



EDERICO II

PhD in Earth, Environmental and Resource Sciences

PhD thesis in Economic Geology Mineralogy and geochemistry of Ni-Co in lateritic profiles



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Inspiration exists, but it has to find you working.

- Pablo Picasso



University of Naples Federico II PhD in Earth, Environmental and Resource Sciences XXXIII cycle Head of the Doctorate: Prof. Maurizio Fedi

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Abstract

Nickel (Ni) and cobalt (Co) laterites are supergene deposits formed under tropical climatic conditions, through the weathering of olivine-bearing mafic to ultramafic rocks. The mineralogical and geochemical study of laterites has been always considered to be a knotty challenge, due to their complex mineralogical assemblage that commonly contains amorphous to poorly crystalline ore-carriers. These features also represent a challenge for mining companies when dealing with the classification, processing and metallurgy of lateritic ores. Laterite ores represent viable targets for the supplying of Co, whose vast majority of global production is related to high-risk countries (i.e. Democratic Republic of Congo). Therefore, the studies on the Co deportment and its spatial distribution within laterites are crucial to unlock thousands of tonnes of Co reserves in countries that are more geopolitically and socially stable. Accordingly, the main goals that have been pursued in this study are:

(i) The achievement of an increased knowledge of the metallogenetic processes of the diverse mineralized facies in Ni-Co laterite deposits;

(ii) The study of the challenging aspects when dealing with the evaluation of the modal mineralogy and metal deportment of laterite ores;

(iii) The assessement of the influence of the pre-lateritic and syn-lateritic alteration processes on the Co-endowment in laterite ores.

To pursue these aims, two oxide-type laterites were considered: Wingellina (Musgrave Province, Western Australia) and Santa Fe' (Goiás Province, Central Brazil) deposits. The Wingellina Ni-Co deposit is located close to the border between Northern Territory and Western Australia and likely formed during the episodic weathering events occurred in the Australian continent during Mesozoic to Tertiary. The Santa Fe' Ni-Co laterite is a major undeveloped deposit located in the Goiás State of Central Brazil, which was originated during the Eocene to Oligocene and Miocene-Pliocene stages of tropical weathering.

Significant differences in terms of the nature of parent rocks, alteration histories and ore distribution can be recognized between the selected deposits. The Wingellina deposit formed from the alteration of a Mesoproterozoic mafic to ultramafic intrusion (Giles Complex) with tholeiitic affinity, which comprehends dunite, peridotite, and pyroxenite in the primitive members, and olivine gabbro, gabbronorite, and anorthosite in the relatively more differentiated units. The Santa Fe' laterite formed from a Cretaceous ultramafic-dominated intrusion representing the plutonic portion of a large alkaline province (South Goiás Alkaline Province). The intrusive body consists of a dunite core surrounded by peridotite, pyroxenite and minor gabbro.

The pre-lateritic history of the Wingellina hill intrusion is marked by a first stage of high-pressure and high-temperature metamorphism, which was later superimposed by a lower T° hydrothermalism leading to the serpentinization of the ultramafic units. When the lateritic processes superimposed the aforementioned processes, in the lowermost section of the weathering profiles Nibearing-smectite clays developed after the alteration of ferromagnesian minerals and of former layered silicates, while in the oxide unit Co-rich Mnoxy-hydroxides formed after clay minerals. In the Santa Fe' deposit, the early greenschist facies alteration, leading to the serpentinization of the parent rock, has been later overprinted by an amphibolite facies assemblage consisting of secondary spinels, Ni-rich chlorite, sulfide and amphibole. At Santa Fe', Ni and Co have atypical geochemical footprints, not correlated with geochemical proxy (i.e. Mn and Fe) indicating a typical a lateritic enrichment. At Wingellina Mnoxy-hydroxides are the main Ni and Co carriers in the oxide ore, with lithiophorite and asbolane (with their intermediates) representing that main phases. The lithiophorite-asbolane intermediates occur as late replacements of former Mn-phases, which have a lower ore grade and a high content of more mobile elements (as Ba and K), indicating that the Co enrichment in Mn-oxyhydroxides was controlled by a multistage diagenetic evolution.

Whole-rock geochemical survey enabled to evaluate the Ni-Co enrichment in the Wingellina profile, and its High-Tech metals (REE and Sc) potential. The Ni enrichment was mostly controlled by the paragenetic evolution of the laterite itself, whereas the Co enrichment was related to the formation of Mn-oxyhydroxide-rich horizons in the oxide orebody. Significant REEs concentrations have been observed within the oxide zones, where Ce is decoupled from the other REEs, reflecting either a variable enrichment process among the different REEs and a heterogeneous mineralogy of the REEs-bearing phases. The REEs concentration was found to be higher in the gabbro-derived laterite than in the serpentinite-derived profile due to the higher REE concentration in the more differentiated units of the bedrock and to the higher LREE fractionation in the profile, which likely resulted in the formation of neoformed LREE-bearing phases. Scandium is only partially correlated with Fe_2O_3 , having been most commonly detected in Ni- and SiO₂-rich zones of the saprolite, reflecting its association with epigenetic Fe-oxy-hydroxides derived from relict olivine and/or its adsorbtion into clays.

The study of the Ni-phyllosilicates in the Wingellina saprolite ore was aimed to understand the role of diverse bedrocks (gabbro and serpentinite) and the influence of climate on saprolitization process. In the same suite of samples the mineralogical survey was refined by an investigation with TEM-HRTEM, in order to understand the minerogenetic process of Ni-bearing clays at the nanoscale. The main phyllosilicate in the gabbro-derived saprolite consists of a Al- and Ni-rich montmorillonite, derived from the weathering of pyroxene. In the serpentinite-derived saprolite, the alteration pathway followed a multistage evolution: (i) lateritic alteration of serpentine into smectites (saponite and nontronite); (ii) late precipitation of interstratified Ni-clays as a replacement of former phyllosilicates and as neo-formed minerals. The latest phenomenon is related to the late Miocene shift from humid-and-acid (tropical climate) to saline-and-alkaline conditions (arid to semi-arid climate), and represents an example of post-lateritization processes, rarely observed in laterites located on stable cratons. The aridity-driven precipitation of Ni-rich interstratified clays in the Wingellina laterite can be seen as a new model for explaining the evolution of Ni-laterities in stable cratonic settings experiencing post-lateritization aridity. The nanoscale TEM-HRTEM imaging indicates that Ni-bearing clays occur either as a replacement of the former clay suite (i.e. serpentine and chlorite) or as porous clay aggregates, with the latter occurring in close association with nanometric Co-rich Mn-oxy-hydroxides. This finding provides a better understanding of the early stage formation of Mn-oxy-hydroxides in laterite systems, which were earlier observed only onto kaolinite templates. The detection of nanometric Mn-oxy-hydroxides is also important to constrain the Co distribution and targeting within unconventional laterite ore facies.

In the Wingellina deposit, the occurrence of ore minerals characterized either by complex crystal structures (e.g. smectite and certain Mn-oxy-hydroxides) or by poor structural order (e.g. Fe-oxy-hydroxides), restrict the efficiency of XRPD. In this frame, automated Scanning Electron Microscopy (automated SEM) methods, based on the chemistry and density of various mineral species, offer breakthroughs in defining the mineralogy and the metal deportments, bypassing the issues related to the presence of phases not evaluable by using solely XRPD-based approaches. In this study is demonstrated that the main benefit of using automated SEM is the possibility to detect and identify Ni-Cobearing Mn-oxy-hydroxides (lithiophorite, lithiophorite-asbolane and asbolane) and Ni-bearing clays, which can be hardly distinguished through XRPD because of their poorly crystalline structure and because of their very similar diffraction features. Automated SEM also allowed the determination of the Co deportment, which is essential to predict the optimum achievable metals recoveries.

The Santa Fe' deposit is characterized by both oxide- and phyllosilicatedominated ore zones. The oxide ore consists of Ni- and Co-bearing Fe-oxyhydroxides, while Mn-oxy-hydroxides occur as minor components. In the saprolite, the major Ni-carrying phase is chlorite. Multivariate statistical analyses conducted on the drillcore assays showed that the Ni distribution is not controlled by *in situ* weathering. This is because the highest Ni concentrations have been measured in laterite horizons where Ni-rich minerals (chlorite and goethite) are associated with reworked material. Cobalt has an atypical statistical distribution at Santa Fe' if compared with Wingellina, being correlated not only with Mn, but also with Cr. From microchemical analyses it was observed that residual spinels contains significant elevated Co contents. This feature is atypical for Ni-Co laterite deposits, where Co is normally associated with Mn in supergene oxy-hydroxides. In the Santa Fe' case, the Co concentration in spinels is related to magmatic and post-magmatic processes occurring prior tolateritization, specifically: (i) orthomagmatic enrichment of Co in chromite, due to its high affinity to spinels in alkaline melts; and (ii) trace elements (i.e. Co, Mn, Ni and Zn) redistribution during amphibolite facies metamorphism of chromite into ferritchromite. Based on the interpretation of metallurgical testworks, a fraction of total Co (up to 50%) is locked in spinels.

Chapter 1:

Introduction

1.1 The importance of Ni and Co in the modern industry

Nickel (Ni) and cobalt (Co) are key commodities in many industrial and technological applications. Nickel is widely used in alloys, in petroleum refineries, jet engines, power generation facilities etc. (USGS, 2020). In the last decade Ni alloys have increasingly been used in electronic industries for rechargeable batteries for personal computers, electric vehicles and power tools (Nickel Institute, 2010). Cobalt has been classified by the European Union as a critical raw material (Blengini et al., 2017). The leading use of Co is in the manufacture of rechargeable lithium-ion batteries, where it is fundamental to enhance their stability and to restrict corrosion (Slack et al., 2017). For this reason, Co demand is forecast to increase drastically with the manufacturing of electric vehicles (Blengini et al., 2017). Moreover, Co is widely used in the electronic (mobile devices) and aerospace (jet and gas turbines generators) industries, as well as in the pharmaceutical sector, wherein the use of radioactive cobalt-60 is critical for cancer treatments (USGS, 2020). Indonesia and Philippines represent the world's leading Ni producers (800,000 Mt and 420,000 Mt of Ni in 2019 respectively, USGS, 2020), whereas the Democratic Republic of Congo (DRC) is the main global producer of Co (100,000 Mt of Co in 2019) covering about 66% of the world's supply. The risk of a breakdown in the Co supply could not only be related to its limited resources worldwide, but also to the fact that most cobalt is a by-product of the mining, processing and recovery of more common commodities as Ni and Cu. An additional issue that could become a risk for the future Co supply chain is the child-labour ethical mining factor, as well as the high socio-political instability in DRC (Kapusta, 2006). Therefore, the targeting of new resources is critical in order to sustain the future demand of Co.

1.2 Sources of Ni and Co

The genesis of economic concentrations of Ni and Co is related to both primary (i.e. orthomagmatic and hydrothermal) and secondary (i.e. supergene) processes. Primary Ni mineralisation accounts for about 40% of the land-based global resources, whereas supergene Ni ores represent about 60% of these resources (Butt and Cluzel, 2013; Freyssinet et al., 2005; USGS, 2020). Cobalt

occurs mainly in three deposit types: (i) sediment-hosted stratiform Cu(Co) deposits (Annels and Simmonds, 1984; Hitzman et al., 2005 and references therein); (ii) orthomagmatic Ni-sulfides deposits, such as Sudbury (Canada) and Norilsk (Russia), where Co is exploited as by-product (Naldrett, 2013 and references therein); (iii) Ni-Co laterite deposits, which occur primarily in the tropical to subtropical areas (e.g. Brazil, Caribbean, Cameroon, New Caledonia, Indonesia and Philippines). Other mining districts are also located in Europe (Greece), Urals (Russia) and Australia (Freyssinet et al., 2005, and references therein). The recent decline in new discoveries of Ni-Co-bearing sulfides, has made lateritic ores the main future target for the exploration of these commodities.

1.3 Ni-Co laterite deposits

1.3.1 General features

Nickel and Co laterite deposits are regolith covers formed by chemical alteration of mafic to ultramafic parent rocks, where Ni- and Co-bearing forsteritic olivine occurs in the magmatic mineralogical assemblage (e.g. Freyssinet et al., 2005; Butt and Cluzel, 2013). The lateritization process is favoured at temperatures and rainfall rates characteristic of the tropical to subtropical areas. Under these climatic conditions, the alteration of the magmatic parent rock is triggered by the seeping downwards of acid meteoric waters, ending with the leaching of the most mobile elements (e.g. alkaline earth metals, alkali metal and Si) and the concentration of the least mobile components (e.g. transition metals). The interaction between the magmatic bedrock and meteoric waters leads to the dissolution of metastable phases (ferromagnesian minerals) and the formation of secondary minerals (oxyhydroxides and layered silicates), which at specific pH and Eh conditions can act as metals scavengers for Ni and Co as well as for other potentially valuable elements such as Sc, REE and PGEs (Golightly, 2010; Aiglsperger et al., 2016). In laterite ores, the first stage of the weathering though oxidizing meteoric waters is the hydrolysis of olivine, which in most cases represents the main source of Ni and Co during the primary ore-formation process:

As shown by Eq. 1.1, the hydrolysis of olivine leads to the formation of orebearing Fe-oxy-hydroxides and originates silicic acid, which enhances an acidification of meteoric waters in the regolith system. In well-developed laterite profiles, the acidification process leads to the formation of a vertical gradient of the pH of meteoric solutions, from acid to neutral-slightly basic, proceeding from the surface toward the deepest sections of the weathering profile. This pH variation affects the stability of secondary minerals and thus defines the development of the different units of the regolith (e.g, Golightly, 2010). In an *in-situ* laterite profile the main units from the bottom to the top are (Fig. 1.1):



Fig. 1.1: Stratigraphic column of a Ni-Co laterite profile showing the main regolith units.

- Magmatic bedrock: occurs below the weathering front and consists of magmatic minerals (i.e. ferromagnesian minerals, feldspars and Cr-Ti-oxides). It can show a variable degree of metamorphic and/or hydrothermal overprint, depending on the pre-lateritic alteration history;
- Saprolite: it lies below the Mg-discontinuity and is a clay-rich lithology, where the original texture of the parent rock is totally obliterated. It may also enclose floating blocks of partially altered protolith, where the magmatic features are still partially present (i.e. saprock);
- Mottled horizon: where present, it occurs above the Mg-discontinuity. Similar to the saprolite unit, it consists of a clay-rich horizon. However, at this level in the profile the decomposition of Mg-layered silicates due to the more acid pH of the meteoric waters promotes the formation of kaolinite and/or halloysite;
- Oxide zone: this unit lies either above or within the vertical range of fluctuation of the water table and consists of Fe- and Mn-oxy-hydroxides;
- Duricrust: in most deposits it consists of an unit rich in Fe-oxides, that are formed through the aging and dehydration of former Fe-hydroxides.

1.3.2 Classification, metallogenesis and tectonic setting

Ni-Co laterites are subdivided in three main ore types (e.g. Elias, 2002; Butt and Cluzel, 2013): (i) oxide-type; (ii) clay silicate-type; (iii) hydrous Mgsilicate-type. Oxide-type ores are characterized by the economic Ni and Co concentrations, which are enriched in Fe- and Mn-oxy-hydroxides, within the ferruginous saprolite (hereafter oxide zone), lying above the Mg-discontinuity. Oxide-dominated ore deposits, although being of low grade, commonly have the highest tonnage. The mineralogy of Fe-phases is dominated by goethite, with minor Fe-oxides. The mineralogy of Mn-oxy-hydroxides (Table 1.1) is very variable, with lithiophorite-asbolane representing the main phases, although a wide range of other species are also commonly present. With a few exceptions, these deposits occur in stable cratons (Fig. 1.2). The most significant oxide-type districts are found in Western Australia (Cawse, Ravensthorpe and Wingellina), Brazil (Santa Fe', Onça and Puma), Cuba (Moa Bay), New Caledonia (Goro) and in South Cameroon (Nkamouna) (Freyssinet et al., 2005 and references therein). The genetic process of oxide-dominated laterites is through a *direct formation* model (Fig. 1.3a to c), in which an olivine \pm pyroxene parent rock undergoes a continuous tropical weathering in a stable tectonic environment (i.e. shields and cratons). Under these conditions, the water table remains high in the weathering profile and the free flushing of the ground waters produces a complete leaching of Mg and Si and the formation of a deep regolith enriched in Ni- and Co-bearing oxy-hydroxides (Butt and Cluzel, 2013).

Clay silicate- and hydrous Mg silicate-type deposits (hereafter garnierite-type), are phyllosilicates-endowed deposits where most of the Ni is hosted in the saprolitic units at the bottom of the profiles (e.g. Butt and Cluzel, 2013). Based on the mineralogy of Ni-bearing phyllosilicates, as well as on their distribution and origin within the laterite profiles, clay silicate- and garnierite-type ores display contrasting features (Table 1.1).



Fig. 1.2: Morphoclimatic map showing the location of the main Ni-Co laterite deposits world wide (adapted from Butt and Cluzel, 2013).

The most representative examples of clay silicate-type ores are in the worldclass Ni-laterite deposits of Brazil (e.g. Niquelândia; Colin et al., 1990) and Western Australia (e.g. Murrin Murrin; Gaudin et al., 2004a, 2004b) (Fig. 1.2). In these deposits, Ni-phyllosilicates are commonly concentrated within thick plasmic horizons occurring at the base of the laterite profiles (Golightly, 2010). Clay-type deposits are commonly endowed in Ni-bearing smectites, which are 15Å 2:1 clay minerals belonging to the trioctahedral (i.e. saponite, ferrosaponite and stevenstite) and to the dioctahedral types (nontronite and montmorillonite) (e.g. Gaudin et al., 2004a, 2004b; Christidis and Mitsis, 2006; Kadir et al., 2015). With very few notable exceptions (e.g. Loma Ortega deposit, Dominican Republic; Tauler et al., 2017), the ore grades observed in Ni-bearing smectite

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are generally low, with Ni being an octahedral cation subordinate to Fe, Al and Mg (Butt and Cluzel, 2013). In addition, the economic exploitation of clay silicate-type ores depends mostly on the volumetric extent of the smectiteenriched plasmic unit and on the high smectite/gangue ratio observed in this zone of the laterite profile. Similarly to oxide deposit, clay silicate-type laterites also form in low relief areas under constant weathering rates, although the formation of significant clay silicate deposits is restricted to areas with lower leaching degrees and to profiles developing from protoliths hosting Al-bearing primary minerals as plagioclase (Golightly, 2010). However, significant oxideand clay silicate-type mineralizations can be commonly observed both in the same deposit and in the same district (e.g. Western Australia). Garnierite-type ores are mostly localized on active margins, where obducted sections of the oceanic lithosphere underwent chemical weathering during Tertiary (Freyssinet et al., 2005 and references therein). The most important mineral districts, in which garnierite ores represent the main target for Ni exploration, are New Caledonia, Indonesia and the Caribbean region (e.g. Villanova-de-Benavent et al., 2014; Cathelineau et al., 2017; Fu et al., 2018) (Fig. 1.3d). The genesis of garnierite ores follows a multistage fluid-flow dynamic process (i.e. per descensum model), during which the uplift of the peridotite nappe, coeval to regional lateritization, enhances the formation of fractures and open spaces and the seeping of Ni-saturated solutions toward the bottom of the alteration profile (Fig. 1.3d). These processes end with the formation of high-grade veins- to faults-hosted garnierite ores within a low-grade host rock (i.e. saprolite unit; Cluzel and Vigier, 2008). The first implication of the mode of occurrence of garnierite mineralizations is that, although garnierite has a Ni grade significantly higher than smectite, they also have a lower ratio between the high grade ore and the barren to low-grade saprolite host rock. Nevertheless, these characteristics are beneficial during the preliminary steps of the processing route, as they make garnierite ores amenable to physical beneficiation and concentration treatments to produce ore feed with high Ni grades (Dalvi et al., 2004). As reported by Villanova-de-Benavent et al. (2014 and references therein), garnierite is not recognized as a mineral species by the International Mineralogical Association (IMA). This term is generally used by mine geologists when referring to green, fine-grained and poorly crystallized Nibearing magnesium phyllosilicates, such as serpentine, talc, sepiolite and chlorite, often occurring as mixtures and hence not easily distinguishable between each other.



Fig. 1.3: Schematic model showing the genesis and evolution of laterite ores; a) to c) show the main processes occurring during the direct formation models, while d) shows the dynamic of the per descensum model (adapted from Butt and Cluzel, 2013).

As a consequence of these mineralogical features, the classification of garnierite-type ores is very complex and controversial. However, clay minerals ascribed to the garnierite-type are mainly non-swelling trioctahedral phyllosilicates, with the most common Mg-Ni-bearing mineral series belonging to the following four groups (Table 1.1):

i). serpentine group - lizardite-népouite and chrysotile-pecoraite series, which are 7 Å 1:1 phyllosilicates belonging to the kaolinite-serpentine group (serpentine subgroup);

ii). pyrophyllite-talc group - talc-like 10 Å 2:1 clay minerals, with two series, i.e. the talc-willemseite series, characterized by a 9.3 Å d_{001} reflection according to IMA classification, and the kerolite-pimelite series, not recognized by IMA, which comprehends the hydrated talc-like species having a ca. 10 Å basal reflection and a disordered structure;

iii). chlorite group, consisting of 14 Å 2:1:1 clay minerals, members of the clinochlore-nimite series;

iv). palygorskite-sepiolite group - sepiolite-falcondoite series, having a 12 Å basal spacing and a 2:1 structure (Villanova-de-Benavent et al., 2016 and references therein).

1.3.3 Mineral processing

The Ni mineralogy and chemistry in laterite ores are the first controlling factors defining the choice of the most effective ore treatment and metallurgical routes (e.g. Crundwell et al., 2011). Nickel and Co extraction from laterite ore can be undertaken either via pyrometallurgical or hydrometallurgical methods (Dalvi et al., 2004). In oxide-dominated deposits, the Ni and Co extraction is conducted through the High Pressure Acid Leaching (HPAL) method, under which the ore is leached in autoclaves with H₂SO₄ at 250 °C and 40 bars. Afterwards, both Ni and Co are precipitated from the solution as mixed sulfides by solvent extraction and then refined by hydrogen reduction or electrowinning (e.g. Crundwell et al., 2011). Ni-clays endowed ores (clay silicate- and garnierite-type ores) are generally more problematic, due to their smaller particle size and to their very challenging handling, crushing, screening and minero-chemical variability (Mano et al., 2019). Ni-saprolite ores are treated either via the Smelting or Caron processes. The former is applied mainly to

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garnierite ores and is conducted through three main steps: (i) dehydration of the ore via calcination at 900 °C; (ii) reduction of oxidized Fe and Ni in their metallic form; (iii) smelting in presence of carbon at 1600 °C (Dalvi et al., 2004 and references therein). During this process the composition of the ore (i.e. the SiO₂/MgO ratio) strongly controls the smelting temperature and thus the whole operative costs (Dalvi et al., 2004; Villanova-de-Benavent et al., 2014). Many laterites containing Ni-smectites (e.g. Niquelândia, Brazil) have been processed with the Caron method. The main benefit of the Caron process is that the feed can consist of a mixture of both oxide and saprolitic ores, thus rendering economic both mineralization types when they occur together in a single laterite deposit (Rhamdhani et al., 2009). The Caron process involves a reductionroasting step, during which the ore is roasted at 750 °C to produce a Ni(Co)-Fe metallic alloy. Afterwards, the reduced ore is leached with an ammoniaammonium carbonate solution: during this stage Ni and Co are selectively leached from the solid Ni (Co)-Fe alloy (Rhamdhani et al., 2009). The main issue arising from the treatment of mixed oxide and saprolitic ores via the Caron process is that while the ore recovery from the oxide component can be very high (i.e. 90%), lower Ni recoveries were systematically obtained from the clay component that prevails in the saprolite zone (i.e. up to 65%, De Graaf, 1979, 1980; Rhamdhani et al., 2009). Mano et al. (2019) explained the lower performance of the Caron process on the saprolite component with the mineralogical and chemical heterogeneity of Ni-bearing smectites. These authors observed that the lowest Ni recoveries (10%) are due to trioctahedral Ni- and Mg-rich clays, while the highest recoveries (90%) were generally detected in dioctahedral Fe-rich and relatively Ni-poor dioctahedral smectites. Mano et al. (2019) sustained that this paradoxical outcome is due to the lower Fe content in trioctahedral smectite, which does not allow an effective formation process of Ni-Fe alloys.

Table 1.1: Schematic summary of features of oxide- and phyllosilicate-dominated mineralizations with the ideal formulas (IMA accepted, excepted for minerals in Italics) of common ore-bearing clays occurring in Ni-laterite deposits (adapted from Butt and Cluzel, 2013).

