Greater Antilles, with the location of different laterite mining districts (modified from Wilson et al., 2021). (b) Geological map of the Mayarí-Baracoa Ophiolite Belt (after Pushcharovsky, 1988) with the location of the Moa Bay laterite mining district.

Figure 2: Location of eight of the eleven laterite deposits within Moa Bay mining district. The drill core location of the three studied profiles is marked with a red star. The two metallurgical plants and the tailing pond are also observed. Satellite image taken from Google Earth.

Figure 3: Schematic Ni laterite profile from the Yagrumaje Norte deposit with major, minor and trace element contents.

Figure 4: Schematic Ni laterite profile from the Yamanigüey deposit with major, minor and trace element contents.

Figure 5: Quantitative mineral distribution patterns along the studied profiles of Yagrumaje Norte and Yamanigüey deposits.

Figure 6: Back-scattered electron (BSE) images of (a) botryoidal aggregates of goethite; (b) goethite grain composed by fibrous, elongated crystals; (c-d) maghemite crystals surrounded by goethite grains forming the so-called “baguette-like” texture; (e-f) Mn oxyhydroxides with colloform textures; (g) garnierite vein crosscutting serpentine II; (h) Mn oxyhydroxides growing in a fracture of the saprolite horizon. Note that the fine-grained, darker in the BSE images, matrix from images (a) to (f) corresponds to fine-grained goethite. Abbreviations: Chr: Cr-spinel; Gar: garnierite; Gth: goethite; Mgh: maghemite; Mn-OH: Mn oxyhydroxides; Srp II: serpentine II.

Figure 7: Composition of goethite. (a) Box and whiskers diagram; (b) Fe₂O₃ (wt.%) vs NiO (wt.%) binary diagram; (c) Fe₂O₃ (wt.%) vs CoO (wt.%) binary diagram.

1120 Figure 8: Composition of maghemite. (a) Box and whiskers diagram; (b) Ni (a.p.f.u.) vs
1121 Fe^{3+} (a.p.f.u.) binary diagram; (c) Co (a.p.f.u.) vs Fe^{3+} (a.p.f.u.) binary diagram.

1122 Figure 9: (a) BSE image of a euhedral, isolated maghemite crystal. The locations of the
1123 Raman spectra from (d) and the thin-foil, obtained by FIB, are showed with red circles
1124 and a red line respectively; (b-c) Ni and Co elemental maps of the euhedral maghemite;
1125 (d) Raman spectra of the maghemite and goethite from (a); (e) BSE image of a
1126 “baguette-like” maghemite that has been partially replaced by hematite. The locations of
1127 the Raman spectra from (h) are showed with red circles; (f-g) Ni and Co elemental maps
1128 of the “baguette-like” maghemite; (h) Raman spectra of the maghemite, hematite and
1129 goethite from (e).

1130 Figure 10: (a-e) HAADF image and TEM-EDS elemental maps for Ni, Co, Si and Cr of
1131 the maghemite thin-foil whose extraction location can be found in Fig. 10a; (f) HRTEM
1132 image of maghemite Ni-depleted zone; (g) HRTEM image of maghemite Ni-enriched
1133 zone; (h) HRTEM image of a fracture cross-cutting the maghemite filled with goethite.

1134 Figure 11: Composition of Mn oxyhydroxides. (a) Box and whiskers diagram; Al-Ni-Co
1135 and Al-Fe-Mn ternary diagrams classified according to (b) Ni content of the Mn
1136 oxyhydroxides on the basis of 100 oxygens, and (c) Co content of the Mn
1137 oxyhydroxides on the basis of 100 oxygens.

1138 Figure 12: Binary (a-c) and ternary (d) diagrams representing the chemical composition
1139 of serpentine I and II from Yamanigüey in terms of wt.% Mg, Ni and Fe from EMP data
1140 (this study and Villanova-de-Benavent et al., 2017), compared to other Ni-laterite
1141 serpentines from the literature: Punta Gorda, Loma Caribe (Villanova-de Benavent et
1142 al., 2017), Loma Ortega (Tauler et al., 2017), San Felipe (Tauler et al., 2023), New
1143 Caledonia (Pelletier, 1996), and Indonesia (Golightly and Arancibia, 1979).

1144 Figure 13: BSE (a) and (b) Mg, (c) Fe, (d) Ni, (e) Si and (f) Mn X-ray elemental maps
1145 of a garnierite vein crosscutting the saprolite matrix; (g) ternary plot showing the
1146 composition of the analyzed garnierite grains compared to the garnierite composition
1147 from the Falcondo Ni laterite deposit (Dominican Republic).

1148 Figure 14: Molar ternary plot of $\text{Al}_2\text{O}_3+\text{Fe}_2\text{O}_3$ -MgO-SiO₂ showing the weathering
1149 trends of ultramafic rocks and their relationship with the Ultramafic Index of Alteration
1150 (UMIA). Our dataset is compared with data from Punta Gorda (Aiglsperger et al., 2016)

and other lateritic mining districts from the Caribbean (Cuba, Tauler et al., 2023; Colombia, Gleeson et al., 2004 and Tobón et al., 2020; Dominican Republic, Aiglsperger et al., 2016; Venezuela, Domènech et al., 2022; Guatemala, Tavchandjian and Golightly, 2010).

Figure 15: (a) Scree plot showing the % of explained variance of each Principal Component (PCs) of the dataset; (b) PC1 vs PC2 binary diagram of the studied samples and samples from Punta Gorda (Aiglsperger et al., 2016) and other lateritic mining districts from the Caribbean (Cuba, Tauler et al., 2023; Colombia, Gleeson et al., 2004 and Tobón et al., 2020; Dominican Republic, Aiglsperger et al., 2016; Venezuela, Domènech et al., 2022).

Figure 16: Relationship between the total oxides (wt.%) and (a) Fe_2O_3 (wt.%); (b) NiO (wt.%); (c) CoO (wt.%) of goethite grains from the three studied deposits. Binary diagrams (d) NiO (wt.%) vs $\text{NiO}/\text{Fe}_2\text{O}_3$ ratio, and (e) CoO (wt.%) vs $\text{CoO}/\text{Fe}_2\text{O}_3$ ratio, with data classified according to their total oxides content (in wt.%); (f) BSE image of three goethite types according to their BSE brightness and grain size. Note that goethite in the matrix is relatively more enriched in Ni than coarse-grained goethite.

Supplementary Figure 1: (a) Optical microscope photomicrograph of magnetite being replaced by hematite (martitization), together with their Raman spectra. Both, magnetite and hematite have NiO and CoO contents below the detection limit; (b) BSE image of two euhedral, isolated, maghemite grains, together with the Raman spectrum of the larger crystal. Note the maghemite high contents of NiO and CoO .

Supplementary Figure 2: Cr-spinel grains from the oxide zone with wormy textures.

Supplementary Figure 3: Sc (ppm) vs Fe_2O_3 (wt.%) contents in the bedrock, saprolite and oxide zones of the studied profiles. Data from Punta Gorda is taken from Aiglsperger et al. (2016).