Deposit type	Major mineral districts	Most common parent rocks	Way of occurrence	Group	Mineral	Ideal formula
Oxide-type	Western Australia, Cuba and Brazil	Ultramafic intrusions	Fine-grained to massive layers	Fe-oxy-hydroxides Mn-oxy-hydroxides	Goethite Hematite Lithiophorite Asbolane Romanèchite K-Birnessite Ernienickelite Jianshuite Manganite	$FeO(OH) \\ Fe_2O_3 \\ (A1,Li)MnO_2(OH)_2 \\ (Ni,Co)_{x}Mn(O,OH)_4*nH_2O \\ (Ba, H_2O)_2(Mn)_5O_{10} \\ (K,Na,Ca)_{0.5}(Mn)_2O_4*1.5H_2O \\ NiMn_3O_7*3H_2O \\ (Mg,Mn)Mn_3O_7*3H_2O \\ MnO(OH) \\ MnO(OH) \\ (Mg,Mn)Mn_3O_7*3H_2O \\ MnO(OH) \\ (Mg,Mn)Mn_3O_7*3H_2O \\ MnO(OH) \\ (Mg,Mn)Mn_3O_7*3H_2O \\ MnO(OH) \\ (Mg,Mn)Mn_3O_7*3H_2O \\ (Mg,Mn)Mn_3O_7*MM_2O \\ (Mg,Mn)M_3O_7*MM_2O \\ (Mg,Mn)M_3O_7*MM$
Clay silicate-type	Western Australia and Brazil	Mafic to ultramafic intrusions	At the base of the laterite profiles in thick plasmic horizons or as dispersed aggregates in the oxide zone	Smectite (15 Å)	Clay silicate-type montmorillonite saponite	$Na_{0.3}Fe_2^{3+}(Si,A1)_4O_{10}(OH)_{2}\cdot nH_2O$ $(Na,Ca)_{0.3}(A1,Mg)_2Si_4O_{10}(OH)_{2}\cdot nH_2O$ $(Ca,Na)_{0.3}(Mg,Fe)_3(Si,A1)_4O_{10}(OH_2)\cdot 4H_2O$
					ferrosaponite stevensite beidellite	$\begin{array}{c} Ca_{0.3}(Fe^{2*},Mg,Fe^{2*})_3(Si,A1)_4O_{10}(OH)_2\cdot 4H_2O\\ (Ca,Na)_xMg_{3\cdot y}Si_4O_{10}(OH)_2\\ Na_{0.5}Al_2(Si_{3.5}Al_{0.5})O_{10}(OH)_2\cdot n(H_2O) \end{array}$
				Serpentine (7 Å)	lizardite - népouite	Mg3Si2O5(OH)4 - Ni3Si2O5(OH)4
Garnierite-type	New Caledonia, Indonesia and Caribbean region	Ophiolite suites	As vein- to fracture hosted cements and coatings within the saprolite or in thick serpentinite sections	Pyrophyllite-Talc (9.3 Å to 10 Å)	chrysotile - pecoraite talc - willemseite <i>kerolite -</i> <i>pimelite</i>	$Mg_{3}Si_{4}O_{10}(OH)_{2}$ - $Ni_{3}Si_{4}O_{10}(OH)_{2}$
				Chlorite (14 Å)	clinochlore - nimite	$Mg_{5}Al(Si_{3},Al)O_{10}(OH)_{8} - (Ni,Mg,Al)_{6}(Si,Al)_{4}O_{10}(OH)_{8}$
				Palygorskite-Sepiolite (12 Å)	sepiolite - falcondoite	$Mg_4Si_6O_{15}(OH)_{2^*}6H_2O - Ni_4Si_6O_{15}(OH)_{2^*}6H_2O$

Aim of the study and Thesis outline

The main aim of this study was to achieve a better knowledge of the genetic processes occurring during the formation of Ni-Co laterite ores. In this context a special focus has been devoted to clarify the relationship between the characteristics of the bedrock and its alteration history, investigating the fate of Co during the lateritic process, with the dominant minerogenetic processes leading to the formation of the diverse regolith facies and with critical elements geochemistry. Moreover, as a secondary aim of this study, attention has been paid to the quantitative mineralogical evaluation of the diverse ore facies in a laterite deposit by means of conventional and unconventional analytical techniques, in order to reach a more comprehensive knowledge of the relationship between the deportment of Ni and Co and the presence of poorly crystalline phases.

In order to pursue the aims of this study, we selected a wide range of mineralized samples from the Wingellina (Western Australia) and Santa Fe' (Brazil) deposits, which are world class prospects in the pre-development stage. The general and local geological features of the selected study areas are reported in Chapter 2. Chapter 3 reports the results of a detailed XRPD and EMPA evaluation of Co-bearing Mn-oxy-hydroxides of the Wingellina deposit. The Chapter 4 concerns with lithogeochemistry (ICP-MS and ICP-ES) of Ni-Co and of High-Tech metals (REE and Sc) in the laterite occurring in the Wingellina deposit. Chapters 5 reports on a mineralogical study of the phyllosilicates-rich saprolite facies of the Wingellina by means of XRPD on the clay fraction and by EMPA aimed to assess the control of the parent rock and of the climatic regime of the formation of smectite mineralization. In Chapter 6, the clay-rich samples studied in chapter 5 have been analysed by TEM and HRTEM in order to evaluate the effectiveness of the ion milling technique on challenging regolith samples. In Chapter 7, the analytical challenges associated with the modal mineralogy appraisal of regolith ores were addressed and discussed towards the most common XRPD-Rietveld approach. Lastly, Chapter 8 reports the study on the control of the parent rock on the Co enrichment process in the Santa Fe' deposit by means on an integrated approach between multivariate statistical analysis on lithogeochemical data and the mineralogical features of the deposit. The discussion is focused on the comparison between the two investigated deposits.

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Several parts of this PhD thesis correspond to the content of the following papers published and *in press*:

- **Chapter 3:** Mineralogical association and Ni-Co deportment in the Wingellina oxide-type laterite deposit (Western Australia)

Published in "Ore Geology Reviews"

Reference: Putzolu, F., Balassone, G., Boni, M., Maczurad, M., Mondillo, N., Najorka, J., and Pirajno, F. (2018). Mineralogical association and Ni-Co deportment in the Wingellina oxide-type laterite deposit (Western Australia). Ore Geology Reviews, 97, 21-34. DOI: <u>https://doi.org/10.1016/j.oregeorev.2018.05.005</u>.

Contributions of F. Putzolu to the paper: on-site survey and samples collection, petrological and mineralogical characterization. F. Putzolu implemented the papers conceptualization, the data interpretation and carried out the writing of the first version of the manuscript, which was then reviewed and approved by co-authors.

- **Chapter 4:** Ni-Co enrichment and High-Tech metals geochemistry in the Wingellina Ni-Co oxide-type laterite deposit (Western Australia)

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Reference: Putzolu, F., Boni, M., Mondillo, N., Maczurad, M., and Pirajno, F. (2019). Ni-Co enrichment and High-Tech metals geochemistry in the Wingellina Ni-Co oxide-type laterite deposit (Western Australia). Journal of Geochemical Exploration, 196, 282-296.

DOI: <u>https://doi.org/10.1016/j.gexplo.2018.11.004</u>.

Contributions of F. Putzolu to the paper: on-site survey and samples collection. F. Putzolu implemented the papers conceptualization, and the geochemical data interpretation and carried out the writing of the first version of the manuscript, which was then reviewed and approved by co-authors.

 Chapter 5: Parent rock and climatic evolution control on the genesis of Ni-bearing clays in Ni-Co laterites: New inferences from the Wingellina deposit (Western Australia)

Published in "Ore Geology Reviews"

Reference: Putzolu, F., Abad, I., Balassone, G., Boni, M., Cappelletti, P., Graziano, S. F., Maczurad, M., Mondillo, N., Najorka, J., and Santoro, L. (2020). Parent rock and climatic evolution control on the genesis of Ni-bearing clays in Ni-Co laterites: new inferences from the Wingellina Ni-Co deposit (Western Australia). Ore Geology Reviews, 103431.

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Contributions of F. Putzolu to the paper: F. Putzolu conducted on-site survey and samples collection, the clay fraction separation process and petrological and mineralogical characterization (qualitative and quantitative XRPD, XRPD on clay aggregates and EMPA). F. Putzolu implemented the papers conceptualization, the data interpretation and carried out the writing of the first version of the manuscript, which was then reviewed and approved by co-authors.

- **Chapter 6:** Ni-bearing smectites in the Wingellina laterite deposit (Western Australia) at nanoscale: TEM-HRTEM evidences of the formation mechanisms

Published in "Applied Clay Science"

Reference: Putzolu, F., Abad, I., Balassone, G., Boni, M., and Mondillo, N. (2020). Ni-bearing smectites in the Wingellina laterite deposit (Western Australia) at nanoscale: TEM-HRTEM evidences of the formation mechanisms. Applied Clay Science, 196, 105753. DOI: https://doi.org/10.1016/j.clay.2020.105753.

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data interpretation and carried out the writing of the first version of the manuscript, which was then reviewed and approved by co-authors.

- **Chapter 7:** Quantitative mineralogical evaluation of Ni-Co laterite ores through XRPD-QPA- and automated SEM-based approaches: the Wingellina (Western Australia) case study

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- *Chapter 8:* The influence of the magmatic to post-magmatic evolution of the parent rock on the Co deportment in lateritic systems: the example of the Santa Fe' Ni-Co deposit (Brazil)

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Chapter 2:

Case studies: the Wingellina (Western Australia) and Santa Fe' (Brazil)

2.1 Regional and local geology of the Wingellina laterite deposit

2.1.1 Overview of major Australian Ni-Co laterite districts

Australia is one of the most important producers of Ni and Co of the world (USGS, 2020). Historically, most of the Australian Ni and Co industries were mainly built on the exploration and exploitation of sulfide deposits. However, the advent of hydrometallurgical technologies (e.g. HPAL) unlocked thousands of tons of Ni and Co reserves occurring in laterite deposits that were previously believed to be a too difficult challenge for ore processing and recovery (Elias, 2013). From that moment, the interest of many mineral companies shifted towards laterite deposits, thus initiating a new season for the Ni and Co exploration in the Australian continent. Nowadays, most of the Australia's nickel resources are associated with laterite deposit (about 62.1%; GSWA, 2019). Three main mineral districts can be recognized in the country:

(i) The Yilgarn Block (Western Australia) is the major Ni laterite district of the Australian continent, whereby laterites developed during the Mesozoic and Tertiary on Archean ultramafic rocks, which are part of the greenstone belts occurring in the south-eastern zone of the shield. The Yilgarn district is characterized by the occurrence of laterites of both clay silicate-type (e.g. Murrin Murrin) and of oxide-dominated-type (e.g. Cawse and Ravensthorpe). In other world-class deposits from the same Block (e.g. Bulong and Siberia), despite the Ni grades are controlled by the clays distribution, there is also a well-developed oxide ore body. In the Yilgarn Block deposits, most Co is concentrated at the transition between the clay- and oxide-dominated sections, in association with Mn oxide-rich horizons (Elias et al., 1981; Wells, 2003).

(ii) In the Eastern Australia (EA) district, the Ni laterites formed through Tertiary weathering of Alaskan-type mafic to ultramafic complexes. The major laterite mineralization of this district is the Syrston-Flemington deposit, which despite its oxide-type ore also contains a well-defined saprolite zone enriched in Ni-smectites (Chassé et al., 2016). The most significant characteristic of the Ni laterites from EA is that they are particularly enriched in Sc (up to 500 ppm),

both in the oxide and in the clay zones, associated with goethite and smectite, respectively. The outstanding Sc grades of these deposits is due the high concentration of this element in the parent rock, where it is already enriched in the Sc-bearing clinopyroxene (Chassé et al., 2016, Chassé et al., 2019).

(iii) The Musgrave Province is not widely known as an important district for the presence of laterite ore. In fact, in the past this region of the continent has been explored mainly for orthomagmatic Ni ores, which are commonly associated with a range of other commodities (i.e. Cu-Co-PGEs-V-Ti). The above ores are all associated with the huge magmatic input related to the emplacement of the mafic to ultramafic Giles Complex (Maier et al., 2015). However, during the mid-1950's, INCO Exploration discovered significant laterite sections developed from the weathering of the Giles Complex. The main findings were the Wingellina (the object of this study) and the Claude Hills Ni-Co laterite deposits, as well as the Mt Davies and Scarface exploration prospects. These assets are all part of the so-called Central Musgrave Project, which is a large operation held by Metals X Ltd and encompasses an area of about 2000 km² of prospective exploration for Ni and Co lateritic ores (Metals X Ltd, 2018).

2.1.2 Background information and regional geology

The Wingellina Ni-Co deposit (owned by Metals X Limited, hereafter "the company") is an oxide-dominated laterite. The deposit is located in the Ngaanyatjarraku Shire, close to the border between Northern Territory and Western Australia (Fig. 2.1a, b). In the 2008, the company completed a Phase 1 Feasibility Study (+ 25%) following the JORC Code (2012 Edition), defining a Mining Reserve of 168 Mt of oxide ore grading 0.98% Ni and 0.08% Co with ca a 7:3 oxide to saprolite ore ratio. In this context, the calculated grade of the saprolite ore is 0.83 wt% Ni (Metals X Limited, 2018). Further works defined in 2017 a mining production plan aimed to optimize several high-grade pit designs and to undertake additional assessments for initial smaller scale Ni-Co production scenarios. Metallurgical tests did confirm that High Pressure Acid Leaching (HPAL) is the most suitable method for the treatment of the Wingellina oxide ore type, with a leach recovery of ca. 94 % for Ni and Co and a sulphuric acid consumption rate of 300 kg/t of ore (Metals X Limited, 2018). The final metallurgical step will comprise the production of Ni-Co sulphates as feedstock for the battery industry (Metals X Limited, 2018). The Wingellina Ni-Co laterite deposit occurs within the Musgrave Province (Fig. 2.1b), which is an east-trending Proterozoic orogenic belt lying at the nexus of the Australia's three cratonic provinces (West, North, and South Australian Cratons, Fig. 2.1a) (Howard et al., 2015). The Wingellina ore-bearing laterite is derived from the weathering of the Wingellina Hill mafic to ultramafic layered intrusion (i.e. Hinckley Range Gabbro Formation), which is part of the Mesoproterozoic Warakurna Large Igneous Province (Wingate et al., 2004; Pirajno and Hoatson, 2012) and the 1085–1040 Ma Giles Event (Maier et al., 2014, 2015). These mafic to ultramafic intrusions, called Giles Complex Suite (Maier et al., 2014, 2015), were emplaced in a Paleoproterozoic basement consisting of high-grade granulite facies gneisses (i.e. Musgravian Gneisses) (Major and Conor, 1993; Camacho and Fanning, 1995; Edgoose et al., 2004). Maier et al. (2014 and 2015) classified the intrusive bodies of the Giles Suite into several types (Fig. 2.2): ultramafic intrusions (e.g. Wingellina Hills), gabbroic intrusions, anorthosite and troctolitic intrusions.



Fig. 2.1: a) Map of the Australian continent displaying the locations of Archaean cratons and Palaeo-Mesoproterozoic terrains (after Wade et al., 2006 modified). The rectangle highlights

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the position of Musgrave Province, displayed in Fig. b. b) Geology of the Musgrave Province (after Wade et al., 2006 modified) showing the location of the Wingellina Ni-Co laterite deposit.

The coeval lithologies of the Bentley Supergroup and the Tjauwata Group represent the volcanic products and subordinate rift sediments related to the magmatism of the Giles event (Sun et al., 1996). The most recent (0.63–0.53 Ga) tectonic event that shaped the Musgrave Province is the Petermann Orogeny (Camacho et al., 1997; Camacho and McDougall, 2000).



Fig. 2.2: a) Schematic model of emplacement of the Giles Complex indicating the supposed position of the ultramafic and mafic portions of the orthomagmatic system (after Maier et al.,

2014, modified; b) Simplified geological map of the Giles Complex showing the location of the Wingellina hill intrusion (after Nesbitt et al., 1970, modified).

This orogeny triggered the exhumation in sub-aerial environment of the Musgrave Province (e.g. Hoskins and Lemon, 1995; Walter et al., 1995; Hand and Sandiford, 1999; Wade et al., 2005). In this tectonic framework, the Australia's weathering history has been variable and complex, with parts of the continent (e.g. Yilgarn Craton, Musgrave Province) that have experienced a subaerial exposure since the Precambrian (Anand and Paine, 2002). According to Pillans et al. (2005), the geochronology of the Australian regolith covers suggests that the whole Phanerozoic of the Australian continent has been characterized by several stages of warm and humid climatic conditions, which enhanced the intensive weathering and alteration of the exposed rocks. The Quaternary (Late Miocene or Pliocene) shift to more arid to semi-arid conditions played an important control on the evolution experienced by Australia's regolith (Tardy and Roquin, 1998; Anand and Paine, 2002). However, in the specific case of the Musgrave Province, it must be highlighted that the age of the weathering event associated with the Wingellina lateritization process still remains undefined.

2.1.3 The mafic to ultramafic-layered-intrusion of the Wingellina Hills

The Wingellina Hills mafic to ultramafic intrusion (Fig. 2.3), a member of the Hinckley Range Gabbro, is the parent rock of the Wingellina laterite deposit. The intrusive body has a length of about 12 km along strike and a width of 3 km, and comprises a southeast-trending and southwest-dipping mafic–ultramafic set of ridges (Fig. 2.4). The magmatic sequence has a thickness of 2.5 km (not considering the tectonic thickening), and is composed of several cyclic units (Fig. 2.3). These consist of a basal pegmatoid orthopyroxenite, followed by a clinopyroxenite, a peridotite (olivine-espinel cumulate), a wehrlite and gabbronorite (Ballhaus and Glikson, 1989). The magmatic rocks outcropping in the deposit area are weathered gabbro/gabbronorite units, with subordinate pyroxenite lenses (Fig. 2.4). The Wingellina Hills intrusion is deformed by south-east trending shear zones that produced intensively sheared mylonites, and by east-west sinistral brittle cross-structures, which offset the layered intrusion mainly in its central part.

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2.1.4 The Wingellina laterite profile

The Wingellina lateritic ore body is located in elongated valleys parallel to the local deformation trend (Figs. 2.4, 2.5.a and b), meaning that the lateritization of the magmatic suite has been likely controlled by the existence of former structural elements that locally enhanced the weathering and drainage degrees (Putzolu et al., 2018). Based on the surface geology, the Wingellina deposit can be subdivided in three main zones: northern, central and southern (Fig. 2.4).



Fig. 2.3: Stratigraphic column showing the general features of the mafic to ultramafic lithologies occurring in the Wingellina Hill intrusion (after Ballhaus and Glikson, 1989).

It must be observed that several "exclusion" zones occur throughout the tenement, which consist of archaeological and ethnographic sites that the Ngaanyatjarra Council and the Traditional Owners heritage survey judged of importance for the local aboriginal communities. These zones cannot, therefore, be considered for expanding further mineral exploration in the Wingellina mineralized area.



Fig. 2.4: Geological map of the Wingellina Ni-Co laterite deposit, including the location of the studied drillcores (after Putzolu et al., 2018, modified).

The central zone of the deposit is occupied by a massive silica- and magnesiterich horizon, which the project geologists call "jasperoid laterite". The "jasperoid" facies developed directly from the weathering of a variably serpentinized dunite body, which at depth coincides with the main magmatic unit occurring in the central sector of the tenure. The jasperoid laterite is locally characterized by a sheared texture (Fig. 2.5c), whose stretching lineation is parallel to the deformative trend measured on the outcropping mafic units, meaning that such lineation witnesses the structures occurring in the former dunite body. The northern and southern zones of the deposit have very similar characteristics resembling that of an oxide-dominated laterite. In these zones

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the orebody occurring in the valleys is capped either by a massive Fe-oxyhydroxide-rich gossan (i.e. ferricrete, Fig. 2.5d) or by a silica and/ or nodular carbonate-rich duricrust (i.e. silcrete-calcrete, Fig. 2.5e). To better assess the areal extent and the vertical-lateral variation of the oxide zone, during the very early stage of exploration the INCO Exploration dug several trenches that intercepted the uppermost section of the ore body (i.e. duricrust and upper oxide zone, Fig. 2.5f).



Fig. 2.5: Wingellina surface geology: a) and b) Panoramic views of the southern zone of the deposit showing the spatial relationship between the oxide ore body, the magmatic ridges and ferricrete cap; c) Sheared jasperoid laterite; d) Massive ferricrete enriched in Fe-oxides (bluish to black) and Fe-hydroxides (yellow to orange); e) Calcrete-silcrete enclosing nodular

magnesite; f) Lateral view of an exploration trench intercepting the upper oxide ore body; g) Ochre oxide ore coated by Mn-(hydr) oxides; h) Ni-clays + carbonates vein cutting the oxide ore.

The oxide zone is enriched in red-brown Fe-oxy-hydroxides, locally coated by Mn-oxy- hydroxides (Fig. 2.5g and h). The latest represent the main target for Co as they deport most of the amount of this element contained in the oxide zone (Putzolu et al., 2018, 2019). Moreover, despite the oxide zone is dominated by oxy-hydroxides, both drillcore logging and trench survey revealed that also pale green and potentially Ni-enriched phyllosilicates are disseminated throughout the oxide ore (Fig. 2.5h). The saprolite zone of the deposit has never been intercepted by the trenches, but is only visible in the cores drilled by the company to assess the vertical extent of the weathering front (Fig. 2.6). Based on the drillcore analysis conducted in the frame of this study, the typical Wingellina lateritic is on average made of (Fig. 2.6):

(i). The duricust is 0.5 m to 2 m thick and contains abundant nodular to massive carbonates (Fig. 2.6a). It has a detrital texture and a high degree of cementation, likely associated with silicification and calcification processes;

(ii). The oxide horizon is generally red-brown and fine-grained, and contains Mn-oxy-hydroxides both disseminated in the matrix, as well as filling/coating cracks and fractures (Fig. 2.6b). The oxide unit is well developed and its thickness in the drill holes selected for this study varies between 20 m and 100 m. At the base of the oxide zone, a mottled kaolinite-rich horizon (Fig. 2.6c) is also locally observed;

(iii). The saprolite is a massive, greenish to brownish, clayey unit with occasional joints that may contain carbonates and secondary silica (Fig. 2.6d). The saprolite is poorly developed, with an average thickness of 17 m in the studied drill holes.



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Fig. 2.6: Stratigraphic column of the Wingellina laterite profile and aspect of samples representative of the observed lithologies.

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2.2 Regional and local geology of the Santa Fe' laterite deposit

2.2.1 Overview of major Brazilian Ni-Co laterite districts

Like the Australia's case, Brazil is one of the global leading producers of Ni, with most of the Ni production based on laterite ores. The Brazilian Ni reserves consist of 11,000,000 t, which correspond approximately to 12% of the total worldwide reserves (USGS, 2020). However, unlike Australian ores, the Co (and Sc) exploration and exploitation from laterite ores in Brazil have never been significant, making laterite projects from Brazil less valuable and more sensitive to marked fluctuations. The main mineral districts in the country are (Golighlty, 2010):

(i) The Jacupiranga district (São Paulo state) occurs in the southern part of the country, where Ni-laterite ores are developed from the weathering of the ultramafic portions of the Early Cretaceous Jacupiranga Alkaline Igneous Complex (Marker et al., 1991). In this district, laterite ores consist in allochthonous oxide-dominated ores, mixed with serpentine- and chlorite-bearing saprolitic units (Marker et al., 1991);

(ii) The Goiás district (State of Goiás) is host of the major Ni-laterite deposits of the country. The Niquelândia and Barro Alto deposits, which are developed from Precambrian layered mafic–ultramafic intrusions, are the most relevant deposit of the Goiás region. Although in this district both oxide- and saprolite-dominated regolith zones are recognized, the most significant Ni concentrations are observed in association with the smectite-rich layers, making the Niquelândia and Barro Alto deposits the most significant case studies for the clay-silicate laterite type (e.g. Colin et al., 1990). In addition, in this region laterite ores developed also from ultramafic alkaline complexes. These deposits (e.g. Santa Fe'), were studied in this thesis and thus their geology will be further discussed later in this chapter;

(iii) The Amazon district, occurring in the northern zone of the country, is home of several laterites deposits (e.g. Vermelho, Onça-Puma, Jacaré and Araguaia deposits), which are developed from serpentinized peridotites intercalated with pyroxenite lenses. These deposits belong to the oxide-type and show several common features, such as a pervasive silicification on top of the profiles and lack of a significant phyllosilicate-bearing mineralization (de Oliveira et al., 1992);

(iv) In the Piaui district Ni-laterite profiles lying above Neoproterozoic layered mafic-ultramafic complex, in which the main protolith consists of a serpentinized dunite. In this region, laterite ores comprehend both oxide- and saprolite-dominated ores. Moreover, an intense silicification is observed throughout the weathering profiles, which were likely formed during the on-set of the recent arid climate nowadays present in this area (de Oliveira et al., 1992);

2.2.2 Background information and regional geology

The Santa Fe' Ni-Co laterite deposit (property of Companhia Niquel Santa Fe' Ltda., held 75% by Mineradora INVI Ltda.) is one of the largest unexploited deposits of the South Goiás alkaline Province (GAP, Brod et al., 2005), with an indicated resource of 35.7 Mt, grading 1.14% Ni and 0.083% Co and inferred resources of 104.3 Mt, grading 1.03% Ni and 0.054% Co (Dreisinger et al., 2008). This deposit was first discovered during in the 1970's and undergone an extensive exploration and drilling campaign during 2000. The Santa Fe' Ni-Co laterite deposit originated from the weathering of the Santa Fe' ultramafic massif (Fig. 2.7a, b). Mafic to ultramafic complexes crop out throughout the Brazilian shield and represent common exploration targets for both hypogene and supergene Ni-ores. The Goiás state in Central Brazil is home to Niresources associated with two types of ultramafic complexes, which differ in emplacement ages and petrological characteristics (de Oliveira et al., 1992 and references therein). The oldest ultramafic massif is the Tonian Goiás Stratiform Complex (TGSC), which is part of the Goiás Massif. The TGSC is located in the northeastern sector of the Goiás state and is considered one of the biggest mafic to ultramafic complexes worldwide. The emplacement of the TGSC is believed to be Mesoproterozoic to Neoproterozoic in age (770-800 Ma, Pimentel et al., 2000; Giovanardi et al., 2017), although its geodynamic setting is still a matter of debate. Many authors (e.g. Pimentel et al., 2004, 2006; Giovanardi et al., 2017) suggested that continental rift and back-arc extension in continental crust settings are the most appropriate geodynamic scenarios for the TGSC emplacement. The TGSC magmatic sequence consists of layered mafic to ultramafic units, such as norites, gabbros, peridotites, pyroxenites and

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anorthosites. The mafic basal zone hosts elevated Cu and Ni sulfide concentrations, whereas chromite pods occur in the ultramafic zone of TGSC (de Oliveira et al., 1992). Lateritic weathering of the Proterozoic massifs has produced the world class Niquelândia and Barro Alto Ni deposits (Colin et al., 1990; de Oliveira et al., 1992). The youngest ultramafic massif is the Late Cretaceous (86.7 Ma) South Goiás Alkaline Province (GAP; Barbour, 1978; Sonoki and Garda, 1988; de Oliveira and Trescases, 1992), which hosts the Santa Fe' deposit. The GAP lithologies are located in the southwestern sector of the Goiás state, surrounded by the Paleozoic to Cretaceous Paraná Basin (Fig. 2.7a).



Fig. 2.7: a) Geological map of the south Goiás region showing the location of Goiás Alkaline Province (modified after Lacerda et al., 2000); b) Simplified geological map of the Santa Fe' ultramafic massif (modified after Golightly, 2010) with the drill hole grid. The drill holes used in this work are shown in colours: red circles indicate the location of the drillcores used for the geochemical survey, while the dark green circles show the location of the drillcores sampled for the mineralogical study.

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The alkaline ultramafic massif consists of scattered and relatively small plutons, which intruded into the Precambrian basement of the Brazilian belt (Valeriano et al., 2008). Almeida (1967 and 1983) proposed that GAP occurred during multiple alkaline magmatic events related to the opening of the Southern Atlantic Ocean. In contrast, other authors (Gibson et al., 1995; Van Decar et al., 1995) suggested that alkaline magmatism in the Goiàs region could have been due to a mantle plume impacting the Brazilian basement. The GAP is characterized by significant spatial changes in the dominant magmatic and volcanic lithologies: the plutonic alkaline mafic to ultramafic complexes are mainly located in the northern zone, whereas the subvolcanic bodies and their volcanic products are dominant in the central and southern zones, respectively (Brod et al., 2005 and references therein). The subvolcanic bodies are mainly kamafugites, whereas the volcanic products consist of a kamafugite-carbonatite association. The Santa Fe' alkaline ultramafic massif is one of the plutonic bodies belonging to the GAP and has a sub-circular to ellipsoidal shape, with the ultramafic units (i.e. serpentinized dunite, peridotite and pyroxenite) in the center of the intrusion and the more differentiated mafic to intermediate products (i.e. alkali gabbros and syenites) at its border. In a few localities, as in Santa Fe', peralkaline and ultrapotassic subvolcanic tabular bodies, such as lamprophyre and phonolite dikes, crosscut the main pluton (Barbour et al., 1979; Brod et al., 2005). Supergene alteration of the Brazilian ultramafic massifs started during the Eocene to Oligocene and was coincident with the onset of the Sul-Americano geomorphological cycle (Braun, 1971). During this cycle, the main alteration dynamics were: silicification under arid to semi-arid conditions and lateritization of the ultramafic bodies during warm and humid periods (de Oliveira et al., 1992). During Miocene-Pliocene, the onset of the Velhas geomorphological cycle led to the dismantling of the Sul-Americano surface and partial reworking and sedimentation of the ancient regolith profiles in the lowlands. Silicified horizons protected the profiles from erosion during the Velhas cycle (de Oliveira et al., 1992 and reference therein). Weathering continues today in the majority of the lateritic districts, with the exception of the São João do Piauì, where the current climatic conditions are arid to semiarid, and mechanical erosion dominates over chemical weathering (de Oliveira et al., 1992).

2.2.3 Local geology and laterite profile

The studied Ni-Co laterite lies upon the ultramafic massif of Santa Fe' (Fig. 2.7b), which consists of a sub-circular pluton with an area of about 38 km². The intrusive body comprises a serpentinized dunite core surrounded by peridotite, clinopyroxenite and minor alkaline gabbro (Barbour, 1979; Dreisinger et al., 2008; Golightly, 2010). The laterite cover is mainly located in the flat lying lowlands (Fig. 2.8), which correspond to the Velhas surface. The remnants of this surface, developed during the Sul-Americano cycle, are still visible and form topographic highs capped by silcrete. De Oliveira et al. (1992) first described the Santa Fe' laterite profile as composed of four main horizons, and observed that despite the highest Ni grades being associated with ferruginous saprolite (up to 1.65 wt% Ni), the better-developed and largest ore zone corresponds to the coarse saprolite (minimum Ni content 1.25 wt% NiO).



Fig. 2.8: Schematic cross-section of the Santa Fe' massif (Machado et al., under review) and stratigraphic column of laterite profile.

For our study the chemistry and features of the regolith have been analysed in 613 drill holes and in a number of pits and open cuts, leading to the recognition of eight regolith units within the laterite profile and of three main lithologies in the ultramafic bedrock. The ultramafic bedrock consists of: (i) serpentinized and locally oxidized dunite (lithological code = U1); (ii) peridotite (lithological code = U2); (iii) pyroxenite (lithological code = U3). The laterite profile is

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displayed schematically in Figure 2.8. The thickness of each unit represents the median value taken from the drill holes. The preliminary step in classifying the regolith facies was based on geochemistry, initially defining the oxide- and phyllosilicate-dominated units of the deposit using Mg, recognizing the Mg-discontinuity, i.e. the geochemical surface at which Mg-phyllosilicates decomposed in the laterite profile (Freyssinet et al., 2005; Butt and Cluzel, 2013). Further discrimination of regolith units was based on macroscopic features, aimed at recognizing deposit facies affected by mechanical reworking. The laterite profile demonstrates three distinct zones, further subdivided into seven units from bottom to top:

The lowermost zone preserving the original structures and texture of the magmatic parent rock comprises: (i) Saprock (lithological code = R8): a greenish rock with silica-filled fractures, occurring in all drillcores. Its median thickness is 4 m, measured in all drill holes regardless they reached bedrock or not. (ii) Green saprolite horizon (lithological code = R7, median thickness = 3 m): this unit is ubiquitous and consists of a brownish to greenish clayey saprolite preserving the original structure of the parent rock. The textures and primary minerals are partly replaced by fine-grained phyllosilicates and oxides.

The ferruginous zones of the profile have been subdivided in two horizons: (iii) ferruginous saprolite (lithological code = R6, median thickness = 1.2 m): this rock is only present in about 50 % of drill holes; and (iv) ochre saprolite (lithological code = R5, median thickness = 1 m), which occurs only in about 20 % of the drill holes and shows the highest Ni grades (mean. Ni = 1.44 wt%). The R5 unit marks the transition between saprolite and the ferruginous zones *sensu lato*. In the ochre saprolite, the original rock features are completely destroyed.

The uppermost ferruginous zones are characterized by reddish hematite-rich layers, subdivided into further three units: (v) a lowermost transition zone (lithological code = R3, median thickness = 0.8 m), comprising a fine-grained and reddish horizon; (vi) an overlying inducated ferruginous lateritic crust (lithological code = R2, median thickness = 1.1 m), which has a pisolitic texture with local coatings of Mn-oxy-hydroxides. This unit has been observed in only about 10 % of the drill holes and show the highest Co grades (mean. Co = 0.12

wt%); (vii) an uppermost pisolitic topsoil layer (lithological code = R1, median thickness = 3 m) that covers the whole project area. It has a granular texture composed of loose ferruginous pisolites and oolites in a silty to clayey matrix. Another common lithology is silcrete (lithological code = R4), which consists of an indurated chalcedony-rich layer sporadically occurring on hilltops. The silcrete also occurs as more irregular, discontinuous and thinner intervals across the regolith units.

Chapter 3:

Mineralogical association and Ni-Co deportment in the Wingellina oxide-type laterite deposit (Western Australia)

3.1 Introduction

This part of the study is a preliminary investigation of the ore assemblage in the oxide zone of the Wingellina deposit by mean of XRPD, optical microscopy, SEM-EDS and EMPA. The main aim is to provide insights into the mineralogy, texture and chemistry of complex and poorly studied Mn-oxy-hydroxides and to assess their role in controlling Ni and Co deportment. Moreover, the obtained results will be also discussed in the framework of the potential implications for the ore processing.

3.2 Sampling strategy and analytical methods

Mineralogical and petrographic analyses have been performed on twelve samples of the oxide horizon, collected from three mineralized cores (WPDD0019, WPDD0012 and WPRC0576; Fig. 3.1). The selected holes were drilled by Metals X Ltd. in 2007 in high-grade zones of the laterite s.s.. Major minerals were identified through X-ray powder diffraction (XRPD) analyses, carried out with a Panalytical X'Pert PRO MPD diffractometer equipped with an X'celerator PSD 2.1° detector at the Natural History Museum (London, UK). The instrument was operated using cobalt Ka radiation at 40 kV, and 40 mA° with an Fe filter and a 1/4° divergence slit. XRPD patterns were collected between an incident angle of 5 and $100^{\circ} 2\theta$ at a step size of $0.02^{\circ} 2\theta$. The run time per step was 75 s. The analyses were interpreted with the "X powder" software using the PDF2.DAT database of the 'The International Centre for Diffraction Data (ICDD)'. Mineralogical and textural analyses were carried out on standard polished thin sections using transmitted and reflected light Optical Microscopy (OM) and Scanning Electron Microscopy equipped with Energy Dispersive X-ray Spectroscopy (SEM-EDS). Scanning Electron Microscopy analyses were carried out at the Dipartimento di Scienze della Terra, dell'Ambiente e delle Risorse (DiSTAR), University of Naples "Federico II" (Italy), using a Jeol JSM 5310 instrument. Energy Dispersive X-ray

Spectroscopy microanalyses were obtained by the INCA system (Oxford Instruments).

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Fig. 3.1: Stratigraphic columns of the Wingellina laterite based on three drill holes: a) Drill hole WPDD0019. b) Drill hole WPDD0012. c) Drill hole WPRC0576.

Electron probe microanalyses (EPMA) were performed on two representative thin sections at the Istituto di Geologia Ambientale e Geoingegneria (CNR-IGAG, Rome), using a Cameca SX50 Electron Microprobe Analyser with five Wavelength Dispersive Spectrometry (WDS) Bragg spectrometers. The analytical conditions were a current of 15.1 nA, an accelerating voltage of 15 kV and a 1 μ m beam diameter. The instrument calibration was performed using natural and synthetic reference materials: zircon (Zr, PET, L α), orthoclase (K, PET, K α), jadeite (Na, PET, K α), V₂O₃ (V, PET, K α), metallic chromium (Cr, PET, K α), periclase (Mg, TAP, K α), rutile (Ti, PET, K α), wollastonite (Si, TAP, K α), corundum (Al, TAP, K α), wollastonite (Ca, PET, K α), celestine (Sr, PET, K α), barite (Ba, PET, L α), metallic cobalt (Co, LIF, K α), metallic nickel (Ni, LIF, K α), rhodonite (Mn, LIF, K α) and magnetite (Fe, LIF, K α).

3.3 Results

3.3.1 Mineralogy and petrography of the oxide zone

According to the XRPD analyses (Table 3.1; XRPD patterns of representative samples W19527, W19529, W19532 and W19450 from drill hole WPRC0576, are shown in Fig. 3.2), the potentially ore-bearing phases of the oxide zone consist of Fe- and Mn-oxy-hydroxides and minor Mg-phyllosilicates. Goethite is the main Fe-oxy-hydroxides, and lithiophorite-asbolane intermediate is the main Mn-bearing phase. Lithiophorite and asbolane have similar crystal structures and are characterized by a wide overlap of their XRPD patterns; for this reason, they can be easily misidentified (Burlet and Vanbrabant, 2015). However, some of the samples rich in Mn-oxy-hydroxides show a decoupling of the peaks at 4.70 Å and 4.84 Å (Fig. 3.2a and f), thus suggesting the presence of both lithiophorite and asbolane. The minor reflection at 6.84 Å (Fig. 3.2c) should be probably assigned to ernienickelite. The analyses also indicate the presence of two types of Mg-phyllosilicates with variably strong reflections at 15.25 Å and at 7.15 to 3.57 Å. The 15.25 Å peak corresponds to the d_{001} reflection of the smectite group clays, whereas the reflections between 7.15 Å and 3.57 Å highlight the occurrence of kaolinite-serpentine phases and of the chlorite group minerals including lizardite (7.15 Å), kaolinite (7.14 Å and 3.56 Å) and chlorite (7.25 Å, 4.77 Å and 3.57 Å; Fig. 3.2d–e). Other important constituents of the oxide are gibbsite, quartz, dolomite and spinel. The texture of the oxide varies from a pseudo-layering of both Fe and Mn phases to a spheroidal one (Fig. 3.3a-c). In some cases, detrital clasts of Fe-oxy-hydroxides are embedded in a kaolinite matrix (Fig. 3.3d and e). Lithophorite-asbolane intermediates occur as skeletal, poorly crystalline masses that sometimes replace birnessite, manganite, and other Mn phases (Fig. 3.3f and g). Ernienickelite occurs both as irregular crusts (Fig. 3.3b) and as radial "needles" replacing colloform jianshuiite (Fig. 3.3h). Two generations of romanèchite (romanèchite I and romanechite II) have been observed in one of the samples. Romanèchite I occurs as detrital clasts, cemented by encrustations of romanèchite II (Fig. 3.3i). The Mg-phyllosilicates occur as minor phases in the oxide zone and form fine-grained coatings on spheroidal Fe-oxy-hydroxides (Fig. 3.3c). Several detrital minerals including monazite, zircon, hematite, and picotite were also detected in the oxide (Fig. 3.3e). The observed picotite – a Mg and Cr-bearing variety of hercynite - is partially weathered (Fig. 3.3c).



Fig. 3.2: X-ray Powder Diffraction patterns of representative oxide samples from drillhole WPRC0576: a) Sample W19527; b) Sample W91529; c) Sample W19532; d) Sample W19540. In rectangles e) and f) are displayed the diagnostic reflections of kaolinite-serpentine/chlorite and Mn-oxy-hydroxides respectively. *=Ni and Co assays (by courtesy of Metals X Ltd).

3.3.2 Ore mineral chemistry

In Table 3.2 are summarized the average chemical compositions and the average structural formulae of the ore-bearing oxy-hydroxides, whereas selected EDS and WDS microanalyses are listed in Tables 3.3 to 3.5. Goethite has average NiO and CoO content of 1.40 and 0.86 wt%, respectively (apfu Ni and Co: 0.02 and 0.01 respectively). Goethite displays a marked deficiency in Fe (average FeO_t value = 54.99 wt%), which is probably due to substitutions of Mn, Cr and Al for Fe in the crystal lattice. Goethite commonly shows traces of SiO₂, which could be related to the occurrence of secondary silica intergrowths. Hematite has lower NiO and CoO enrichment (0.64 and 0.68 wt%, 0.01 and 0.01 apfu, respectively), compared to goethite. Both goethite and hematite contain variable amounts of Cr₂O₃, ranging from 0 to 4.37 wt% (average Cr₂O₃ = 0.88 wt%). In general, the Cr-bearing Fe-oxy-hydroxides are associated with detrital picotite.



Fig. 3.3: OP (a) and BSE (b–i) photomicrographs showing the oxide textures: a) Reflected light (crossed polar) showing a goethite (Ght) encrustation, which grows upon pseudomophic Mn-oxy-hydroxides (MnOH). b) Irregular encrustations of ernienickelite (Ern) and goethite in a kaolinite (Kln) matrix. c) Spheroidal goethite associated a fine-grained smectite (Smc) coating and detrital spinel (Spn). d) Matrix-supported oxide, with angular to sub-angular goethite. e) Detrital clasts of monazite (Mnz), Al-goethite (Al-Ght), zircon (Zrc) and hematite (Hmt) in a kaolinite matrix. f) Cryptocrystalline lithiophorite-asbolane replacing birnessite. g) Cryptocrystalline lithiophorite-asbolane replacing manganite (Mng). h) Colloform jianshuiite

(Jns) replaced by radial "flakes" of ernienickelite. i) Sub-angular romanèchite I (Rmn I) clasts cemented by romanèchite II (Rmn II) encrustations.

Lithiophorite-asbolane has the highest NiO and CoO values, ranging between 3.96 and 19.88 wt% NiO (0.01-0.51 apfu) and 0 and 15.68 wt % CoO (0.00-0.36 apfu). The lithium content in the lithiophorite was not evaluated, because the low energy of the characteristic radiation of this element did not allow its detection by the SEM-EDS and EMPA analyses used in this study. The concentrations of Al₂O₃, MnO, and FeOt in lithiophorite-asbolane vary between 1.58 and 22.77 wt% Al₂O₃ (0.04–0.88 apfu), 17.16–48.39 wt% MnO (0.38– 1.11 apfu) and 0.01–10.41 wt% FeOt (0–0.39 apfu), in a few cases, there are also traces of MgO (0-4.80 wt%, 0-0.23 apfu). The average structural formula for the lithiophorite is $(Al_{0.45}, Ni_{0.24}, Co_{0.12}^{3+})(Mn_{0.69}^{4+}, Fe_{0.15}^{3+}, Mg^{0.11})O_2(OH)_2$. In the Co-Ni-Al ternary system (Fig. 3.4), the chemical composition of the Wingellina lithiophorite plots within an intermediate field between the stoichiometric lithiophorite and the Ni- and Co-asbolanes, with a marked Aldepletion and a high Ni and Co enrichment. Based on their chemical composition, these "lithiophorite-asbolane" intermediates can be subdivided into four types. Type I has a marked enrichment in both NiO and CoO, and a moderate Al₂O₃ depletion (average values 10.36, 8.48 and 8.85 wt% respectively). Type II lithiophorite-asbolane has a lower Al₂O₃ and CoO content (2.22 and 2.55 wt% respectively) and a significant enrichment in NiO (16.35 wt% Ni), and plots within the Ni-rich asbolane field. Type III lithiophorite-asbolane intermediate has the highest Al₂O₃ content, a significant Ni enrichment (average $Al_2O_3 = 18.96$ wt% and average NiO = 12.32 wt%), and a minor Co content (average CoO = 0.35 wt%). Type IV has the highest variation in Al₂O₃ content (from 2.31 to 19.31 wt%), and a marked Nienrichment (NiO average value = 9.37 wt%) relative to Co (CoO average value = 3.19 wt%). The chemical variation of the lithiophorite-asbolane intermediates strongly affects the Co/Ni ratio, which is generally higher in Type I (average Co/Ni ratio of 0.85), with respect to that of Types II, III and IV (average Co/Ni ratio of 0.17, 0.03 and 0.34 respectively). The Co-Ni-Al ternary diagram also shows the compositions of lithiophorite-asbolane intermediates from oxide-type laterite deposits in Moa Bay, Cuba (Roqué-Rosell et al., 2010) and Nkamouna, southeast Cameroon (Lambiv Dzemua et al., 2013) and from the hydrous Mgsilicate lateritic ore in New Caledonia (Manceau et al., 1987). In general, the lithiophorite-asbolane intermediates detected in Wingellina are quite different from those of the Nkamouna and New Caledonia ores. On the contrary, the lithiophorite-asbolane intermediates from Moa Bay have a composition similar to that of Types I, III and IV lithiophorite- asbolane intermediates from Wingellina. The two romanèchite generations (Fig. 3.3i) also display remarkable differences in their chemistry. Romanèchite I has a higher BaO content (BaO average value = 7.64 wt%) and a limited Ni and Co enrichment (NiO and CoO average values = 1.21 and 0.72 wt%, respectively), whereas romanèchite II has less BaO (average value = 2.68 wt%) and higher Ni and Co contents (NiO and CoO average values = 2.90 and 1.48 wt% respectively).



Fig. 3.4: Co-Ni-Al ternary plot (cationic composition wt%) displaying the mineral chemistry of the lithiophorite-asbolane intermediates from Wingellina and comparing their composition to those from Moa Bay, Cuba (Roqué-Rosell et al., 2010); Nkamouna, SE Cameroon (Lambiv Dzemua et al., 2013); New Caledonia (Manceau et al., 1987).

The negative correlations observed in the Ni vs. Ba and Co vs. Ba binary plots (Fig. 3.5a and b) support, despite the scattering of data, the chemical variability of the two romanechite generations. Traces of Fe and Al are contained in both romanechite generations, and their amounts slightly increase from generation I

to II (FeO_t average values of 4.54 and 5.80 wt% respectively; Al_2O_3 average values of 0.83 and 1.38 wt% respectively).



Fig. 3.5: Comparison between the BaO and the NiO (a) and CoO (b) contents (apfu) of romanèchite.

The average structural formulae of romanèchite I and II are (Ba_{0.30},Na_{0.05}, K_{0.04}) (Mn_{3.99}⁴⁺,Fe_{0.35}³⁺,Mg_{0.26},Si_{0.17},Al_{0.14},Ni_{0.10},Co_{0.05}³⁺)O₁₀ and (Ba_{0.11},Na_{0.10}, K_{0.06}) (Mn_{3.81}⁴⁺,Fe_{0.45}³⁺,Mg_{0.42},Al_{0.24},Ni_{0.23},Si_{0.12},Co_{0.11}³⁺)O₁₀, respectively. K-bearing birnessite has a moderate Ni- and Co-enrichment (average values of 1.67 and 0.42 wt%, respectively), and displays a slight depletion in Mn, Na and Ca. Its formula is: $(K_{0,18}, Na_{0.04}, Ca_{0.01})(Mn_{1.85}^{4+}, Ni_{0.06}, Mg_{0.02}, Mg_{0.02})$ average structural $Co_{0.01}^{3+}$) O₄. The composition of ernienickelite-like phases is intermediate between the Mg- and Ni-rich end members (jianshuiite-ernienickelite) of the isomorphic solid solution (Fig. 3.6). In the studied samples, the ernienikelitejianshuiite intermediates are moderately enriched in Ni and Co (average NiO value = 4.98 wt%) and strongly depleted in Mn relative to the common compositions (Jambor and Grew, 1994; Jambor et al., 1995; Gorshkov et al., 1992; Grice et al., 1994; Yan et al., 1992). In addition, these intermediate phases display an average CoO content of 1.81 wt%. The calculated average structural formula for the ernienickelite-jianshuiite intermediate phases is: $(Mg_{0.34}, Ni_{0.30}, Co_{0.10}, Na_{0.04}, Ca_{0.03})(Mn_{2.75}^{4+}, Al_{0.25}, Fe_{0.12}^{3+})O_7$. In the Mg vs. Ni (apfu) binary plot (Fig. 3.6), the composition measured with this study and those of nominal ernienickelite and jianshuiite from other deposits are reported. It is possible to observe that the ernienickelite-jianshuiite phases do not occur at Wingellina as pure "end-members", but have an intermediate chemistry with a general Mg-enrichment relative to Ni. Lastly, manganite displays the lowest Ni and Co contents (NiO and CoO average values of 1.43 and 0.61 wt% respectively), and has an average structural formula of $(Mn_{0.91}^{4+}, Ni_{0.02}, Co_{0.01}^{3+})O(OH)$.



Fig. 3.6: Mg (apfu) vs. Ni (apfu) binary plot showing the compositional variation of the ernienickelite-jianshuiite "solid solutions" identified at Wingellina. The jianshuiite and ernienickelite fields have been drawn of the basis of their composition taken from the International Mineralogical Association (IMA) database.

3.4 Discussion

3.4.1 Ni-Co mineralogical association

The XRDP, SEM-EDS and EMPA analyses have shown the complex mineralogy and chemistry of the Wingellina limonitic ore. Manganese and Feoxy-hydroxides are the main ore minerals hosting both Ni and Co. The strong chemical affinity of Co to Mn-oxy-hydroxides has already been examined by many authors (Burns, 1976; Kay et al., 2001; Manceau et al., 1992; McKenzie, 1989), who argued about the capability of these minerals to retain Co and other trace metals because of their large surface area. Burns (1976) proposed that hydrated Co²⁺ ions are adsorbed on the surface of Mn-oxy-hydroxides within Mn⁴⁺ vacancies, whereas the cobalt fixation is enhanced by its oxidation in the trivalent state as Co³⁺ ions. At Wingellina, the main Mn-oxy-hydroxide is the lithiophorite-asbolane intermediate. This mineral has a high degree of chemical variability, which significantly affects its Ni and Co enrichment and thus the Co/Ni ratio. The formation of the lithiophorite-asbolane intermediate, as well as its enrichment in metals, has been associated with the replacement of Al by Ni and Co in the gibbsite-like octahedral sites of the lithiophorite, which consequently triggers the development of an asbolane-type layer when Al is entirely replaced (Ostwald, 1984). This model implies the formation of a stacked-layers structure with intermediate characteristics comprised between the lithiophorite and the asbolane end-members. Similarly, Roberts et al. (1999) inferred that in presence of Al and at a pH above 6, Ni is rapidly adsorbed by lithiophorite due to the development of Al-Ni precipitates in the form of gibbsite-like layers. In contrast, in an Al-free environment and at neutral pH Ni would be adsorbed in the Mn-oxide type layer, likely on Mn vacancies (Peacock, 2009; Roqué-Rosell et al., 2010). The chemistry of the lithiophoriteasbolane intermediates in the Wingellina oxide suggests that the Ni and Co enrichment in the Al-rich Type I, III and IV intermediates can be better explained with the models proposed by Ostwald (1984) and Roberts et al. (1999), whereas Peacock (2009)'s model is applicable for the Al- and Co-poor and Ni-rich Type III lithiophorite-asbolane. Other less abundant ore-bearing Mn-oxy-hydroxides at Wingellina include romanèchite, ernienickelitejianshuiite, manganite, and birnessite. Romanèchite shows very variable chemical composition, where Co and Ni enrichments seems to be particularly controlled by Ba contents. The crystal structure of romanèchite consists of double and triple chains of edge-shearing MnO₆ octahedral layers, which form

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large tunnel structures filled with adsorbed Ba and water (Post, 1999). Mukherjee (1965), while defining the crystallography of the psilomelane (romanèchite) group, affirmed that both Ni and Co in the crystal lattice are located in the octahedral sites. This model fits partially with the chemistry of the Wingellina romanèchite, which shows moderate negative between Ni vs. Ba and Co vs. Ba binary concentrations (Fig. 3.5a and b). In addition, the Ba-poor romanèchite (romanèchite II) shows a significant gain of several transition metals together with Ni and Co. This peculiar relationship between Ba and Ni-Co contents of romanechite could be related to the Ni- and Co-enrichment processes occurred in the laterite. In particular, the possible leaching of Ba^{2+} from the tunnel structures of romanèchite, producing a charge disequilibrium in the minerals, could have been balanced by an increase of the amount of the transition metals in the octahedral sites. Goethite and hematite, the main Feoxy-hydroxides, are able to capture Ni²⁺ either by sorption on their surfaces or by substitutions for Fe^{3+} (e.g. Trivedi and Axe, 2001), whereas Co^{2+} and Co^{3+} sequestration is associated with sorption under 8-10 pH conditions (Schenck et al., 1983). The Co-bearing goethite has been recently investigated by Dublet et al. (2017), who suggested that the Co enrichment in the Fe-oxy-hydroxides is the product of the dissolution of Co-bearing Mn-oxy-hydroxides, caused by the acidification of the soil solution in the uppermost zone of the weathering profile. This model fits only partially with the characteristics of the oxide zone at Wingellina, where Co-goethite is indeed common, but the Co-bearing Mnoxy-hydroxides not only occur in the lowermost part of the profile, but also in the upper part of the oxide profiles (see chapter 2 for field evidences).

3.4.2 Paragenesis of the Mn-oxy-hydroxides: A proxy for Ni and Co deportment?

Lithiophorite-asbolane intermediates have been observed also several other Ni-Co laterites (e.g., Moa Bay, Cuba, Roqué-Rosell et al., 2010; New Caledonia mining district, Manceau et al., 1987; Nkamouna, Cameroon, Lambiv Dzemua et al., 2013). Their wide occurrence led many authors (Taylor et al., 1964; McKenzie, 1989; Dowding and Fey, 2007) to suggest that they could have been formed from the oxidation of other relatively less stable Mn-oxy-hydroxides such as birnessite, todorokite, or hollandite. This process may be associated with the leaching of alkali and alkaline-earth metals from the Mn-oxyhydroxides, and with the addition of Al. The above hypotheses are confirmed by the common associations between lithiophorite-asbolane and birnessite and

between lithiophorite-asbolane and manganite at Wingellina (Fig. 3.3f and g), providing further insights of the late-stage formation of lithiophorite. However, the formation of lithiophorite requires a high input of Al (Cui et al., 2009; Golden et al., 1993), which in the case of Wingellina is likely sourced from the hydrolysis of the sialic minerals (e.g., plagioclase) that occur in the gabbro/gabbronorite units. The multistage evolution of the manganiferous phases is also supported by the presence of two generations of romanèchite, with the younger phase characterized by a sharp decrease in Ba and an increase in Ni, Co and other transition metals as Al and Fe. Therefore, romanèchite II can be interpreted as a possibly intermediate oxidation stage between the older cation-rich Mn-oxy-hydroxides and the younger lithiophorite. However, there is no textural evidence for a lithiophorite-romanèchite II association in the analyzed samples. Notwithstanding, the replacement of K- and Ba-rich Mnoxy-hydroxides (e.g., romanèchite I and birnessite) by late stage metals-rich Mn-oxy-hydroxides seems to be the primary controlling factor for the Ni and Co deportment during the formation of the limonitic ore at Wingellina.

3.4.3 Considerations on the ore treatment

Based on the similarities of the Wingellina ore with that of Moa Bay (Elias, 2002), the mineralogy and chemistry of the analyzed samples suggest the Wingellina ore is also amenable to the High-Pressure Acid Leaching (HPAL). The costs and efficiency of HPAL processing are strongly controlled by the chemistry of the ore minerals. One of the critical components is acid consumption. Magnesium-rich ores, such as smectite and hydrous Mg-silicates, generally consume large volumes of acid. The Wingellina mineralization, even though representing an oxide-type laterite, contains a significant Mg amount associated with some lithiophorite-asbolane intermediates (MgO content up to 5 wt%). Also aluminum has negative effects on HPAL performance, because the presence of Al in the slurry can trigger the formation of alunite encrustations in the autoclave during acid leaching (Elias, 2002). In the Wingellina oxide zone, Al occurs in several mineral phases including gibbsite and Co- and Ni-rich lithiophorite-asbolane intermediates, with an average Al_2O_3 content of 9.42 wt%. Nickel- and Co-bearing Mn-oxy-hydroxides occur mainly as fine-grained aggregates (Fig. 3.3), and according to metallurgical test work carried out by Metals X Ltd., the ore is not amenable to physical beneficiation involving scrubbing and size classification. Kaya and Topkaya (2011) demonstrated that during HPAL processing, the autoclave feed size strongly affects Ni and Co

extraction. Excessive fine-grained ore provides extra surface area for enhanced Fe and Al precipitation, which in turn enhances Ni and Co extractions (Chou et al., 1977). However, overgrinding increases both the energy consumption and technological challenges separating ores from tailings. Depending on the processing method chosen, the dominance of fine-grained and soft limonitic ore at Wingellina could be advantageous because it would require relatively less energy in the grinding step. Other factors to consider include the presence of nickeliferous and cobaltiferous hematite, which is relatively refractory to leaching and could result in low metals recoveries (Kaya and Topkaya, 2011). The neo-formation of hematite, together with alunite in the autoclaves can coprecipitate dissolved Ni and Co, also resulting in lower recoveries (Papangelakiset al., 1996; Whittington and Muir, 2000). However, hematite represents a minor mineral in the Wingellina orebody in comparison with goethite and Mn-hydroxides and has also low Co-and Ni-grades (NiO and CoO average values = 0.64 and 0.68 wt%, respectively). The association of Ni and Co with Mn in the Wingellina ore may also be problematic. Acid leaching of the Wingellina ore would dissolve not only Co and Ni but also Mn, and separation of Mn from Ni and Co from acid leach liquor is generally inefficient (Ferron, 2002). In many other Ni-Co laterite deposits (e.g., Cawse, Western Australia), Ni and Co are recovered as mixed hydroxide precipitate (MHP) using magnesia (MgO) as a precipitant (Kyle and Furfaro, 1992). This method selectively precipitates Ni and Co although higher cobalt recoveries involve some Mn co-precipitation. In Moa Bay, intermediate sulfide concentrates of Ni and Co are produced using H₂S precipitation. This method allows a high selectivity of Co and Ni against Mn (Chalkley and Toirac, 1992).

3.5 Conclusions

The Wingellina Ni-Co laterite contains several types of Ni- and Co-bearing Feand Mn-oxy-hydroxides. High concentrations of Ni and Co have been detected in both goethite and hematite in all the analysed samples. High Ni- and Cogrades occur in lithiophorite-asbolane intermediates with a heterogeneous chemical signature, which probably reflects variable mechanisms of metalsenrichment. Minor amounts of other ore-bearing Mn-oxy-hydroxides (manganite, romanèchite, ernienickelite-jianshuiite and birnessite) were also observed in the oxide zone. The enrichment of Ni and Co in the Wingellina laterite profile was probably controlled by the post-formation evolution of the Mn-oxy-hydroxides. Francesco Putzolu

			(Qualitat	ive XF	RPD in	terprea	atations							
		Ore-bearing minerals										Gangu	0		
				Oxyhydroxides				Phyl	Phyllosilicates				Gallgue		
Core ID	Sample ID	Depth (m)	Ght	Hmt	Asb	Lth	Brn	Ern	Smc	Lzr	Chl	Kln	Qtz	Spn	Gbb
WPDD0012	WPDD0012-2	9	0	0	0	0	_	0	_	_	_	_	_	_	-
WPDD0012	WPDD0012-5	30.7	0	-	0	-	-	-	-	-	-	-	-	-	0
WPDD0012	WPDD0012-6	31	0	0	0	-	-	-	-	-	-	-	-	-	0
WPDD0012	WPDD0012-8	47.1	0	0	-	0	-	-	-	-	-	Ο	-	-	0
WPDD0012	WPDD0012-13	68	0	-	0	0	-	-	-	-	-	-	-	-	-
WPDD0019	WPDD0019-2	13.8	0	-	0	0	0	_	_	-	_	_	0	0	-
WPDD0019	WPDD0019-3	23	0	-	0	-	-	0	0	-	-	-	-	-	-
WPRC0575	W19527	76-78	0	0	0	0	-	_	0	-	_	0	-	0	-
WPRC0576	W19529	80-82	0	-	-	0	-	-	0	-	-	Ο	0	-	-
WPRC0576	W19532	84-86	0	-	-	-	-	0	0	-	-	Ο	0	-	-
WPRC0576	W19536	92-94	0	-	0	0	-	0	0	-	-	Ο	0	0	-
WPRC0576	W19540	100-102	0	-	0	-	-	-	-	0	0	-	0	0	-

Table 3.1: Qualitative XRPD analyses of cores WPDD0012, WPDD0019 and WPRC0576.

Ght= goethite; Hmt= hematite; Asb= asbolane; Lth= lithiophorite; Brn= birnessite; Ern= ernienickelite; Smc= smectite; Lzr= lizardite; Chl= chlorite; Kln= kaolinite; Qtz= quartz; Spn= spinel; Dlm= dolomite; Gbs= Gibbsite; O= detected; -= not detected.

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Table 3.2: Summary	of the averag	e structural f	formula and	chemical	composition of	of the ore-	bearing of	xy-hydroxides
2	<i>U</i>				1		0	2 2

Mineral name	Ideal structural formula	Average structural formula (apfu)	Туре	Average chemistry (wt%)												
				SiO ₂	Cr_2O_3	MnO	FeOt	Al_2O_3	MgO	CoO	NiO	K_2O	Na ₂ O	CaO	BaO	Total
			Ι	1.69	0.16	36.38	6.51	8.85	2.69	8.48	10.36	0.30	0.43	0.39	0.20	76.43
Lithiophorite	(Al,Li)MnO ₂ (OH) ₂	(A1 N' C_{1} $3+)(M_{1}$ $4+\Gamma_{2}$ $3+M_{1}$)O (OII)		2.28	0.17	34.60	11.87	2.22	3.31	2.55	16.35	0.14	0.44	0.28	0.00	74.20
Asbolane	(Ni,Co) _x Mn(O,OH) ₄ *nH ₂ O	$(AI_{0.45}, NI_{0.24}, CO_{0.12}) (MII_{0.69}, Fe_{0.15}, Mg_{0.11}) O_2(OH)_2$	III	1.13	0.08	35.77	6.26	18.96	0.44	0.35	12.32	0.04	0.26	0.01	0.17	75.79
			IV	2.48	0.06	33.87	9.80	9.56	2.27	3.19	9.37	0.24	0.31	0.22	0.10	71.48
Romanèchite	(Ba, H ₂ O) ₂ (Mn) ₅ O ₁₀	$(Ba_{0.30}, Na_{0.05}, K_{0.04})(Mn_{3.99}^{4+}, Fe_{0.35}^{3+}, Mg_{0.26}, \\Si_{0.17}, Al_{0.14}, Ni_{0.10}, Co_{0.05}^{3+})O_{10}\\Ba_{0.11}, Na_{0.10}, K_{0.06})(Mn_{3.81}^{4+}, Fe_{0.45}^{3+}Mg_{0.42}, Al_{0.24}, Ni_{0.23}, Si_{0.12}, Co_{0.11}^{3+})O_{10}$		1.73	0.12	56.52	4.54	0.83	1.72	0.72	1.21	0.32	0.24	0.33	7.64	75.93
				1.33	0.07	54.41	5.80	1.39	2.88	1.48	2.90	0.43	0.51	0.30	2.68	74.19
K-Birnessite	(K,Na,Ca) _{0.5} (Mn) ₂ O ₄ *1.5H ₂ O	$(K_{0.18}, Na_{0.04}, Ca_{0.01})(Mn_{1.85}{}^{4+}Ni_{0.06}, Mg_{0.02}, Co_{0.01}{}^{3+})O_4.$	-	0.28	0.07	71.64	0.51	0.74	0.30	0.54	2.13	3.73	0.67	0.27	0.26	81.14
Ernienickelite	NiMn ₃ O _{7*} 3H ₂ O	$(Mg_{0.34}, Ni_{0.30}, Co_{0.10}, Na_{0.04}, Ca_{0.03})(Mn_{2.75}^{4+}, Al_{0.25}, Fe_{0.12}^{3+})O_{7}$	_	0.80	0.00) 53.	57 2	.25	2.12	3.03	1.81	4.	98 0).71	0.24	0.41
Jianshuiite	$(Mg,Mn)Mn_3 O_7*3H_2O$	(1v120.34,1v10.30,000.10,1v40.04,040.03)(1v112.75,1v10.25,1 00.12, 707		0.10	69.32											
Manganite	MnO(OH)	$(Mn_{0.91}^{4+}, Ni_{0.02}, Co_{0.01}^{3+})O(OH))$	-	0.82	0.14	74.92	0.38	0.71	0.28	0.61	1.43	0.30	0.24	0.20	0.49	80.51
Goethite	FeO(OH)	$(Fe^{3+}_{0.67}, Si_{0.11}, Ni_{0.02}, Co^{3+}_{0.01})O(OH)$	-	6.59	0.88	3.09	54.99	3.35	1.09	0.86	1.40	0.15	0.09	0.48	0.44	73.41
Hematite	Fe ₂ O ₃	(Fe ³⁺ 0.90,Ni0.01,Co0.01)O(OH)	-	1.61	0.89	2.07	81.71	0.61	0.78	0.68	0.64	0.02	0.07	0.14	0.15	89.37

Table 3.3: Chemical composition (EMPA and EDS microanalyses) and structural formulae (apfu) of lithiophorite-asbolane intermediates from Wingellina.

Sampl	WPDD0012	WPDD0012	WPDD001	WPDD001	W19529	W19529	WPDD001	W19529
Coro	-12	-12	2-12 WDDD001	9-3 WDD001	WDDC057	WDDC057	2-12 WDDD001	WDDC057
ID	WPDD0012	WPDD0012	2-12	9	6 wrkc037	6 wrkcos7	2	6 wrkcos <i>i</i>
Туре	I*	I*	II*	II**	III*	III*	IV*	IV*
wt%								
SiO2	0.67	0.38	0.24	1.36	2.63	1.21	1.48	1.66
Cr_2O_3	-	0.03	-	-	0.08	0.09	0.02	-
MgO	2.99	2.98	0.98	3.13	0.42	0.99	2.04	2.92
MnO	38.43	37.71	44.15	44.96	27.46	33.70	35.32	39.75
FeO	2.02	2.51	-	1.68	17.31	11.33	5.91	2.03
Al_2O_3	7.03	7.09	7.41	1.94	16.43	13.46	10.30	12.17
CoO	6.02	5.56	2.96	2.54	0.14	0.33	4.35	5.13
NiO	13.69	14.72	14.07	14.12	10.47	12.80	10.62	11.43
Total	70.85	70.99	69.81	69.74	74.94	73.91	70.05	75.10
Co/Ni	0.44	0.38	0.21	0.18	0.01	0.03	0.41	0.45
apfu				On the basis of	f 3 Oxygens			
Si	0.02	0.01	0.01	0.04	0.08	0.04	0.05	0.05
Cr	-	-	-	-	-	-	-	-
Mg	0.15	0.15	0.05	0.15	0.02	0.05	0.10	0.13
Mn	0.87	0.86	1.01	1.01	0.56	0.71	0.79	0.81
Fe	0.05	0.06	-	0.04	0.39	0.26	0.14	0.05
Σ_{OMn}	1.09	1.08	1.07	1.25	1.05	1.06	1.08	1.04
Al	0.27	0.28	0.29	0.10	0.57	0.49	0.39	0.42
Co	0.14	0.13	0.07	0.06	-	0.01	0.10	0.11
Ni	0.36	0.39	0.37	0.37	0.25	0.32	0.28	0.27
Σ_{OAl}	0.78	0.80	0.73	0.53	0.82	0.81	0.77	0.81
*: EMPA gibbsite-	A; **: EDS; Σα like octahedral	omn= sum of th site; -= not dete	e elements in ected.	the Mn-oxide	type octahedra	al site; Σ_{OAI} =	sum of the ele	ments in the

Table 3.4: Chemical composition	on (EMPA and EDS micro	oanalyses) and structural f	formulae (apfu) of the Ni	- and Co-bearing	Mn-oxy-hydroxides
from Wingellina.					

Sample	WPDD0012-	WPDD0012-	W19536	W19529	W19527	W19527		WPDD0012-12	WPDD0019-
<u>ID</u>	8	8							3
Core ID	WPDD0012	WPDD0012	WPRC0576	WPRC0576	WPRC0576	WPRC0576		WPDD0012	WPDD0019- 3
Mineral	Romanèchite I**	Romanèchite II**	K- Birnessite**	K- Birnessite*	Manganite**	Manganite**		"Ernienickelite*"	"Jainsuiite**"
wt%									
SiO ₂	0.62	0.85	0.32	0.26	0.36	0.61	SiO ₂	0.24	0.48
Cr_2O_3	-	-	-	0.01	0.22	0.25	Cr_2O_3	-	-
MnO	60.66	51.87	74.06	70.02	73.11	75.64	MnO	44.15	54.72
FeO	0.30	4.41	0.61	-	-	0.13	FeO	-	1.70
Al_2O_3	0.59	1.46	0.56	0.80	0.89	0.97	Al_2O_3	7.41	0.46
MgO	1.09	1.70	0.17	0.27	0.10	0.22	MgO	0.98	5.83
CoO	0.95	1.59	0.65	0.18	0.93	1.21	CoO	2.96	0.63
NiO	1.12	2.51	3.03	2.58	2.34	3.17	NiO	14.07	3.25
K ₂ O	0.25	0.40	3.86	3.74	0.67	0.48	K_2O	0.15	0.03
Na ₂ O	0.07	0.81	0.70	0.61	0.08	0.56	Na ₂ O	0.09	-
CaO	0.13	0.14	0.32	0.23	0.14	0.18	CaO	0.14	0.16
BaO	9.81	4.65	0.14	0.29	-	-	BaO	0.12	1.81
Total	75.58	70.40	84.43	79.00	78.84	83.42	Total	70.31	69.07
apfu	On the basis	of 5 Oxygens	On the basis	of 4 Oxygens	On the basis	of 2 Oxygens		On the basis of	f 7 Oxygens
Si	0.07	0.09	0.01	0.01	0.01	0.01	Si	0.02	0.04
Cr	-	-	-	-	-	-	Cr	-	-
Mn	4.40	3.88	1.83	1.85	0.91	0.89	Mn	2.35	2.89
Fe	0.02	0.36	0.02	-	-	-	Fe	-	0.10
Al	0.10	0.25	0.03	0.04	0.03	0.03	Al	0.67	0.06
Mg	0.17	0.27	0.01	0.02	0.00	0.01	Σ_{OMn}	3.04	2.99
Co	0.07	0.12	0.03	0.01	0.01	0.01	Mg	0.11	0.66
Ni	0.09	0.22	0.08	0.08	0.03	0.04	Co	0.17	0.03
Σ_{OMn}	4.92	5.20	2.01	1.99	0.99	0.99	Ni	0.87	0.20
Κ	0.03	0.05	0.16	0.18	0.02	0.01	Κ	0.01	-
Na	0.01	0.17	0.04	0.05	0.00	0.02	Na	0.01	-
Ca	0.01	0.02	0.01	0.01	0.00	0.00	Ca	0.01	0.01
Ba	0.40	0.20	-	-	-	-	Ba	0.00	0.05
Σ_{cat}	0.46	0.44	0.22	0.24	0.02	0.03	$\Sigma_{\rm cat}$	1.19	0.97

*: EMPA; **: EDS; Σ_{OMn} = sum of the elements in the Mn-oxide type octahedral site; Σ_{cat} = sum of the adsorbed cations; -= not detected.

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 Table 3.5: Chemical composition (EDS microanalyses) of Fe-oxy-hydroxides from Wingellina.

Sample ID	W19536	W19529	WPDD0012-12	W19536	WPDD0019-3	W19529	W19527	W19527
Core ID	WPRC0576	WPRC0576	WPDD0012	WPRC0576	WPDD0019	WPRC0576	WPRC0576	WPRC0576
Mineral	Goethite**	Goethite**	Goethite**	Goethite**	Hematite**	Hematite**	Hematite**	Hematite**
wt%								
SiO ₂	6.29	6.15	7.28	5.92	1.10	0.33	0.74	0.79
Cr_2O_3	0.30	0.28	-	0.08	1.99	0.95	4.37	4.08
MnO	1.75	0.31	0.80	9.56	0.24	4.13	1.57	1.85
FeO	70.22	63.03	62.39	59.01	82.80	82.49	79.91	79.70
TiO ₂	-	0.40	0.00	0.16	0.60	0.58	0.67	0.86
Al_2O_3	3.49	3.68	4.08	4.36	0.22	0.72	0.62	0.68
MgO	0.49	0.60	0.59	0.51	0.66	0.16	0.27	0.39
CoO	1.01	0.91	0.84	0.78	0.41	2.06	0.41	-
NiO	0.77	0.25	0.31	1.36	0.12	1.10	0.47	0.93
K ₂ O	-	0.21	0.12	-	-	0.09	0.01	-
Na ₂ O	-	0.26	0.00	0.20	-	-	0.24	-
CaO	0.09	-	0.05	0.27	0.18	-	0.10	0.07
Total	84.42	76.07	76.45	82.20	88.31	92.62	89.38	89.37

**: EDS; -= not detected.

Chapter 4:

Ni-Co enrichment and High-Tech metals geochemistry in the Wingellina Ni-Co oxide-type laterite deposit (Western Australia)

4.1 Introduction

In this part of the study an evaluation of the geochemistry of two mineralized drillcores, characterized by distinct mineralogy (one is oxide-prevailing, whereas the other is saprolite-prevailing) from the Wingellina deposit is presented based on ICP-MS and ICP-ES data, as well as on the facies detected by drillcore logging. The aim is to better constrain the behaviour of the major elements plus Ni and Co, in relationship with facies and mineralogical variations in the laterite profiles. A particular emphasis has been given to the assessment of the main ore-forming processes that accounted for the development of a variable range of facies within the laterite profiles, and to the geochemistry of REEs and Sc, which could represent potential by-products of Ni and Co extraction.

4.2 Description of the cores, sampling and analytical methods

This study was carried out on two mineralized drillcores (WPDD0012 and WPDD0019) drilled by the Metals X Ltd in 2007 in the high-grade zone of the laterite *s.s.*

4.2.1 Drillcore WPDD0012

The core WPDD0012 (7117583N; 497093E; Dip: -60; Azimuth: 49) was drilled in the southern zone of the deposit and reached a depth of 78.6m (Fig. 4.1a). In the uppermost zone of the drillhole (0–2 m) the duricrust occurs as a reddish and relatively indurated unit crosscut by veinlets of carbonates and Feoxy-hydroxides (Fig. 4.1b). The oxide zone occurring in this core is intercepted at depths of between 2 and 72 m, and therefore is the most developed unit. This

unit consists of a brittle and fine-grained lithotype, locally characterized by disseminated (Fig. 4.1c) or massive Mn-oxy-hydroxides (Fig. 4.1d). Within the same oxide unit (Fig. 4.1a), several clay-rich mottled horizons occur between 36 and 45m and 68 to 72m in depth. From 72 to 76m depth, the core comprises the silicates-rich saprolite zone, which consists of a massive, bright green lithology locally spotted by reddish to black coatings of Fe-oxy-hydroxides (Fig. 4.1f). The bottom part of the drillcore intercepts the local magmatic bedrock corresponding to relatively unweathered gabbro/gabbronorite (Fig. 4.1g).

4.2.2 Drillcore WPDD0019

The core WPDD0019 (7117900N; 495336E; Dip: -60; Azimuth: 49) was drilled in the north-western sector of the southern zone of the tenement and reaches a depth of 56.8 m. In comparison to the other analyzed core (WPDD0012), here the lateritic profile has a better developed silicate-rich saprolite, whereas the residual oxy-hydroxide zone is only subordinate (Fig. 4.2a). The surficial zone of the weathering profile (0-2.5 m) is occupied by the silica- and carbonate-rich duricrust (Fig. 4.2b), which is characterized by a higher cementation degree compared to that of the other drillcore (WPDD0012). In addition, the duricrust in this locality is characterized by the occurrence of nodular carbonates and by sub-angular and silicified oxide fragments, all of this suggesting a partial reworking of the regolith profile (Fig. 4.2b). The oxide zone starts at a depth of 2.5m and continues down to 25 m; this zone is locally coated by pseudo-layered Mn-oxy-hydroxides and by microcrystalline carbonates (Fig. 4.2c). The core intersects the silicates-rich saprolite horizon between 25 and 55.5m in depth. In this zone the saprolite unit has different features compared to the saprolite zone in core WPDD0012. In particular, the uppermost portion of the saprolite unit (25 to 45 m, Fig. 4.2d) consists of brownish clays, locally crosscut by pale green silicate-rich veins associated with a silica boxwork (Fig. 4.2e). The lower saprolite (45 to 55m in depth, Fig. 4.2f and g) occurs as a waxy and pale green unit. In this zone, carbonate veins are common (Fig. 4.2f). In the lowermost saprolite interval (54.5m in depth), carbonates occur as partially oxidized microcrystalline nodules (Fig. 4.2h). At the bottom of the core, several green and dense saprock blocks, likely corresponding to relicts of serpentinized peridotites, are cemented by saprolitic silicates (Fig. 4.2i).



Fig. 4.1: Wingellina lateritic profile at the drilling site WPDD0012 and images of representative specimens. a) Stratigraphic column based on drillhole WPDD0012 showing the core samples locations (after Putzolu et al., 2018, modified); b) Duricrust sample (depth: 0.5

m); c) and d) Manganesiferous oxide samples (depth: 9 and 68m respectively); e) Mottled clays sample (depth: 71.2 m); f) Saprolite sample (depth: 73 m) g) Parent rock sample (depth: 75.8 m). The asterisk indicates the position of the displayed representative samples.

4.2.3 Sampling and methods

For the present study 31 core samples were collected from drillcores WPDD0012 (18 samples) and WPDD0019 (13 samples). The down hole sample positions are shown in Figs. 4.1a and 4.2a. The adopted sampling strategy was aimed primarily to best represent the lithological, facies and textural variability of the identified horizons within the laterite profiles. The chemical analyses of major, minor and trace elements on the core samples were carried out at the Bureau Veritas Laboratory in Canada. Prior to the analyses, the samples were prepared through drying at 105 °C. For the major and minor element determinations, 0.5 g of pulp has been leached with "aqua regia" and then flux fused with LiBO₂/Li₂B₄O₇ for Inductively Coupled Plasma Emission Spectrometry (ICP-ES) analyses. Major oxides and minor elements have been analyzed with a Method Detection Limit (MDL) between 0.01 and 0.001 wt%. Loss on ignition (LOI) has been evaluated at 1000 °C, with a MDL of -5.1wt%. Trace element determinations (including REEs, Sc) have been carried undertaken by Inductively Coupled Plasma Mass Spectrometry (ICP-MS), with a MDL between 0.01 and 8 ppm. Finally, Ni, Co and Cu have been analyzed with acid digestion through IPC-ES with a MDL of 0.001 wt%.

4.3 Results

4.3.1 Major oxides composition and the Ni-Co grades

The geochemical data of major, minor and trace elements of drillcores WPDD0012 and WPDD0019 are summarized in Tables 4.1 and 4.2 respectively.

4.3.1.1 Drillcore WPDD0012

Fig. 4.3a shows the geochemical trends observed in the lateritic profile of the core WPDD0012 (from sample 12-1 to sample 12-18). The dominant oxides are

Fe₂O₃, SiO₂ and Al₂O₃, with average values of 35.61, 21.61 and 16.38 wt%. Fe₂O₃ has an increasing trend from the weathered gabbro bedrock (WPDD0012-18) to the uppermost zone of the oxide, whereas it shows a sharp decrease in correspondence of the mottled clays horizons (WPDD0012-8, WPDD0012-9 and WPDD0012-11) and in the duricrust (WPDD0012-1). SiO₂ and Al₂O₃ have both inverted tendencies compared to Fe₂O₃. In particular, SiO₂ undergoes a slight increase from the gabbro to the saprolite horizon, where it reaches its highest values (55.38 wt% SiO₂, WPDD0012-17). Silica then remains very low throughout the oxide zone, except for the mottled clays horizons from 25.62 and 34.53 wt% SiO₂. In addition, a SiO₂ increase has been observed also in the duricrust (8.18 wt%). The geochemical trend is quite irregular for Al₂O₃, whose values decrease from the gabbro (WPDD0012-18, 11.81 wt%) to the duricrust (WPDD0012-1, 4.39 wt%). Al₂O₃ reaches the highest content in oxide samples (up to 33.29 wt% in WPDD0012-7). In addition, the Al₂O₃ trend from the gabbro bedrock to the mottled clay sample WPDD0012-8 is similar to that of SiO_2 , whereas in the uppermost zone of the profile this correlation is not observed. MgO and CaO have similar trends, characterized by sharply decreasing concentrations from the bottom gabbro (WPDD0012-18) to the upper oxide zone (WPDD0012-2), and by a sharp increase in the duricrust (sample WPDD0012-1). Differently from CaO, in the saprolite zone (samples WPDD0012-17 to WPDD0012-15) MgO has still remarkably high values (average 4.64 wt%), which rapidly drop the at the interface with the oxide zone (WPDD0012-14, 0.64 wt%). MnO shows negligible concentration values both in the gabbro (WPDD0012-18, 0.09 wt% MnO) and in the saprolite zone (WPDD0012-15 to WPDD0012-17, average value: 0.40 wt%), whereas it is significantly enriched within the oxide, with average values of 4.00 wt%. The MnO concentration strongly decreases in the duricrust (0.36 wt%). The Co-grade generally increases from the gabbro (WPDD0012-18, 0.003 wt% Co) to the oxide, where it reaches its highest average values (0.37 wt% Co), and sharply decreases in the duricrust (WPDD0012-1,0.025 wt%). The Co trend within the oxide is very similar to that of MnO. Nickel shows a rapid increase in the transition zone from the gabbro (WPDD0012-18, 0.07 wt%) to the saprolite, where a sharp positive peak could be observed (WPDD0012-16, 3.33 wt%).



Fig. 4.2: Wingellina lateritic profile at the drilling site WPDD0019 and images of representative specimens. a) Stratigraphic column based on drillhole WPDD0019 (after Putzolu et al., 2018, modified) showing the core samples locations; b) Duricrust sample (depth: 1.6 m); c) Manganesiferous oxide samples (depth: 23 m); d) saprolite sample (depth: 25 m) e) silicarich boxwork within the saprolite sample WPDD0019.4; f) and g) saprolite sample (depth: 44.5 and 46.5m respectively); h) carbonate pod sample (depth: 54.5 m); i) serpentinized parent rock

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sample (depth: 56 m). The asterisk indicates the position of the displayed representative samples. N.B.: the carbonate sample WPDD0019-12 (drillcore WPDD0019) is not included in the geochemical analyses.

Nickel displays a relative decrease in the oxide zone, with average values of 1.24 wt%. The duricrust sample has a Ni content of 0.50 wt%. The Ni trend is quite variable and is generally correlated to the abundance of MnO (and thus of Co) within the oxide, whereas in the saprolite zone a SiO₂-Ni geochemical association is far more evident.



Fig. 4.3: Geochemical logs for drill cores WPDD0012 (a) and WPDD0019 (b): Ni, Co, Fe₂O₃, SiO₂, Al₂O₃, CaO, MgO and MnO are expressed in weigh percent (wt%); Sc and Sum REEs in parts per million (ppm).

4.3.1.2 Drillcore WPDD0019

The major and minor chemical compositions measured along the core WPDD0019 are shown in Fig. 4.3b (19-1 to 19-14). Compared to the core

WPDD0012, in this case a sharp enrichment of SiO₂ and MgO (average values: 30.16 and 13.45 wt% respectively) and a depletion of Fe_2O_3 and Al_2O_3 (average values: 19.32 and 4.40 wt% respectively) have been observed. Silica undergoes a strong increase in the transition from the gabbro (WPDD0019-14, 8.33 wt%) toward the saprolite, where it reaches its highest values (WPDD0019-4 to WPDD0019-13, average value: 37.83 wt%), even though with an irregular trend. In the oxide zone (WPDD0019-2 to WPDD0019-3) the SiO₂ amount decreases, however still maintaining remarkably high values (average value: 18 wt%) if compared to those of the uppermost zone of core WPDD0012, whereas SiO₂ in the duricrust (WPDD0019-1) decreases to values of 7.23 wt% SiO₂. Fe_2O_3 sharply increases from the parent rock (5.38 wt%) to the saprolite horizon (where it averages 18.47 wt%). In this zone of the lateritic profile, Fe₂O₃ has a behavior similar to SiO₂, except for the upper saprolite sample WPDD0019-6, where Fe₂O₃ sharply increases and SiO₂ decreases. Similar to core WPDD0012, Fe₂O₃ reaches its highest values in the oxide zone (average value: 32.23 wt%), and then decreases toward the duricrust (14.99 wt%). Al₂O₃ shows remarkable differences in its geochemical behavior and, generally, the weathering profile intercepted by the core WPDD0019 is sharply "Al₂O₃depleted" if compared to that of the core WPDD0012. This difference can be observed starting from the locally serpentinized protolith, where Al₂O₃ has very low values (0.85 wt%). Al₂O₃ slightly increases in the saprolite (5.21 wt%) and in the oxide (4.19 wt%) zones, and decreases in the duricrust (1.18 wt%). On the whole, a similarity between the behavior of this oxide and that of Fe₂O₃ in the whole profile has been observed. The geochemical trends of MgO and CaO are significantly different in the WPDD0019 drillcore if compared to the WPDD0012 core. The MgO content of the local parent rock is sharply higher (18.93 wt%), compared to that of the parent rock of WPDD0012. This oxide has an articulated trend: it initially experiences a decrease in correspondence of the transition zone to the lower saprolite, then undergoes a strong enrichment in the lower saprolite zone (WPDD0019-8 to WPDD0019-13), where it reaches its highest values (average value: 18.79 wt%). MgO content then decreases significantly at the transition to the upper saprolite (WPDD0019-4 to WPDD0019-7, average value: 12.95 wt%) and to the oxide zone (1.50 wt%). Finally, MgO increases to a value of 7.18 wt% in the duricrust. CaO is the dominant oxide in the local weathered parent rock, with a value of 25.36 wt%. CaO displays very low baseline values (between 0.1 and 1 wt%) throughout the lateritic profile, except for positive peak values corresponding to the saprolite

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samples WPDD0019-9 and WPDD0019-11 (22.07 and 10.66 wt% respectively) and to the duricrust (32.82 wt%). MnO and Co have very similar trends to those observed in WPDD0012. The initial MnO content (0.05 wt%) of the local weathered parent rock is lower than that of the core WPDD0012, whereas its Co value is significantly higher (0.01 wt%). The MnO and Co values of the whole saprolite zone are negligible (average values: 0.24 and 0.02 wt% respectively), whereas a strong increase is observable within the oxide zone (average values: 25.69 and 0.57 wt% respectively). The concentration of both elements decreases in the duricrust, reaching values of 0.03 and 0.004 wt% respectively. Similar to Co, the Ni grade of the local parent rock (0.14 wt%) is higher than that of WPDD0012. Nickel exhibits a strong enrichment within the saprolite zone (average value: 1.83 wt%), and the distinctive features of its geochemical behaviour can be commonly observed between the lower and the upper saprolite zones. In particular, the lower saprolite has a poorer Nienrichment (average value: 1.32 wt%) in comparison to the upper saprolite zone (2.47 wt%). In addition, the Ni trend in the lower saprolite is very similar to the SiO₂ and Fe₂O₃ trends and, with the exception of sample WPDD0019-13, to that of MgO. In contrast, the Ni-SiO₂-Fe₂O₃ correlation cannot be observed in the upper saprolite zone, where the tendency in the highest Ni value (WPDD0019-6, 3.10 wt%) is positively correlated to that of Fe₂O₃. Ni undergoes a strong increase in the transition to the oxide (average value: 2.04 wt%), then it decreases toward the duricrust (0.20 wt%). Similar to the core WPDD0012, Ni tendency in the oxide zone highlights the geochemical affinity of this element with Co and Mn.

4.3.2 High-tech metals geochemistry

4.3.2.1 Drillcore WPDD0012

The REEs and Sc trends throughout the laterite profile intercepted by the core WPDD0012 are shown in Fig. 4.3a. The dominant REEs are Ce, Nd and La with low average values of 62, 27 and 21 ppm in the whole profile. The REEs concentration in the local magmatic bedrock is significantly lower (WPDD0012-18, 6 ppm). These elements undergo a slight increase in the saprolite unit (WPDD0012-15 to WPDD0012-17, average value=40 ppm in total). The highest total REEs values can be observed in correspondence of the

Mn-oxy-hydroxides-rich zones (sample WPDD0012-13, 404 ppm) and in the mottled layers within the oxide unit (samples WPDD0012-8 and WPDD0012-9, 891 and 336 ppm respectively). The REEs concentration decreases significantly in the duricrust (WPDD0012-1, 13 ppm). The REEs/chondrite normalized patterns of core samples from the core WPDD0012 (Fig. 4.4a) show a progressive REEs-enrichment starting from the bedrock (WPDD0012-18, average REEs/cho value: 2 times) to the saprolite (WPDD0012-15 to WPDD0012-17, average REEs/cho value: 17 times) and then to the oxide zones (WPDD0012-2 to WPDD0012-14, average REEs/cho value: 50 times). The duricrust unit shows a sharp depletion in REEs (WPDD0012-1, average REEs/cho value: 3 times). The majority of samples display distinctive features, such as Ce and Eu anomalies, flat HREEs patterns and steep LREEs patterns. The Ce and Eu anomalies have been quantified with the Ce/Ce*, Eu/Eu* indexes (Fig. 4.4b). The Ce/Ce* index varies broadly (0.04 to 8.23) and, with the exception of the oxide sample WPDD0012-7, it displays positive values in the uppermost zone of the local weathering profile (WPDD0012-1 to WPDD0012-9). In contrast, the Ce/Ce* negative values have been observed mostly in the lower oxide zone down core. The Eu/Eu* index ranges between 0.21 and 0.88. The highest Eu/Eu* values are observed in the gabbro bedrock (WPDD0012-18, 0.88), whereas variably strong negative anomalies occur throughout the local laterite profile, with the lowest values associated with the mottled clays horizon between samples WPDD0012-8 and WPDD0012-9 (0.21 and 0.42 respectively). As shown in Fig. 4.4a, Sc sharply increases at the boundary between the gabbro (sample WPDD0012-18, 42 ppm) and the saprolite zone (samples WPDD0012-17 to WPDD0012-15). In the latter zone, scandium reaches the highest values of the core (average of 111 ppm). Toward the upper part of the profile, this element has a constant negative trend, reaching very low values (average value: 50 ppm). In addition, the Sc trend does not show any type of correlation to Fe₂O₃ wt% (Fig. 4.5a), whereas a similarity between the Ni and the Sc trends has been observed throughout the profile (Fig. 4.3a). To better constrain the High-Tech (HT) metals geochemical deportment, and to infer about their possible mineralogical association, a correlation matrix between the HT metals and the most representative major oxides as well as Ni and Co has been calculated (Table 4.3). It must be specified that during this analysis Ce, Eu and the other REE (i.e. REE*) have been processed separately. In general, the correlation matrix confirms that the REE* are chiefly associated with both MnO (r = 0.54, *p*-value = 0.02) and Co (r = 0.50, *p*-value = 0.04). As expected, Ce and Eu behave differently from the other REEs. Firstly, although the Ce-REE* (r = 0.56, *p*-value = 0.01) and Eu-REE* (r = 0.75, *p*-value = 0.00) correlations are positively high, they are quite lower than the unity. In addition, differently from the other REEs*, Ce is not correlated to MnO (r = 0.05, *p*-value = 0.86).



Fig. 4.4: a) REEs/Chondrite normalized diagrams of core WPDD0012. The chondrite reference values are taken from McDonough and Sun (1995); b) Ce/Ce* and Eu/Eu* geochemical logs of core WPDD0012; c) REEs/Chondrite normalized diagrams of core WPDD0019; d) Ce/Ce* and Eu/Eu* geochemical logs of core WPDD0019. The chondrite reference values are taken from McDonough and Sun (1995); The Ce/Ce* and Eu/Eu* anomalies have been quantified following the formulae proposed by $[Eu/Eu* = [Eu_n / \sqrt{(Sm_n \cdot Gd_n)}; Ce/Ce* = Ce_n / \sqrt{(La_n \cdot Pr_n)}]$, (Mongelli et al., 2014)].

However, the most striking feature of the Ce behaviour is its positive correlation with Al_2O_3 (r = 0.49, *p*-value = 0.04). Eu displays a sharp positive correlation with REE* (r = 0.75, *p*-value = 0.00), and similar to other REE*, it is correlated with Co (r = 0.78, *p*-value = 0.00) and MnO (r = 0.76, *p*-value =
0.00). Finally, Sc shows remarkable positive correlations with Ni (r = 0.68, *p*-value = 0.00) and SiO₂ (r = 0.50, *p*-value = 0.03), whereas it does not show any correlations with Fe₂O₃ (r = -0.16, *p*-value = 0.54).

4.3.2.2 Drillcore WPDD0019

Fig. 4.4b shows the REEs and Sc geochemical trends in WPDD0019. Also in this core La, Nd, and Ce are the main REEs with average values of 13, 10 and 6 ppm. In this core, even though the local parent rock displays a similar total REEs concentration (WPDD0019-14, 5 ppm) to that of the WPDD0012 core, the lateritic profile shows a general REEs depletion. In particular, the total REEs concentration remains very low in the whole saprolite unit (WPDD0019-4 to WPDD0019-13, average value: 4 ppm), whereas a significant increase is observed in the oxide zone (WPDD0019-2 to WPDD0019-3, average value: 247 ppm). REEs sharply decrease in the duricust (WPDD0019-1, 13 ppm). In this core the strong REEs enrichment within the oxide zone is positively correlated with a Fe₂O₃ (Fig. 4.3b). As shown by the REEs/cho diagram in Fig. 4.4c, the highest REEs/cho values occur in the oxide zone (WPDD0019-2 to WPDD0019-3, average REE/cho: 83 times), whereas very low REEs/cho enrichments characterize the serpentinized parent rock (WPDD0019-14, average REEs/cho: 1.4 times), the saprolite zone (WPDD0019-4 to WPDD0019-13, average REEs/cho: 1.5 times) and the duricrust (WPDD0019-1, average REEs/cho: 4 times). Cerium and Eu display several differences in their geochemical behaviours in this core. In particular, Ce always shows negative anomalies throughout the local weathering profile. In addition, the Ce/Ce* index has a very irregular trend (Fig. 4.4d), and a narrow range of values (0.01-0.77). Another remarkable difference in the geochemical behaviour of REEs in this core respect to the previous core, regards Eu. The initial Eu/Eu* ratio of the serpentinized parent rock in this core (WPDD0019-14, 0.93) is higher than in the core WPDD0012. In addition, differently from the latter drillcore, Eu does not yield anomalies (Fig. 4.4c) and, as shown by Fig. 4.4d, the Eu/Eu* ratio is relatively more constant, with values ranging between 0.80 and 1.15. Fig. 4.3b shows the scandium trend in the core WPDD0019. Even though in this core Sc has very low concentrations (5-27 ppm), its geochemical trend is significantly different to that measured in the core WPDD0012. In particular, the geochemical behaviour of Sc in

WPDD0019 is very similar to the behaviour of Fe_2O_3 and Ni (Fig. 4.3b). Nevertheless, the highest Sc concentrations are detected in the oxide sample WPDD0019-2 and in the saprolite sample WPDD0019-6 (23 and 27 ppm respectively). The correlation matrix of the core WPDD0019 (Table 4.4) confirms that the High-Tech metals deportment in this core is different from WPDD0012. In particular, although the REE*-Co (r = 0.76, *p*-value = 0.00) and the REE*-MnO (r = 0.70, *p*-value = 0.01) correlations are high, a strong REE* correlation has been observed also with Fe_2O_3 (r = 0.71, p-value = 0.01). Furthermore, the REE*-Ce (r = 0.93, *p*-value = 0.00) and REE*-Eu (r = 1.00, *p*value = 0.00) associations are remarkably higher, if compared to those of the previous core. As a corollary, Eu and REE*, and less Ce, display variably similar positive correlations with Fe_2O_3 (r = 0.68, p-value = 0.01; r = 0.71, pvalue = 0.01; r = 0.79; p-value = 0.00, respectively), MnO (r = 0.75, p-value = 0.00; r = 0.70, p-value = 0.01; r = 0.39, p-value = 0.19, respectively) and Co (r = 0.82, p-value = 0.00; r = 0.76, p-value = 0.00; r = 0.48, p-value = 0.10, respectively). Finally, the strong Ce-Al₂O₃ positive correlation observed in the WPDD0012 core is not present in the WPDD0019 profile (r = 0.18, *p*-value = 0.55). Regarding Sc, although also in this drillcore positive correlations have been observed with SiO₂ and Ni (r = 0.46, *p*-value = 0.11; r = 0.75, *p*-value = 0.00 respectively), the correlation matrix confirms its strongly different deportment. In fact, remarkable positive correlations have been detected also with Al₂O₃ and Fe₂O₃ (r = 0.85, p-value = 0.00; r = 0.74, p-value = 0.00, respectively).

4.3.3 The ultramafic index of alteration (UMIA)

In order to assess the geochemical variations triggered by the chemical weathering, the ultramafic index of alteration (UMIA) has been calculated in the considered profiles. This calculation has been performed following the formula proposed by Babechuk et al. (2014) and by Aiglsperger et al. (2016):

$$UMIA = 100 \times [(Al_2O_3 + Fe_2O_{3(t)})/(Al_2O_3 + Fe_2O_3 + SiO_2 + MgO)]$$

In the MgO-SiO₂-(Al₂O₃+Fe₂O_{3(t)}) ternary plot (Fig. 4.5) the geochemical trend of the profile intercepted by core WPDD0012 is characterized by an initial loss of MgO in the transition between the gabbro (WPDD0012-18, UMIA: 13.45)

and the saprolite zone (WPDD0012-15 to WPDD0012-17, average UMIA value: 22.55). Afterwards, a strong SiO_2 depletion has been observed in the oxide zone, where the UMIA index reaches its highest values (UMIA range values in oxide: 47.24–89.68), with the exception of relatively low UMIA values detected in the mottled clays-rich horizons (e.g. WPDD0012-8 to WPDD0012-9, average UMIA value: 46.61). The duricrust (WPDD0012-1) lies outside the "classic" lateritization trend, because it shows a lower UMIA (27.22) and a relative gain in both MgO and SiO₂. In the core WPDD0019, the serpentinized protolith (WPDD0019-14) has a low UMIA value (6.89) and, if compared to the gabbro of the core WPDD0012, it has a higher MgO content. Also in this case the saprolite unit shows a progressive loss in MgO and, if compared to the losses occurring in the WPDD0012 drillcore, it results in a lower UMIA average value (about 15). In general, the thin oxide zone of the core WPDD0019 shows a lower UMIA (WPDD0019-2 to WPDD0019-3, average UMIA value: 46.05), if compared to the values calculated in the previous core.



Fig. 4.5: MgO-SiO₂-(Al₂O₃+Fe₂O₃) molar ternary plot, showing the geochemical variations during the chemical weathering of cores WPDD0012 and WPDD0019 and the comparison to

those of the mineralized laterites of Moa Bay, Cuba (Aiglsperger et al., 2016) and Loma Ortega, Dominican Republic (Tauler et al., 2017).

In particular, the bottom specimen of the oxide zone (WPDD0019-3) falls within the saprolite field, whereas the oxide sample WPDD0019-2 has a similar UMIA value (74.24) to that calculated in oxide core samples from the core WPDD0012. Also in this core, the duricrust (WPDD0019-1) is located outside the general trend, with an UMIA value of 26.86.

4.4 Discussion

4.4.1 Ni- and Co-grades and geochemical evolution of the studied profiles

The results of the whole-rock chemical analysis have shown the geochemical complexity of the Wingellina orebody. The laterite profiles intercepted by the two studied drillcores show similar Ni-grades (WPDD0012: 1.42 wt% Ni; WPDD0019: 1.73 wt% Ni). The results obtained indicate that, even though the Wingellina laterite is an oxide-type deposit, the silicate zones (i.e. saprolite horizon) also display remarkably high Ni-grades (WPDD0012, average Nigrade: 2.52 wt%; WPDD0019, average Ni-grade: 1.83 wt%). Therefore, as proposed by many authors (e.g. Berger et al., 2011; Tauler et al., 2017), the classification of the Ni-laterites based on the dominant ore-bearing mineralogy (i.e. oxide-type, clay silicate-type and hydrous Mg silicate-type, e.g. Freyssinet et al., 2005; Golightly, 2010) is an oversimplification, which must be applied with care. Cobalt displays high values in the core WPDD0012 (0.28 wt% Co), whereas it is less enriched in the core WPDD0019 (0.09 wt% Co); in general the highest Co concentrations are found within the oxide zones (WPDD0012, average Co-grade: 0.39 wt%; WPDD0019 average Co-grade: 0.57 wt%). The geochemical evolution of the Wingellina laterite profiles, together with the drillcore characteristics, have provided useful insights about the influence of a range of external controlling factors (e.g. bedrock lithology, drainage conditions, climate etc.) on the local ore-forming processes. The two mineralized laterite profiles of WPDD0012 and WPDD0019 drillcores have both similar, as well as different features. As shown by the geochemical logs (Fig. 4.3a, b), exemplified in the MgO-SiO₂-(Al₂O₃+Fe₂O₃) ternary plot (Fig. 4.5), the transition zones between the parent rocks and the saprolite units of the two laterite profiles are both characterized by a sharp drop in the MgO

concentration and by a gain of SiO₂ and Ni. Nevertheless, the genesis of the silicate-rich unit of the core WPDD0012 is marked by a significantly higher Al₂O₃ gain (Al₂O₃ average values in the saprolite: 13.32 wt%), if compared with that of the core WPDD0019 (Al₂O₃ average values in the lower saprolite: 4.34 wt%). This remarkable geochemical difference between the two laterite profiles suggests the occurrence of different saprolitization processes, which are likely related to the variable bedrock mineralogy and geochemistry. Regarding the WPDD0012 profile, the above-mentioned geochemical evolution suggests that the hydrolysis of the primary minerals of the local parent rock (clinopyroxenes, orthopyroxenes, plagioclase and subordinate forsterite) has enhanced the formation of a smectite-rich saprolite horizon (Putzolu, 2017). This characteristic is consistent with the observations of other authors (Nahon et al., 1982; Colin et al., 1990), who discovered that under intense weathering conditions the incongruent dissolution of pyroxenes is the main trigger for the neo-formation of Ni-bearing smectites. In addition, the Al₂O₃ gain in the saprolite zone is consistent with the direct precipitation (neo-formation) of smectite (e.g. montmorillonite) from pyroxenes (Freyssinet et al., 2005). In the silicate-dominant laterite of the WPDD0019 profile, the unweathered bedrock is not intersected by the drillhole. However, the geochemical characteristics of the deeply serpentinized protolith (i.e. saprock), occurring within the local saprolite, suggest a potential variation of the parent rock lithology. In particular, the Eu/Eu* ratio observed in the WPDD0019 saprock is slightly higher (Eu/Eu* = 0.93) than that of the fresh parent rock intercepted by the core WPDD0012 (WPDD0012-18, $Eu/Eu^* = 0.88$). This geochemical difference would suggest that the WPDD0019 laterite profile is developed from a more primitive lithology, likely corresponding to one of several peridotite units occurring in the Wingellina Hill mafic to ultramafic layered intrusion (Ballhaus and Glikson, 1989). The primary components of the Wingellina Hill magmatic sequence correspond mainly to websterite and wehrlite (Ballhaus and Glikson, 1989). Therefore, the geochemical and mineralogical characteristics (Putzolu, 2017) observed in the lower saprolite in the drillcore from this locality suggest a strong control of the parent rock mineralogy (mostly ferromagnesian minerals) on the ore-forming process, which was probably dominated by hydrothermal alteration and serpentinization, rather than by neoformation of clays after weathering (as in the case of drillcore WPDD0012). This fact is in agreement with previous literature data, which consider the serpentinization process to be commonly affecting the olivine- and pyroxenerich protoliths, i.e. prevailingly ultramafic rocks (McCollom and Seewald, 2013). Another characteristic of the saprolite horizon in the core WPDD0019 is the "zoned" geochemical trend of MgO. More in detail, the MgO amount strongly increases in the lower saprolite, whereas it decreases within the upper saprolite. The progressive MgO loss is coeval with a significant increase in concentration of Fe_2O_3 and locally even with a high Ni-grade. This particular feature suggests an instability increase in the serpentines occurring in the lower saprolite, and hence the neo-formation of secondary serpentines, and of clay minerals and Fe-hydroxides (Golightly and Arancibia, 1979; Freyssinet et al., 2005), according to the following reactions:

 $Mg_{3}Si_{2}O_{5}(OH)_{4} + Ni^{2+} = (Mg,Ni)_{3}Si_{2}O_{5}(OH)_{4} + Mg^{2+}$

primary serpentine

Ni serpentine

 $2(Mg, Fe)_3Si_2O_5(OH)_4 + 3H_2O = Mg_3Si_4O_{10}(OH)_2*4H_2O + 2Mg^{2+} + FeOOH$

primary serpentine smectite goethite
$$(Mg, Fe)_3Si_2O_5(OH)_4 + 3H^+ = FeOOH + 2SiO_2 + 2Mg + + 3H_2O$$

primary serpentine goethite quartz

The occurrence of secondary silica veins and box-works within the local upper saprolite zone (Fig. 4.2e) is consistent with the observations carried out by other authors on other deposits (e.g. Golightly, 1981; Tauler et al., 2017), who affirmed that in poorly drained systems the weathering of serpentines enhances the formation of quartz and clay minerals. In the specific case of the profile intersected by the core WPDD0019, the occurrence of a thick, massive and poorly jointed serpentinite could have prevented the complete leaching of silica, thus explaining also the poor development of the local limonitic orebody and the generally low UMIA values (Fig. 4.5). Several analogies in the geochemistry of the oxide zones in the two studied profiles have been detected. Firstly, the transition toward the oxide zone in both profiles is marked by the complete leaching of MgO (the "Mg-discontinuity"; Brand et al., 1998), SiO₂ and Al₂O₃ and by a significant gain of Fe₂O₃ (Figs. 4.3a, b and 4.5). These geochemical trends could reflect the progressive acidification of the soil

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solutions, commonly occurring in the uppermost zone of the weathering profile (Golightly, 2010), thus enhancing the instability of the silicate phases (i.e. smectitic clay and/or serpentine) and the precipitation of late-stage Fe-oxyhydroxides (Nahon et al., 1982). In this framework, it is known that the vertical variation in pH strongly affects the paragenetic evolution of the mineralogical association within the laterite profiles, thus controlling the Ni deportment and its speciation (Golightly, 1981, 2010). This process is well displayed by the Ni geochemistry in both the studied profiles. In particular, the Ni distribution (Fig. 4.3a and b) is positively correlated with SiO_2 in the saprolite, whereas within the oxide zone it is correlated with MnO, Co and to a less extent to Fe₂O₃, thus confirming that the highest-grade zones of the limonitic orebody are characterized mainly by the occurrence of Mn-oxy-hydroxides (Putzolu et al., 2018). In this context, Co is found to be strictly associated with MnO throughout the laterite profiles of both drillcores, with the highest grade observed within the oxide units. This geochemical affinity has been described by many authors (e.g. McKenzie, 1989), who argued about the capability of the Mn-oxy-hydroxides to uptake Co due to their fine particle sizes, which offer a large surface area for metal adsorption. During lateritization also the Mn distribution, and thus the precipitation of Co(Ni)-bearing Mn-oxy-hydroxides, is controlled by the Eh-pH variation in the weathering profile. In both the studied profiles, the first significant gain of MnO occurs in the lowermost part of the oxide zones, at the transition with the saprolite sections. This MnO behaviour is quite common in Ni-Co laterite. In fact, as shown by Dublet et al. (2017), the early stage weathering (i.e. saprolitization) of the parent rock promotes the oxidation of Mn^{2+} to Mn^{3+} and lastly to the most stable ionic species, Mn⁴⁺. This process stimulates an efficient precipitation of Mn-oxyhydroxides at the transition from the saprolite toward the oxide zone, along which higher humidity and a slightly more alkaline pH enhance the stabilization of such phases (Dublet et al., 2017). The main geochemical difference between the two oxide units is that the oxide orebody of the core WPDD0012 is locally characterized by the occurrence of few Al₂O₃-rich and Fe₂O₃-poor zones, which are mirrored by the kaolinite-rich mottled clay horizons. This difference can be mainly ascribed to the higher input of Al₂O₃ provided by the local gabbro/gabbronorite bedrock, which resulted in the neo-formation of kaoliniterich zones within the limonitic body. A significant enrichment of the mobile elements (i.e. Mg, Ca and Si) and a decrease in Fe, Al, and Mn (together with the Ni- and Co-grades) occurs at the boundary between the oxide and the duricrust in both drillcores (Figs. 4.3a, b and 4.5). These geochemical trends can provide interesting information about the post-formation process that affected the geochemical evolution of the Wingellina orebody, because they can reflect a significant climatic variation, leading to a decrease of the weathering rate and to calcification and silicification processes in the uppermost zone of the laterite profile (Golightly, 2010). In the Australian Ni-Co laterite deposits of the Yilgarn craton, this post-formation process was caused by the north-easterly drifting of the continent starting in Tertiary (mid-Miocene), which consequently produced an increased aridity during Late Miocene-Pliocene. Thus, both calcification and silicification processes prevailed over ferruginization in the uppermost sections of the laterite profiles (Tardy and Roquin, 1998; Anand and Paine, 2002).

4.4.2 Geochemical behaviour of REEs and Sc

4.4.2.1. Rare Earth Elements

The geochemical behaviour of REEs is very variable in the Wingellina laterite. In the analyzed samples, these elements are preferentially concentrated within the oxide zones of the studied profiles, where their concentration reaches values up to 890 ppm. The REEs speciation is strongly controlled by the mineralogical characteristics of the limonitic ore. In particular, a positive correlation of the REEs with MnO (Tables 4.3 and 4.4) could suggest that the remobilization of lanthanides and their accumulation in Mn-oxy-hydroxides was due to chemical weathering, which is commonly enhanced by bacterial activity (Davranche et al., 2005; Laskou and Economou-Eliopoulos, 2007; Pourret et al., 2010; Vodyanitskii, 2012; Kalatha and Economou-Eliopoulos, 2015; Aiglsperger et al., 2016). In addition, the correlation of REEs with the most representative oxides, as well as with Ni and Co in the core WPDD0012 (Table 4.3) shows that a significant geochemical and mineralogical decoupling occurred between Ce, Eu and the other REE (i.e. REE*). In particular, REE* and Eu are chiefly associated with MnO and Co. As reported by Putzolu et al. (2018), the MnOand Co-rich horizons of the Wingellina limonitic orebody contain lithiophoriteasbolane intermediates, which, as reported by Mongelli et al. (2015), can scavenge REEs through sorption processes in supergene settings. Cerium has a very different behavior, which is highlighted both by the positive correlation with Al₂O₃ (Table 4.3), and by the REEs chondrite normalized patterns (Fig.

4.4a and c), where several Ce positive and negative anomalies can be observed. In general, these anomalies produced under a weathering regime, are mainly due to the oxidation of cerium from trivalent (Ce^{3+}) to tetravalent state (Ce^{4+}). This process could also trigger the precipitation of supergene REEs-bearing minerals such as fluoro-carbonates, Ce-oxides and phosphates (Braun et al., 1990), as already observed in other Ni-Co laterite deposits (e.g. Moa Bay in Cuba and Falcondo in the Dominican Republic, Aiglsperger et al., 2016). The higher Ce-Al₂O₃ positive correlation occurs in the WPDD0012 drillcore. The local laterite profile also shows that the highest Ce/Ce* values occur in the uppermost zone of the oxide unit, whereas the negative values occur in the lower oxide zone. This characteristic is consistent with a REEs redistribution within the orebody, and with Ce fractionation and concentration in the uppermost zone of the deposit (Mongelli et al., 2014). Another interesting feature of the REEs geochemistry of the WPDD0012 samples is the significant REE concentration (highest REEs amount 891 ppm) observed in the relatively MnO-poor (2.04 wt% MnO) and Al₂O₃-rich mottled zone (sample WPDD0012-8). As reported by Putzolu et al. (2018), the mottled zone of the limonitic orebody mainly consists of kaolinite, with only minor lithiophorite. The above quoted sample lies outside the MnO-REEs correlation trend (Fig. 4.3a), thus suggesting a different mode of REEs enrichment. Similar significant REEsenrichments in the MnO-poor zones of the lateritic profile have been observed by Aiglsperger et al. (2016) in the mottled zones of the limonitic orebody of the Moa Bay laterite deposit (Cuba), and have been considered to be related to REE adsorption into clays, following a ion adsorption-type concentration process. However, in our case, the mottled clay sample (WPDD0012-8) is also characterized by a significant P_2O_5 concentration (0.15 wt% P_2O_5), which together with positive correlation of Ce with Al₂O₃, could also suggest the occurrence of REEs into LREE-Al-bearing phosphates. Nevertheless, both the occurrence modes need to be verified through dedicated mineralogical investigations. The REEs patterns of the core WPDD0012 display negative Eu anomalies. As reported in the existing literature (McLennan et al., 1993) Eu should have a refractory behavior during weathering, therefore the Eu/Eu* ratio of the many horizons of the laterite profile should reflect that of the local parent rock. In the Wingellina case, the Eu/Eu* index not only varies broadly (0.21-0.83) through the laterite profile, but it is also quite different from that measured in the gabbro/gabbronorite bedrock (0.88). This anomalous behaviour of Eu could be related to the original deportment of REE in the different

minerals of the gabbro/gabbronorite protolith. As shown by Weill and Drake (1973), the Eu enrichment or depletion in igneous rocks is mainly due to the Eu tendency to be incorporated into plagioclases, preferentially over other minerals. Therefore, in the Wingellina case, Eu could have been mostly hosted in the plagioclases of the parent rock, whereas the other REEs were mainly hosted by accessory minerals, such as sphene, zircon and apatite (Frey et al., 1968). Therefore, the Eu/Eu* variation could be attributed to the different response to chemical weathering of REE-bearing accessory phases compared to plagioclase, which likely produced a preferential leaching of Eu in the supergene environment from the highly unstable plagioclases of the protolith, whereas the other REEs remained in the more stable REEs-bearing accessory minerals. This is in agreement with previous literature (Babechuk et al., 2014), which argued about the contribution of the occurrence of plagioclase-bearing parent rocks on the loss of Eu in the weathering products. The REEs geochemical deportment in the profile WPDD0019 is characterized by several differences, if compared to that of the WPDD0012 drillcore. Firstly, the REEs enrichment in the WPDD0019 oxide zone (up to 377 ppm) is much lower if compared to the former drillcore. The lower gain of REEs observed within core WPDD0019, together with the higher Eu/Eu* ratio, is in agreement with the development of the local laterite profile from a predominantly ultramafic protolith, depleted of incompatible elements (such as REEs). In addition, according to the correlation parameters (Table 4.4) and to the relatively flat REEs patterns (Fig. 4.4c) observed in WPDD0019, the REE*-Eu-Ce fractionation is lower if compared to that of the core WPDD0012. Therefore, one the main controlling factor of the lower REEs enrichment in the WPDD0019 laterite profile could be the less significant LREE-HREE fractionation, which prevented the neo-formation of LREE-bearing phases (Braun et al., 1990; Mongelli, 1997; Mameli et al., 2007; Mondillo et al., 2011), leading to REEs uptaking mainly in the Fe-oxy-hydroxides and less in the Mnoxy-hydroxides. Another important variation of the REEs deportment, and more specifically of that of Ce, is their correlation with Fe_2O_3 (Fig. 4.3b and Table 4.4) that confirms the observation of other authors (e.g. Vodyanitskii, 2012), who suggested that lanthanides behave not only as manganophilic but also as siderophilic elements. Other important characteristics of the REEs geochemistry in core WPDD0019 are the absence of Eu anomalies (Fig. 4.4d) and the almost constant Eu/Eu* ratio (0.80–1.15, Fig. 4.4c), which support the absence of plagioclase from the local protolith and, differently from core WPDD0012, a homogenous leaching of REEs from the primary minerals of the protolith.

4.4.2.2 Scandium

The Sc content of the studied profiles of the Wingellina Ni-Co laterite deposit is significantly lower (WPDD0012, average Sc content: 54 ppm; WPDD0019, average Sc content: 15 ppm) if compared to economic deposits, where this element reaches concentration values up to 800 ppm (e.g. Syerston-Flemington, New South Wales, Australia; Chassé et al., 2016). However, the current study can provide useful information about its geochemical deportment. Firstly, the highest Sc concentrations are found within the silicate-rich zones of the sets of core samples from both WPDD0012 and WPDD0019 (maximum Sc values of 140 and 27 ppm respectively). This characteristic is in contrast with the observations carried out by Audet (2008) and Aiglsperger et al. (2016), who observed a clear tendency of Sc to concentrate in the uppermost horizons of the laterite profiles (i.e. oxide units). Secondly, the sharp difference of the Scgrades in the two profiles considered could be interpreted in terms of a variation of the enrichment modality, and hence of the nature of Sc-bearing minerals. In fact, the Sc trend in core WPDD0019 is positively correlated with that of Fe₂O₃ (Fig. 4.3b and Table 4.4), this suggesting the uptaking of Sc^{3+} into neo-formed Fe-oxy-hydroxides (Chassé et al., 2016), which occur as subordinate minerals in the saprolite unit (Putzolu, 2017). Regarding to the core WPDD0012, the Sc-Fe₂O₃ geochemical affinity was not detected and Sc is chiefly associated with and Si and Ni. This association can be interpreted as a proxy of the Sc remobilization during the lateritization process. However, the positive correlations of Sc with SiO₂ (cores WPDD0012 and WPDD0019) and with Al_2O_3 (core WPDD0019) are quite atypical. The Sc-Si association in the phyllosilicate-rich saprolite sections could potentially reflect the Sc occurrence in clay minerals. In fact, as reported by Birgu (1981), in the Fe³⁺-bearing layered silicates (such as montmorillonite and chlorite), Sc could be able to enter in the crystal lattice as substituting for Fe^{3+} in the (di)octahedral site. However, further and more detailed mineralogical investigations are needed to better constrain the mineral deportment of this element in the Wingellina deposit.

4.5 Conclusions

The study of the Wingellina Ni-Co laterite deposit (Western Australia) has shown that the combination of geochemical and mineralogical data, together with a targeted analysis of the facies variability can provide an useful tool to define the controlling factors affecting the Ni and Co supergene enrichment and the main ore-forming processes acting during lateritization. The geochemical evolution of the deposit, the Ni-Co enrichment and the development of several different facies in the laterite profile are strongly affected by the heterogeneity of the parent rock lithology, which likely controlled the degree of hydrothermal serpentinization, the efficiency of the drainage system and thus the dynamics of the lateritization process. The High-Tech metals have a variable geochemical deportment at Wingellina:

(i) REEs are remarkably concentrated within specific zones of the oxide units, which primarily correspond to Mn- and Fe-oxy-hydroxides rich horizons and locally to mottled clayey Al-rich units. A significant geochemical decoupling of REEs has been also observed. The Ce deportment suggests that its speciation was locally controlled by its oxidation from Ce^{3+} to Ce^{4+} and potentially by its uptaking in Fe-oxy-hydroxides at the top of the laterite profile. The other REEs are enriched within the MnO- and Fe₂O₃-rich zones of the orebody, which suggests their capture in Mn- and Fe-oxy-hydroxides.

(ii) Even though the Sc enrichment in the studied laterite profiles is negligible, several geochemical proxies suggesting its remobilization and enrichment during the weathering process have been identified. The Sc geochemical behavior is variable and complex, with the higher Sc-grades observed in the silicate zones of the deposit. This feature is in contrast with previous studies carried out on other Ni-Co laterite deposits and, therefore, more detailed mineralogical assessments will be necessary to better constrain the mineralogical deportment of REEs and Sc within the Wingellina orebody.

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 Table 4.1: Chemical composition of the laterite profile of drillcore WPDD0012

	Sample ID	WPDD0012-1	WPDD0012-2	WPDD0012-3	WPDD0012-4	WPDD0012-5	WPDD0012-6	WPDD0012-7	WPDD0012-8	WPDD0012-9	WPDD0012-10	WPDD0012-11	WPDD0012-12	WPDD0012-13	WPDD0012-14	WPDD0012-15	WPDD0012-16	WPDD0012-17	WPDD0012-18
	Unit*	D	L	L	L	L	L	L	L	L	L	L	L	L	L	S	S	S	Р
SiO ₂	wt%	8.18	2.22	2.70	3.05	3.56	3.50	16.07	30.53	34.83	10.28	25.62	11.21	4.38	31.81	46.46	49.50	55.38	49.70
Al_2O_3	wt%	4.39	4.76	19.59	19.20	19.02	18.50	33.29	26.42	29.26	8.43	20.77	9.25	5.14	25.08	13.61	10.60	15.76	11.81
Fe ₂ O ₃	wt%	16.57	64.02	54.70	54.48	53.99	55.65	25.95	23.99	12.55	60.18	30.28	54.49	58.38	24.56	21.72	18.12	7.03	4.34
MgO	wt%	12.00	1.24	0.99	0.77	0.83	0.68	0.67	0.42	0.69	1.08	1.08	0.80	0.63	0.64	3.24	4.45	6.25	14.53
CaO	wt%	21.86	0.35	0.07	0.06	0.08	0.07	0.05	0.06	0.09	0.07	0.11	0.12	0.20	0.07	0.25	0.32	0.51	17.68
Na ₂ O	wt%	0.09	0.51	0.12	0.04	0.18	0.10	0.07	0.10	0.15	0.05	0.10	0.07	0.05	0.07	0.12	0.17	0.15	0.52
K_2O	wt%	0.12	0.07	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.02	0.03	< 0.01	0.02	< 0.01	0.11	< 0.01	< 0.01	0.02	0.02	< 0.01
TiO ₂	wt%	0.24	0.34	0.24	0.28	0.27	0.20	1.52	3.43	0.36	0.29	0.86	0.24	0.07	0.10	0.39	0.31	0.14	0.10
P_2O_5	wt%	0.01	< 0.01	< 0.01	< 0.01	0.02	0.02	0.20	0.15	< 0.01	< 0.01	< 0.01	0.02	0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
MnO	wt%	0.36	9.13	1.55	1.86	1.99	2.02	0.22	2.04	5.79	0.84	5.04	5.76	12.95	2.83	0.82	0.17	0.22	0.09
Cr_2O_3	wt%	0.97	0.56	0.43	0.64	0.27	0.35	2.65	0.17	0.25	4.13	0.26	0.54	0.55	0.09	1.18	2.75	1.05	0.39
Ni	wt%	0.50	2.10	0.83	1.24	1.14	1.21	0.33	0.43	1.21	1.07	1.80	2.10	1.78	0.95	2.13	3.33	2.10	0.07
Co	wt%	0.03	0.57	0.10	0.13	0.20	0.10	0.02	0.06	0.60	0.14	0.63	0.92	1.23	0.41	0.04	0.01	0.01	0.00
LOI	wt%	34.05	13.18	18.27	17.66	17.90	17.05	18.62	11.40	13.45	12.91	12.76	13.49	13.57	12.96	9.13	9.11	10.49	0.38
Sc	ppm	13	48	37	53	38	37	44	28	11	52	40	51	52	80	129	140	66	42
Cu	ppm	30	60	60	60	100	60	110	40	20	70	60	50	50	10	10	20	10	20
Nb	ppm	<5	<5	<5	<5	<5	<5	<5	128	84	<5	10	<5	<5	<5	<5	<5	<5	7
Ba	ppm	239	336	92	310	197	244	9	346	400	18	132	176	805	14	41	8	34	17
Be	ppm	<1	<1	<1	<1	<1	<1	<1	2	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Cs	ppm	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Ga	ppm	4.3	20.7	14.7	17.8	16.7	18	28.6	35.8	59.7	15.1	23.8	16.6	16.8	13.4	10.8	8.8	6.8	7.7
Hf	ppm	3.5	0.4	0.2	0.3	0.4	0.2	3.4	75	2.6	0.4	1.9	0.4	0.1	< 0.1	0.5	0.4	0.2	0.1
Nb	ppm	1.7	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	8.5	129.2	87.6	0.4	8.7	0.2	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	0.8
Rb	ppm	3.9	1	< 0.1	< 0.1	0.3	0.1	0.6	1	1.7	0.8	0.8	0.4	1.7	< 0.1	0.7	1.3	0.8	< 0.1
Sr	ppm	933.8	126.1	15.3	19.6	23.3	39.3	11.4	47.6	32.6	12.3	46.1	67.6	290.9	25.7	46.8	41	47.8	53.7
Та	ppm	0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	0.5	6.4	4.7	< 0.1	0.6	< 0.1	< 0.1	<0.1	< 0.1	< 0.1	< 0.1	< 0.1
Th	ppm	0.5	< 0.2	< 0.2	< 0.2	<0.2	< 0.2	1	10.5	30.6	<0.2	1.4	0.4	< 0.2	<0.2	< 0.2	0.2	< 0.2	< 0.2
U	ppm	1.2	< 0.1	< 0.1	<0.1	0.2	0.2	1.2	2.6	1.8	1.4	0.8	0.6	0.5	0.4	0.1	0.3	0.2	< 0.1
v	ppm	97	190	184	240	259	295	347	190	78	267	194	336	243	196	275	140	116	169
W	ppm	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	4.3	<0.5	0.7	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Zr	ppm	142	11.8	9	8.5	10.6	7.5	136.6	3073.9	49.6	12.5	54.5	11.2	4.9	2.2	11.5	9.5	6.3	3.4
Y	ppm	3.2	20.7	7.2	7.8	15.8	7.5	8.7	50.3	29.4	24.2	17.6	38.1	51.5	5.7	9	11.9	34.4	4.1
La	ppm	2	7.3	3.1	4.7	3.5	4.5	14.6	165.2	19.3	13.5	19.9	20	84	2.5	10.2	3.4	12	1.5
Ce	ppm	5.2	23.3	32.1	46.8	60.3	96.7	12.1	501.3	268.1	4.7	57.6	2.4	12.2	2.3	1.9	0.8	1.8	0.9
Pr	ppm	0.57	2.28	2.05	1.58	1.79	1.78	2.83	35.51	5.05	2.69	8.62	11.15	36.26	1.15	3.04	0.81	4.14	0.19
Nd	ppm	2.5	11	9.1	7.1	9	8.2	11.5	127.4	19.4	13.2	38.4	50	144.3	5	11.7	3.2	17	0.9
Sm	ppm	0.58	1.94	2.75	2.5	3.87	2.54	2.37	18.77	4.5	4.63	7.42	12.43	32.46	1.08	1.89	0.86	3.46	0.31
Eu	ppm	0.15	0.62	0.76	0.67	1.14	0.66	0.48	1.19	0.69	0.93	1.35	2.55	6.45	0.24	0.46	0.29	1.08	0.12
Gd	ppm	0.58	3.37	2.55	2.25	4.43	2.38	2.16	13.99	4.99	4.2	6.09	11.57	26.68	1.22	2.31	1.58	5.8	0.5
Tb	ppm	0.09	0.4	0.44	0.45	0.95	0.45	0.34	1.71	0.83	0.87	0.97	2.2	4.77	0.21	0.35	0.34	1.07	0.1
Dy	ppm	0.57	2.66	2.74	2.79	5.81	2.63	2.15	9.42	5.21	5.3	5.53	13.2	26.59	1.44	2.3	2.34	7.38	0.72
Ho	ppm	0.1	0.6	0.51	0.55	1.17	0.5	0.41	1.9	1.08	1.03	1.07	2.48	4.98	0.25	0.5	0.54	1.61	0.15
Er	ppm	0.34	1.48	1.42	1.64	3.53	1.46	1.29	5.97	3.26	3.11	2.98	6.92	13.13	0.75	1.36	1.75	4.67	0.45
Tm	ppm	0.05	0.14	0.15	0.24	0.47	0.22	0.19	0.96	0.49	0.5	0.44	0.98	1.75	0.09	0.18	0.25	0.55	0.05
Yb	ppm	0.43	0.82	1.01	1.57	2.29	1.25	1.39	7.18	2.99	3.55	2.61	5.53	9.56	0.51	1.06	1.64	3.2	0.31
Lu	ppm	0.05	0.11	0.13	0.21	0.35	0.18	0.2	1.23	0.46	0.5	0.41	0.83	1.35	0.07	0.16	0.27	0.51	0.05
KEES	ppm	13.21	56.02	58.81	/3.05	98.60	123.45	52.01	891.73	336.35	58.71	153.39	142.24	404.48	16.81	37.41	18.07	64.27	6.25
Ce/Ce*		1.17	1.38	3.07	4.14	5.80	8.23	0.45	1.58	6.54	0.19	1.06	0.04	0.05	0.33	0.08	0.12	0.06	0.41
Eu/Eu*		0.75	0.70	0.83	0.82	0.79	0.77	0.61	0.21	0.42	0.61	0.58	0.61	0.63	0.60	0.64	0.72	0.70	0.88
UMIA		27.22	87.27	89.68	89.53	88.11	88.79	68.10	49.22	43.99	71.20	50.73	69.24	83.06	47.24	27.11	21.43	19.10	13.46

Unit abbreviations: D= duricrust; L= oxide; S= Saprolite; P= Protolith.

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Table 4.2: Chemical composition of the laterite profile of drillcore WPDD0019

	Sample ID	WPDD0019-1	WPDD0019-2	WPDD0019-3	WPDD0019-4	WPDD0019-5	WPDD0019-6	WPDD0019-7	WPDD0019-8	WPDD0019-9	WPDD0019-10	WPDD0019-11	WPDD0019-13	WPDD0019-14
	Unit*	D	L	L	S	S	S	S	S	S	S	S	S	S-P
SiO ₂	wt%	7.23	6.47	29.53	62.87	39.82	28.72	44.38	38.16	11.88	40.72	29.23	44.73	8.33
Al_2O_3	wt%	1.18	6.09	2.28	2.97	5.98	9.34	6.62	5	2.02	3.87	4.61	6.44	0.85
Fe ₂ O ₃	wt%	14.99	50.75	13.71	10.6	24.66	30.75	22.74	17.16	6.28	17.98	12.95	23.15	5.38
MgO	wt%	7.18	1.24	1.75	11.79	14.24	13.56	12.21	23.14	18.92	21.64	17.71	12.52	18.93
CaO	wt%	32.82	0.09	0.4	1.04	0.06	0.08	0.06	0.09	22.07	0.11	10.66	0.36	25.36
Na ₂ O	wt%	0.04	0.21	0.33	0.19	0.11	0.14	0.1	0.07	0.07	0.09	0.1	0.16	0.02
K ₂ O	wt%	0.09	0.14	0.4	0.02	<0.01	<0.01	< 0.01	<0.01	< 0.01	< 0.01	< 0.01	< 0.01	<0.01
11O ₂	wt%	0.17	0.08	0.07	0.05	0.13	0.13	0.09	0.05	0.02	0.08	0.05	0.08	0.02
P2O5	wt%	0.01	0.06	< 0.01	<0.01	<0.01	< 0.01	0.01	<0.01	< 0.01	< 0.01	<0.01	< 0.01	<0.01
MnO Cr.O.	wt%	0.03	17.51	55.8/	0.52	0.3	0.33	0.51	0.2	0.07	0.21	0.17	0.24	0.05
CI2O3	W1%	0.377	0.23	0.55	0.015	1.507	1.639	1.41/	0.969	0.545	1.243	0.85	1.422	0.385
Co	wt%	0.203	0.45	2.8	0.010	0.028	0.033	0.029	2.0	0.007	2.4	0.347	0.080	0.135
LOI	wt%	35 33	13.58	11.85	6.6	0.028	10.6	8.74	11.27	36.08	10.4	22.79	0.024	40.13
LOI	wt/0	35.55	15.56	11.05	0.0	9.42	10.0	0.74	11.27	50.98	10.4	22.19	9.09	40.15
Sc	nnm	5	23	12	18	21	27	21	17	5	17	8	16	6
Cu	ppm	40	320	140	20	60	40	40	20	20	30	30	70	20
Nb	ppm	17	<5	23	<5	<5	7	8		20	<5	<5	<5	9
Ba	ppm	169	10669	10011	153	28	33	19	33	30	84	52	57	17
Be	ppm	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Cs	ppm	< 0.1	0.3	1.9	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Ga	ppm	2	17	26.4	13.5	10.7	10.3	7.9	5.8	1.6	4.1	3.5	4.9	< 0.5
Hf	ppm	2.4	0.1	< 0.1	< 0.1	0.1	0.2	0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Nb	ppm	2.2	< 0.1	< 0.1	0.8	0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Rb	ppm	3.4	5.8	29.7	1.1	0.4	0.2	0.5	< 0.1	< 0.1	0.1	0.4	0.8	< 0.1
Sr	ppm	438.3	636.3	646.6	35.1	20.3	25.3	22.1	22.3	151.4	26	101.4	50.8	133.9
Та	ppm	0.1	0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Th	ppm	0.7	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2
U	ppm	0.4	0.6	< 0.1	< 0.1	0.2	0.2	0.1	0.1	0.1	0.6	0.2	0.4	< 0.1
V	ppm	45	124	48	24	63	69	72	74	62	101	77	54	40
W	ppm	< 0.5	< 0.5	< 0.5	0.7	<0.5	<0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
Zr	ppm	99.1	2.8	3	1.5	3.1	4.5	3.4	2.6	1	2.2	1.9	2.3	0.6
Y	ppm	3.2	37.1	46.7	6.3	3.1	2.7	2.3	1	2.2	0.7	1.2	<0.1	1.8
La	ppm	3.1	111.3	44.2	3.5	1.8	0.6	1.2	0.8	1.5	1.6	1.5	0.9	1.3
Ce	ppm	4.6	69.1	0.5	0.4	0.6	0.8	1.1	0.7	0.6	0.8	0.8	<0.1	0.5
PT NJ	ppm	0.68	27.03	7.05	0.41	0.14	0.15	0.15	0.06	0.11	0.08	0.09	0.03	0.12
INU Sm	ppin	2.4	17.08	50.8	0.26	0.8	0.9	0.8	<0.5	0.5	0.4	0.4	< 0.5	0.7
5III En	ppin	0.42	5 22	0.77	0.50	0.18	0.24	0.21	0.08	0.09	0.08	0.13	< 0.03	0.18
Gd	ppin	0.13	15.2	2.49	0.15	0.08	0.11	0.1	0.04	0.03	0.03	0.03	<0.02	0.07
Th	ppm	0.02	2 29	1 24	0.09	0.05	0.07	0.04	0.02	0.22	0.02	0.02	<0.03	0.03
Dv	ppm	0.49	12.89	7.11	0.51	0.05	0.43	0.34	0.02	0.18	0.18	0.16	<0.01	0.03
Ho	ppm	0.1	2.3	1 47	0.12	0.06	0.09	0.06	0.03	0.04	0.03	0.03	<0.02	0.06
Er	ppm	0.31	6.19	3.93	0.3	0.2	0.3	0.23	0.11	0.11	0.09	0.12	< 0.03	0.18
Tm	ppm	0.05	0.85	0.46	0.04	0.03	0.03	0.03	0.01	0.02	0.02	0.01	< 0.01	0.01
Yb	ppm	0.35	5.35	2.53	0.22	0.17	0.25	0.19	0.1	0.05	0.1	0.08	<0.05	0.19
Lu	ppm	0.05	0.78	0.4	0.03	0.03	0.03	0.03	0.01	< 0.01	0.02	< 0.01	< 0.01	0.02
REEs	ppm	13.29	377.19	116.83	8.69	4.74	4.36	4.82	2.27	3.49	3.57	3.58	0.93	3.89
Ce/Ce*		0.76	0.30	0.01	0.08	0.29	0.64	0.62	0.77	0.36	0.54	0.52	0.15	0.31
Eu/Eu*		0.80	0.93	0.98	0.96	0.99	1.08	1.08	1.05	1.03	0.88	0.90	1.15	0.93
UMIA		26.86	74.24	17.85	7.34	18.73	28.02	18.13	12.59	9.03	11.91	13.34	17.95	6.89

Unit abbreviations: D= duricrust; L= oxide; S= Saprolite; S-P= Serpenitized protolith.

Francesco Putzolu	Mineralogy and	geochemistry	of Ni and	Co in	lateritic profile.
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	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	CaO	MnO	Ni	Co	Sc	REE*	Ce	Eu
SiO ₂	1.00	0.16	-0.85	0.42	0.11	-0.38	0.23	-0.31	0.50	-0.09	0.08	-0.29
Al ₂ O ₃	0.16	1.00	-0.29	-0.40	-0.37	-0.28	-0.39	-0.23	-0.20	-0.01	0.49	-0.31
Fe ₂ O ₃	-0.85	-0.29	1.00	-0.60	-0.44	0.47	0.12	0.40	-0.16	0.14	-0.16	0.40
MgO	0.42	-0.40	-0.60	1.00	0.91	-0.40	-0.23	-0.39	-0.02	-0.31	-0.27	-0.29
CaO	0.11	-0.37	-0.44	0.91	1.00	-0.28	-0.45	-0.27	-0.28	-0.23	-0.18	-0.24
MnO	-0.38	-0.28	0.47	-0.40	-0.28	1.00	0.28	0.93	-0.20	0.54	0.05	0.76
Ni	0.23	-0.39	0.12	-0.23	-0.45	0.28	1.00	0.29	0.68	-0.02	-0.29	0.22
Co	-0.31	-0.23	0.40	-0.39	-0.27	0.93	0.29	1.00	-0.17	0.50	-0.04	0.78
Sc	0.50	-0.20	-0.16	-0.02	-0.28	-0.20	0.68	-0.17	1.00	-0.18	-0.39	-0.08
REE*	-0.09	-0.01	0.14	-0.31	-0.23	0.54	-0.02	0.50	-0.18	1.00	0.56	0.75
Ce	0.08	0.49	-0.16	-0.27	-0.18	0.05	-0.29	-0.04	-0.39	0.56	1.00	-0.03
Eu	-0.29	-0.31	0.40	-0.29	-0.24	0.76	0.22	0.78	-0.08	0.75	-0.03	1.00

REE* = total Rare Earth Elements expect for Ce and

Eu.

 Table 4.4: Correlation matrix for drillcore WPDD0019 (data expressed as Pearson Correlation Coefficient)

	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	CaO	MnO	Ni	Co	Sc	REE	Ce	Eu
SiO ₂	1.00	0.34	-0.11	0.21	-0.68	-0.20	0.52	-0.21	0.46	-0.40	-0.43	-0.39
Al ₂ O ₃	0.34	1.00	0.70	-0.03	-0.70	-0.13	0.52	-0.07	0.85	0.10	0.18	0.08
Fe ₂ O ₃	-0.11	0.70	1.00	-0.49	-0.51	0.25	0.30	0.34	0.74	0.71	0.79	0.68
MgO	0.21	-0.03	-0.49	1.00	0.10	-0.72	-0.04	-0.75	-0.17	-0.71	-0.55	-0.73
CaO	-0.68	-0.70	-0.51	0.10	1.00	-0.25	-0.77	-0.29	-0.83	-0.23	-0.14	-0.24
MnO	-0.20	-0.13	0.25	-0.72	-0.25	1.00	0.26	0.99	0.05	0.70	0.39	0.75
Ni	0.52	0.52	0.30	-0.04	-0.77	0.26	1.00	0.27	0.75	0.03	-0.11	0.06
Co	-0.21	-0.07	0.34	-0.75	-0.29	0.99	0.27	1.00	0.11	0.76	0.48	0.82
Sc	0.46	0.85	0.74	-0.17	-0.83	0.05	0.75	0.11	1.00	0.27	0.31	0.26
REE*	-0.40	0.10	0.71	-0.71	-0.23	0.70	0.03	0.76	0.27	1.00	0.93	1.00
Ce	-0.43	0.18	0.79	-0.55	-0.14	0.39	-0.11	0.48	0.31	0.93	1.00	0.90
Eu	-0.39	0.08	0.68	-0.73	-0.24	0.75	0.06	0.82	0.26	1.00	0.90	1.00

REE* = total Rare Earth Elements expect for Ce and E_{22}

Eu.

Chapter 5:

Parent rock and climatic evolution control on the genesis of Ni-bearing clays in Ni-Co laterites: New inferences from the Wingellina deposit (Western Australia)

5.1 Introduction

Although the Wingellina Ni-Co deposit is an oxides-dominated laterite, where most of the economically exploitable Ni and Co reserves are hosted in the Mn/Fe-oxy-hydroxides-rich layers within the oxide zone (Putzolu et al., 2018), the extensive drilling program conducted by the company in the last ten years revealed that the laterite profile also contains a well-defined saprolite ore zone that represents a significant proportion of the total reserves (i.e. 35%). Furthermore, the geochemical survey conducted on the saprolite facies highlighted that Ni grades are locally even higher than those detected in the oxide ore, making the clay-endowed section of the Wingellina deposit a key asset for the increase of the exploitable ore resources in the future (Putzolu et al., 2019). Therefore, in this chapter are presented the results of an accurate mineralogical investigation through Quantitative XRPD, One-dimensional modelling of XRPD, EMPA and TEM-HRTEM of the Ni-phyllosilicates occurring in the saprolite horizon of the Wingellina laterite, with the aim of understanding the alteration dynamics controlling the ore mineral genesis and the Ni enrichment during saprolitization of the different magmatic precursors. A particular focus is devoted to the assessment of the main alteration stages that promoted the formation of distinct Ni-phyllosilicates in the context of the climatic evolution of the Australian continent.

5.2 Background information

The ore modelling performed by the company (Phase One Feasibility study) defined a Mineral Reserve of 168 Mt of oxide ore grading 0.98% Ni and 0.08% Co, with an average depth of the oxide zone-saprolite boundary placed at 80 m below the topographic surface. Despite the great extent of the oxide ore, the highest Ni concentrations at Wingellina are measured within the saprolite zone (Putzolu et al., 2019). To distinguish the two ore types and to establish the tonnage and grade of the saprolite zone, the

company used a Fe₂O₃ cut-off at 43 wt% (Fe₂O₃ \ge 43% = oxide ore; Fe₂O₃ < 43% = saprolite). According to this cut-off limit, the saprolite zone represents about 35% of the total reserves and has an average Ni grade of 0.83 wt%. At Wingellina, the saprolite unit is characterized by heterogeneous facies and geochemistry, which were inherited from the different parent rocks (Putzolu et al., 2019). The main facies and lithological features of the saprolite zone are well represented in the drillcores WPDD0012 and WPDD0019 (Fig. 5.1), which we used for the current study. The drillcore WPDD0012, located in the southern zone of the Wingellina prospect, reaches a depth of 78.6 m and intercepts the saprolite formed above a gabbro parent rock at depths between 72 and 76 m (Fig. 5.1a and b). The local phyllosilicate-rich horizon consists of a massive, bright green clayey lithology (Fig. 5.3b and c). The drillcore WPDD0019 (Fig. 5.1d and e), located in the north-western sector of the southern zone of the tenure, reaches a total depth of 56.8 m, and intercepts a serpentinitederived saprolite, between 25 and 55.5 m in depth. In this zone the uppermost portion of the saprolite unit (from 25 to 45 m) consists of brownish clays, locally showing pale green talc-like and quartz-rich coatings (Fig. 5.1e and f). The lower saprolite (from 45 to 55 m) is a waxy and pale green serpentinite unit, wherein carbonate veins are common (Fig. 5.1g and h). In the selected saprolite sections, Ni shows remarkable concentrations (WPDD0012 between 72 and 76 m, average Ni-grade = 2.52wt%; WPDD0019 between 25 and 55.5, average Ni-grade = 1.83 wt%), which are higher than those measured in the overlying oxide units (WPDD0012 = 1.42 wt% Ni; WPDD0019 = 1.73 wt% Ni; Putzolu et al.,2019).

5.3 Sampling strategy and analytical methods

As in all Australian laterite deposits, at Wingellina the intense Mesozoic– Tertiary peneplanation resulted in a flat lying topography that locally intercepts only the uppermost horizons (i.e. duricrust and upper oxide zones) of the weathering profile. Therefore, due to the absence of outcrops with exposures of the saprolite ore, for this study we logged and sampled two saprolite horizons intercepted by drill holes carried out for exploration purposes. The current study was conducted on 8 samples from drillcores WPDD0012 and WPDD0019 (Fig. 5.1a and d): two bedrock samples (gabbro/gabbronorite, sample WPDD0012-18, and serpentinite, sample WPDD0019-11) and three saprolite samples from each drillcore (WPDD0012-17, WPDD000012-16 and WPDD0012-15, and WPDD0019-8, WPDD0019-5 and WPDD0019-4). For the bulk rock mineralogical characterization (patterns BR), about 1 g of powdered sample was examined through X-Ray Powder Diffraction (XRPD) analyses with a Panalytical X'Pert PRO MPD diffractometer, equipped with an X'celerator PSD detector at the Natural History Museum (NHM, London, UK).



Fig. 5.1: a) Stratigraphic column based on drillhole WPDD0012 showing the core samples locations (after Putzolu et al., 2018, modified); b) Drillcore from the saprolite unit of hole

WPDD0012 (depth between 72.3 and 76.5 m, after Putzolu et al., 2018, modified); c) Saprolite sample WPDD0012-15 (depth: 73 m); d) Stratigraphic column based on drillhole WPDD0019 showing the core samples locations (after Putzolu et al., 2018, modified); e) Drillcore from the upper saprolite unit of hole WPDD0019 (depth between 21.1 and 26.8 m); f) Upper Saprolite sample WPDD0019-4 (depth: 25 m); g) Drillcore from the lower saprolite unit of hole WPDD0019 (depth between 49.3 and 55.3 m); h) Serpentinite sample WPDD0019-11 (depth: 54 m). The asterisks indicate the position of the displayed representative samples.

To avoid the effect of Fe fluorescence, as a result of the interaction of the Cu radiation with Fe-rich phases, the XRPD patterns were acquired using a Co K α radiation (K α 1 = 1.78897 Å; K α 2 = 1.79285 Å), operating at 40 kV, and 40 mA, with a Fe filter and a 0.76 mm divergence slit. XRPD patterns were collected between an incident angle of 5 and 100° 2 θ at a step size of $0.02^{\circ} 2\theta$. The run time per step was 75 s. The qualitative data interpretation was conducted with the HighScore Plus (Panalytical) and the PDF-4 database from ICDD (International Centre for Diffraction Data). The mineral quantification was obtained by full profile Rietveld refinement using the TOPAS software (version 4.2). The quantitative mineral analyses were performed through the internal standard Rietveld method, with the addition of 10 wt% of corundum to the bulk rock specimens. The internal standard method allowed the quantification of poorly ordered phyllosilicates (i.e. smectite) by difference from 100% (Cesarano et al., 2018 and references therein). In this context, the contribution of smectite to the bulkrock patterns has been modelled on the basis of the whole-rock geochemical data (Putzolu et al., 2019). The potential contribution of partially disordered or disordered interstratified clays (T/S and C/S) was not determined during the bulk rock Rietveld refinement. The preferred orientation of crystallites was refined through the March function (Dollase, 1986), while the contribution from the instrument was modeled with a Lorentzian crystallite size, a strain component, and a 3rd or 4th order Chebyshev background (Cesarano et al., 2018). To assess the validity of the Rietveld refinement, we used the weighted profile R-factor (Rwp). The XRPD analyses on clay aggregates were carried out on the clay fraction ($\phi < 2 \mu m$) of the saprolite and serpentinite samples. Since that in the gabbro bedrock (WPDD0012-18), the clay component is insignificant this sample has not been subjected to the fine-fraction separation procedure. Separation of the clay fraction from the bulk rock samples was conducted at the Dipartimento di Scienze della Terra, dell'Ambiente e delle Risorse (DiSTAR, University of Naples Federico II, Italy) according to the procedure by Moore and Reynolds

(1997). Each sample was milled at a grain size<1 mm and then quartered. About 25 g of ground material was blended with 500 ml of deionized water in a polypropylene beaker, to undergo a preliminary disaggregation with a SONOPLUS ultrasonic probe for 15 min. After ultrasonic treatment, the <2 µm fraction was obtained by four steps of progressive sedimentation (at 1 min, 5 min, 1 h and 17 h) and two centrifugation cycles (5 min at 5000 rpm, 40 min at 8000 rpm) using a Hettich Rotina centrifuge. During the progressive sedimentation steps, about 3 g of sodium hexametaphosphate [(NaPO₃)₆] was added to the solution, in order to avoid flocculation of clays. The precipitated material after the second centrifugation cycle was blended with 4-5 ml of deionized water, smeared on glass slides and left drying at ambient temperature, to permit the orientation of clays along the d_{001} direction (air dried conditions; patterns AD). Afterwards, the samples were solvated with Ethylene glycol at 80 °C for 24 h (patterns EG), to assess the presence of swelling clay minerals. Phyllosilicates identification was also undertaken by heating the samples at 350 °C (patterns HT-350) and 550 °C (patterns HT-550) for 2 h and 1 h respectively, to assess potential variations in the spacing of the crystal structure (e.g. smectite) or loss of the structure (e.g. kaolinite). XRPD measurements on orientated clay aggregates (patterns AD, EG, HT-350 and HT-550) were carried out at the DiSTAR (Naples, Italy) using a Bruker D2 Phaser diffractometer equipped with a LYNXEYE XE-T detector a Cu K α radiation (K α 1 = 1.54056 Å; K α 2 = 1.54439 Å) operating at 30 kV and 10 mA and with a 0.6 mm divergence slit. The XRPD patterns were collected between 3° and $70^{\circ} 2\theta$, at a step size of 0.02° 2θ and 4 s time per step (464 s eq.). Randomly oriented XRPD patterns on clay aggregates (patterns RO) were acquired to distinguish trioctahedral and dioctahedral phyllosilicates and to identify the nature of polytypes according to their d_{06l} and to their typical d_{hkl} bands, respectively (Moore and Reynolds 1997). The preparations for RO measurement were conducted at the NHM (London, UK). During the preparation of RO mounts, to avoid preferred orientation of the clay fraction samples, the powder was prepared following the side-loading procedure. The RO measurements were conducted with a Panalytical X'Pert PRO MPD diffractometer equipped with an X'celerator PSD 2.1° detector with a Cu K α radiation (K α 1 = 1.54056 Å; K α 2 = 1.54439 Å), operating at 45 kV, and 40 mA°, with a Ni filter and a $1/2^{\circ}$ divergence slit. The XRPD patterns were collected between an incident angle of 3° and 65° 2 θ at a step size of 0.0167° 2 θ and 2 s time per step (250 s eq.). The modeling of one-dimensional XRPD pattern has been carried out with MDI Claysim, a software that uses the original NEWMOD[©] code, with the purpose of assessing the presence of randomly interstratified clay minerals. The modeling was carried out on EG patterns, since in air-dried conditions the d_{001} peak of swelling clays (i.e. smectites) is sensitive to environment conditions, such as ambient humidity (Reynolds and Reynolds, 1996). The one-dimensional modelling of the XRPD patterns was also used to extrapolate other parameters as the Coherent Scattering Domain Size (CSDS), the crystallite size distribution (δ , delta value), and the ordering of the layer stacking in the interstratified clays (R, Reichweite value) (Moore and Reynolds, 1997). Moreover, the size distribution of crystallites was calculated using a defect-broadening model (Moore and Reynolds, 1997). Carbon-coated polished thin sections were examined by Scanning Electron Microscopy (SEM), using back-scattered electron (BSE) images and Energy-Dispersive X-ray (EDX) analysis to obtain textural and chemical data. SEM analyses were carried out at the DiSTAR (Naples, Italy), using a Jeol JSM 5310 instrument. In order to refine the SEM-EDS, Electron Microprobe Analyses EMPA was performed at the NHM (London, UK), using a Cameca SX100 Electron Microprobe Analyzer equipped with five Wavelength Dispersive Spectrometry (WDS) Bragg spectrometers. Peak overlaps corrections were performed prior to matrix correction for the following elements: V (overlapping element: Ti; used standard: RUT STD082), Cr (overlapping element: V; used standard: VAN STDIC), Mn (overlapping element: Cr; used standard: CRO₂ STDIC), Fe (overlapping element: Mn; used standard: MNT STDIC). A beam current of 20 nA, an accelerating voltage of 20 keV were used to quantify the following elements: Al (TAP, Ka), Mg (TAP, Ka), P (TAP, Ka), K (PET, Ka), Ca (PET, Ka), Fe (LIF, Ka), Mn (LIF, Ka), Ti (PET, Ka), Co (LIF, Ka), Ni (LIF, Ka), V (LIF, Ka), Cr (PET, Ka), Na (TAP, Ka), Si (TAP, Ka), Cl (PET, K α) and Zn (PET, K α). The chemical formulas of smectite and serpentine were calculated on the basis of 22 [i.e. $O_{10}(OH)_2$] and 14 [i.e. $O_5(OH)_4$] negative charges, respectively. In the case of randomly interstratified clay minerals, the structural formula of talc-smectite (T/S) was calculated on the basis of 22 negative charges [i.e. $O_{10}(OH)_2$], whereas the formulas of chlorite-smectite (C/S) were calculated on a 50 negative charges basis [i.e. O₂₀(OH)₁₀, Bettison-Varga and Mackinnon (1997)]. In accordance with the accepted stoichiometry of trioctahedral phyllosilicates, Fe was considered with a divalent state (i.e. Fe^{2+} , e.g. Newman and Brown, 1987; Gaudin et al., 2004a). However, since the genesis and the evolution of

lateritic soils are characterized by high Eh values (e.g. Golightly, 1981), the occurrence of ferric iron (Fe^{3+}) cannot be totally discarded. High-Resolution Transmission Electron Microscopy (TEM-HRTEM) analyses were performed on three selected specimens from the serpentinite- derived saprolite (i.e. WPDD0019-4, WPDD0019-5 and WPDD0019-8), where the complex clay assemblage did not allow the assessment of the paragenesis only by using BSE. The copper rings were attached to selected areas of thin sections prepared with Canada balsam and ion-thinned using a Fischione-1010 ion mill. The initial conditions for the ion thinning were 12°, 5 Kv and 5 mA until the first hole opened. Afterwards, the rings underwent an intermediate stage with 8°, 4 Kv and 5 mA, followed by a final stage with 5°, 3 Kv and 5 mA. The TEMHRTEM analyses were performed with a HAADF FEI TITAN G2 microscope at the Centro de Instrumentación Científica (CIC, University of Granada, Spain). The instrument operated at 300 kV and with a point-to point resolution of 0.08 nm in the TEM mode and 0.2 nm in the STEM mode. Quantitative chemical analyses were obtained, using STEM mode, with a SuperX detector. Albite, biotite, muscovite, spessartine, olivine and titanite standards were used to obtain Kfactors for the transformation of intensity ratios to concentration ratios according to Cliff and Lorimer (1975).

5.4 Results

5.4.1 Bulk rock mineralogical composition

According to the IUGS (International Union of Geological Science), Subcommission on the Systematics of Igneous Rocks (Le Maitre et al., 2002), the mineralogical composition of the gabbro was assessed through the CIPW norm calculation on whole-rock geochemical data (Putzolu et al., 2019). The results of the CIPW norm showed that gabbro is dominated by pyroxenes, among which clinopyroxenes (i.e. diopside) are the major components (45.65 vol%), whereas orthopyroxenes (i.e. enstatite) occur in lower quantities (7.65 vol%). Among feldspars, anorthite is dominant (29.89 vol%), whereas albite is significantly minor (4.40 vol%). The olivine concentration is of 10.58 vol%. Other accessory phases are magnetite (0.94 vol%), chromite (0.57 vol%) and ilmenite (0.19 vol%). According to Rietveld refinements (Table 5.1), the bulk rock composition of gabbroderived saprolite (WPDD0012) is characterized by the dominant occurrence of smectite (up to ~98%), while kaolinite occurs only in traces in the uppermost samples (up to ~6%). Quartz and spinel are minor phases (up to ~3% and ~3.5%, respectively). The mineralogical assemblage of the serpentinite-derived saprolite (WPDD0019) is more complex. Also in this locality smectite clays are dominant (up to ~67%) and are accompanied by serpentine (up to ~8%); the latter occurs in all specimens with the exception of the upper saprolite sample WPDD0019-4. Another peculiarity of WPDD0019-4 is the occurrence of talc (~17%) as one of the major phases. Minor ore mineral in the core WPDD0019 is goethite (up to ~20%), and the main gangue phases are quartz, dolomite and spinel (up to ~30%, ~24% and ~3%, respectively).

5.4.2 Clay fraction characterization

5.4.2.1 XRPD on clay aggregates of the gabbro-derived saprolite (WPDD0012)

The AD and EG patterns of samples from core WPDD0012 (Fig. 5.2a, b and c) show the shifting of the ~ 15 Å peaks to ~ 17 Å, which is the typical swelling behaviour of smectites (Moore and Reynolds, 1997 and references therein). The detection of the regular sequences of the d_{001} reflections, the absence of systematic deviations of the d_{002} , d_{003} and d_{005} reflections of smectite in EG conditions from their nominal positions, as well as the symmetric shape of the d_{001} peaks suggests that smectites are present as discrete phases, rather than as interstratified clays (e.g. Moore and Reynolds, 1997). After heating at 550 °C, the smectite structure collapses at ~10 Å with less intense reflections at ~5 Å and ~3 Å. The disappearance of the ~7 Å reflection confirms the presence of kaolinite in sample WPDD0012-15. The occurrence of kaolinite is also testified by the d_{06l} reflection centered at 1.490 Å in RO condition (Fig. 5.4d). The RO patterns (Fig. 5.2d) show that the d06l reflections of smectites fall within a *d*-spacing range diagnostic of dioctahedral Al-bearing smectite, to be likely ascribed to montmorillonite (Moore and Reynolds, 1997). In this context, samples WPDD0012-15 and WPDD0012-16 show very similar smectite reflections occurring in the d_{06l} region occurring at 1.510 Å, whereas in sample WPDD0012-17 the d_{06l} reflection of smectite is shifted towards lower dvalues and occurs at 1.499 Å. This difference suggests a potential variation of the nature of smectite and, more in detail, a shift toward dioctahedral end members (i.e. beidellite-like), as similar d-values have been reported for beidellite both in natural systems (Brindley and Brown, 1980) and in

experimental studies (Yamada et al., 1999). Moreover, the RO patterns show several asymmetrical reflections at 4.50 Å and 2.56 Å (02;11 and 13;20 two dimensional reflections, respectively), related to the rotational disorder of the 2:1 layers of smectites (Moore and Reynolds, 1997).

5.4.2.2 XRPD on clay aggregates of the serpentinite-derived saprolite (WPDD0019)

In drillcore WPDD0019 the AD and EG patterns also suggest that swelling clays (i.e. smectites) are dominant in the mineralogical assemblage, whereas ~10 and ~7 Å-spaced phyllosilicates occur as minor phases (Fig. 5.3a–d). In samples WPDD0019-4, WPDD0019-5 and WPDD0019-8 the broadening of the d_{001} reflections of smectite, the absence of superlattice reflections and the detection of irrational d_{00l} series suggest the presence of randomly interstratified clays (Moore and Reynolds, 1997). Sample WPDD0019-4 (Fig. 5.3a) is characterized by the presence of a talc-smectite random interstratification (T/S). The talc component was ascertained by the occurrence of its d₀₀₁ (9.52 Å), d₀₀₃ (3.11 Å), d₀₆₁ (1.526 Å) reflections in RO mode (Fig. 5.3e and f). The position of the observed d_{001} reflection of talc is significantly higher in comparison with its nominal values (i.e. 9.34 Å). Such enlargement of the basal spacing could be the proxy of the transformation of talc into a hydrated and disordered structure (kerolite-like; e.g. Wells et al., 2009 and references therein), in which the d_{001} reaches 9.6 Å as a result of the disordered stacking of the layers (Brindley, 1978). The talc pattern is overlapped with that of smectite in the low 2θ angle region (Fig. 5.3a). In sample WPDD0019-4, the occurrence of reflections at ~7.2 Å and ~3.6 Å can be ascribed both to chlorite (d_{002} and d_{004} , respectively) and to serpentine (d_{001} and d_{002} , respectively). The contribution of chlorite to the patterns can be inferred also by the loss of intensity of the ~7.2 Å peak after heat-treatment at 550 °C, due to the dehydroxylation of the OH- sheet (Moore and Reynolds, 1997), and by identification of diagnostic d_{hkl} lines of the IIb polytype (i.e. d_{20-4} at 2.25 Å and d_{204} at 2.02 Å; Bailey, 1988) in RO mode (Fig. 5.3f). In this context, the absence of the d_{001} peak of chlorite in the HT-350 patterns can be explained either by the very low amount of chlorite, or by taking into account that many ordered Ni-chlorite polytypes (e.g. di,tri-chlorite) can be characterized by significantly less intense reflections at such d-spacing (Bailey and Lister, 1989). Other important clues on the nature of phyllosilicates are provided by the RO pattern (Fig. 5.3f), of samples WPDD0019-5, WPDD0019-8 and WPDD0019-11, where

in the d_{06l} regions, characteristic peaks of tri- (1.542 Å) and dioctahedral (1.511 Å) phyllosilicates (Brindley and Brown, 1980) occur. Moreover, in these samples, the RO patterns display the typical d_{hkl} of lizardite-1 T at 2.50 Å (d_{201}) and 2.15 Å (d_{202}) (Brindley and Brown, 1980), whose occurrence can explain that the peak at ~7.2 Å is still partially visible after the heat treatment at 550 °C. The main difference in the sample WPDD0019-8 is the occurrence of a minor reflection at ~10.8 Å, which is clearly visible in AD and EG patterns (Fig. 5.3c).



Fig. 5.2: XRPD patterns of the clay fraction of the gabbro-derived saprolite: a), b) and c) XRPD patterns of the oriented clay aggregates of samples WPDD0012-15, WPDD0012-16 and WPDD0012-17 respectively; d) Randomly oriented patterns. XRPD patterns



abbreviations: AD = air-dried; EG = ethylene glycol solvated; HT-550 = after heat-treatment at 550 °C; RO = randomly oriented.

Fig. 5.3: XRPD patterns of the clay fraction of the serpentinite-derived saprolite: a), b), c) and d) XRPD patterns of the oriented clay aggregates of samples WPDD0019-4, WPDD0019-5, WPDD0019-8 and WPDD0019-11 respectively; e) and f) Randomly oriented patterns. XRPD patterns abbreviations: AD = air-dried; EG = glycol ethylene solvated; HT-350 = after heat-treatment at 350 °C; HT-550 = after heat-treatment at 550 °C; RO = randomly oriented.

This peak has an asymmetrical shape and does not shift in EG mode, suggesting the interstratification between a ~10 Å phase (i.e. kerolite-like or mica) and of a>10 Å component (i.e. smectite or vermiculite). Sample WPDD0019-11 (Fig. 5.3d) shows several similarities with samples WPDD0019-5 and WPDD0019-8, being characterized by prevailing smectite and the possible occurrence of both lizardite-1*T* and chlorite-II*b*. The position of the main d_{06l} reflection (Fig. 5.3f) falls within the range of dioctahedral phyllosilicates. However, a broad and less intense reflection at

1.544 Å suggests also the potential occurrence of a trioctahedral clay component.

5.4.2.3 Modelling of one-dimensional XRPD pattern

The simulations of clay-rich samples from the gabbro-derived saprolite (WPDD0012 drillcore, Fig. 5.4a) showed that the EG patterns can be modeled by a dioctahedral smectite composition (Dismectite-2Gly) with a basal spacing in EG state ranging between 16.75 and 16.85 Å, a CSDS value between 1 and 10 and a δ value ranging between 4 and 5. The main diffraction effect from the site occupancy composition is due to Fe, which has been fixed between 0.6 and 1.12 apfu, with the highest value observed in the more surficial specimens. In sample WPDD0012- 15 (Fig. 5.4a), the ~7 Å phase is perfectly fitted by kaolinite, with a d_{001} in EG state of 7.15 Å, a CSDS = 1–30 and a δ = 15. The modeling confirmed the occurrence of randomly interstratified clays in the serpentinite-derived saprolite (WPDD0019 drillcore, Fig. 5.4b–d).



Fig. 5.4: One-dimension modelling of EG pattern of saprolite samples from drillcores WPDD0012 (a) and WPDD0019 (b to d). Black patterns represent the EG measurements carried out on the clay fractions of each specimen.

According to Moore and Reynolds (1997) and Steudel et al. (2017), talc has been modelled with a trioctahedral mica structure with zero K and Fe contents and fixing the basal spacing from 10 Å to 9.33 Å (nominal talc) or 9.6 Å (turbostratic talc, kerolite-like). In our study, there is clear evidence of the T/S occurrence in the sample WPDD0019-4 (Fig. 5.4b), in which the interstratification was modelled by using a trioctahedral swelling component (Trismectite-2Gly, 1 < CSDS < 20, R = 0, $\delta = 10$, smectite content = 5%). Based on the XRPD indications, the randomly interstratified chloritesmectite was modelled in samples WPDD0019-4 and WPDD0019-5 (Fig. 5.4b) by using a di,trichlorite structure. Our results show that the R0 C/S chlorite has a CSDS between 1 and 10, high Fe content (FeT = 1.45 apfu, Feoh = 1.75 apfu) and is characterized by chlorite as dominant component (chlorite contents: 90% in WPDD0019-5, 95% in WPDD0019-5). In sample WPDD0019-8 (Fig. 5.4c and d), the broad peak at ~10.9 Å highlights the occurrence of an interstratification between a 10 Å phase and a>10 Å component. Several attempts have been made to model such a peak. In the first model, we did not consider the existence of interstratifications in this dspacing region and the pattern was modelled with a Trismectite-2Gly with CSDS between 1 and 6 and high Fe amounts (1.7 apfu Fe). In the second attempt, R0 T/S was added to the modeling with low CSDS (1 to 6), and a very low smectite amount (5%). The result of this second modelling indicates that the modelled d_{001}/d_{002} of T/S does not fit properly the 10.9 Å line, in agreement with Moore and Reynolds (1997 and references therein), who argued that the d_{001}/d_{002} can only be in the range of 8.75 to 9.6 Å, according to the variable relative proportion of talc-smectite. In the third attempt, a mica-vermiculite (R0, vermiculite content = 10%, 1 apfu Fe, 0.7 apfu K) was added to the modelling, which resulted in a better fitting of the 10.9 Å line. However, despite this good result, no traces of mica and vermiculite were observed in XRPD. In addition, the whole-rock chemical composition of the serpentinite-derived saprolite is characterized by K₂O amounts below detection limits, ruling out the possible occurrence of mica. The serpentinite sample (WPDD0019-11, Fig. 5.4c) was modelled with a Dismectite-2Gly structure with high Fe amount (1.5 apfu Fe), to adjust the scattering factor. In all samples from the serpentinite-derived saprolite, with the exception of WPDD0019-4, the best fits of the ~7 Å phase was achieved with a serpentine structure ($1 < CSDS < 40, \delta = 20$).

5.4.3 Textures and nanotextures

The mafic bedrock of drillcore WPDD0012 (Fig. 5.5a–f) consists of coarse olivine and clinopyroxene grains, with the latter surrounded by partially recrystallized orthopyroxenes and plagioclase coronas (Fig. 5.5a). Olivine displays radial fractures infilled by reddish-brown fine mixtures of layered silicates and Fe-oxy-hydroxides (Fig. 5.5a, c and d). In addition, olivine is locally replaced by Fe-Mg-clays (i.e. smectites from XRPD analysis) (Fig. 5.5d). However, the majority of the smectites detected as limited alteration of this gabbro occur either as plasmic aluminiferous masses, corresponding to montmorillonites, which enclose and replace pyroxenes grains (Fig. 5.5b, e and g) or as fissure clays growing along their $\{1 \ 1 \ 0\}$ cleavage planes (Fig. 5.5e). In the overlying transition zone to saprolite, pyroxenes are totally replaced by montmorillonite, resulting in a plasmic system sensu stricto (Fig. 5.5f and g), whereas plagioclase crystals (mainly anorthite) appear largely unaffected by alteration (Fig. 5.5h). The saprolite zone is almost entirely composed by montmorillonite, which in the analyzed samples occurs as pelitomorphic masses (Fig. 5.5i). Montmorillonite encloses remnants of other "primary" minerals, such as hercynite (a Mg- and Cr-rich variety named picotite, Fig. 5.5e and g), and it is often coated by massive Fe-oxy-hydroxides encrustations (Fig. 5.5i).



Fig. 5.5: OP and BSE photomicrographs of representative samples showing the textures observed in drillcore WPDD0012: a) Olivine, pyroxenes and plagioclases in the slightly weathered bedrock (crossed polars); b) Smectite masses replacing pyroxene (sample

WPDD0012-18, crossed polars); c) Fe-oxy-hydroxides altering olivine (bedrock, BSE image); d) Forsterite grain replaced by Fe/Mg clays and by Fe-oxy-hydroxides (bedrock, BSE image); e) Clinopyroxene exhibiting orthopyroxene exolution lamellae and replaced by montmorillonite (bedrock, BSE image); f) unaltered clinopyroxene-orthopyroxene-spinel simplectite (bedrock, BSE image); g) weathered clinopyroxene-orthopyroxene-spinel simplectite (bedrock, BSE image); h) unweathered plagioclase and clinopyroxenes crystals (bedrock, BSE image); i) Fe-oxy-hydroxides coatings onto montmorillonite (gabbro-derived saprolite; BSE image). Mineral abbreviations (mainly after Siivola and Schmid, 2007): Ol = olivine; Fo = forsterite; Cpx = clinopyroxene; Opx = orthopyroxene; Pl = plagioclase; An = anorthite; Sme = smectite, Mnt = montmorillonite; Spl = spinel).

In the serpentinite sample (drillcore WPDD0019), serpentine forms veins and rims enveloping and cutting cryptocrystalline silica (i.e. chalcedony) and skeletal goethite cores (Fig. 5.6a). Based on its texture serpentine can be subdivided in mesh-type (Fig. 5.6a) and pseudomorph-type (Fig. 5.6b). Smectitic clays occur as interstitial aggregates developing directly from serpentine (Fig. 5.6a). In this context, C/S and T/S occur either as mineral coatings or as fibers (Fig. 5.6b and c).



Fig. 5.6: BSE photomicrographs of representative samples showing the textures observed in drillcore WPDD0019: a) Mesh serpentines enveloping quartz/Fe-oxy-hydroxides and skeletal goethite (lower saprolite zone of drillcore WPDD0019); b) Quartz + Fe-oxyhydroxides aggregates enveloped by pseudomorph serpentine, trioctahedral smectite, as well as chlorite-smectite (C/S), surrounding and replacing serpentine (serpentinite-derived saprolite; sample WPDD0019-5); c) Fibrous talc-smectite (T/S) coating massive chloritesmectite (serpentinite-derived saprolite; sample WPDD0019-4).

The TEM-HRTEM investigations revelated that the serpentinite bedrock of drill core WPDD0019 is dominated by polygonal serpentine (Fig. 5.7a), with the characteristic basal reflection at ~7 Å (Fig. 5.7b) and confirmed that serpentine minerals weather directly to smectite clays (Fig. 5.7c). Smectite clays occur in the studied samples as compact clay packages (Fig. 5.7c and d) and in HRTEM mode show the typical collapse of the basal

spacing at ~10 Å due to the TEM vacuum (Fig. 5.7e and f). The late-stage layered-silicates that overprint smectite (Fig. 5.7d) consist of disordered sequences of ~14 Å and ~10 Å layers (disordered chlorite-smectite, Fig. 5.7e and f). In this context, crystallites with regularly alternating chlorite and collapsed smectite layers (i.e. corrensite-like) were observed as a very subordinate component of the clay assemblage (Fig. 5.7g). In the uppermost section of the local saprolite zone (i.e sample WPDD0019-4), the talc-like fibrous aggregates occur mainly as open spaces filling in quartz (Fig. 5.7h). In HRTEM mode, the stacking of lattice fringes with basal spacings at ~9 Å and ~10 Å (Fig. 5.7i) confirm the occurrence of T/S interstratifications.



Fig. 5.7: TEM and HRTEM photomicrographs of representative samples from the serpentinite-derived saprolite: a) Textural image showing the typical polygonal shape of serpentine in the serpentinite unit; b) High-resolution lattice fringe images of polygonal serpentine showing the \sim 7 Å basal spacing; c) Textural image showing smectite clay

growing onto serpentine; d) Textural image showing serpentine and smectite overprinted by late-stage layered silicates; e) and f) High-resolution lattice fringe images showing adjacent chlorite (~14 Å) and collapsed smectite (~10 Å) layers; g) High-resolution lattice fringe images showing corrensite-like layers (~24 Å) h) Textural image of fibrous talc-like aggregates in a quartz open space; i) High-resolution lattice fringe image of talc-like (~9 Å) and collapsed smectite (~10 Å) layers in the upper saprolite section.

5.4.4 Phyllosilicates chemistry

5.4.4.1 Chemical composition of montmorillonite from the gabbro-derived saprolite (WPDD0012)

Montmorillonite (Table 5.2) has a Si content in the range 3.29–3.99 apfu/22, reaching the full tetrahedral occupancy in almost all the samples (as a corollary Al^{IV} ranges between 0.01 and 0.71 apfu/ 22, Fig. 5.8a). The octahedral site composition is more variable, with Al^{VI} occurring as dominant cation (0.42 < Al^{VI} < 1.89 apfu/22, Fig. 5.8a and b). The Mg content ranges between 0.09 and 0.73 apfu/22 and shows a progressive decrease from the bottom to the top of the drillcore (Fig. 5.8c). Fe^{VI} and Ni occur in low quantities $(0.13 < \text{Fe}^{VI} < 1.07 \text{ apfu}/22; 0.02 < \text{Ni} < 0.56$ apfu/22, Fig. 5.8d). Based on the Mg-Ni association, three montmorillonite groups were recognized; 1) Mg-rich and Ni-poor type (samples WPDD0012-16); 2) montmorillonite showing a positive correlation between the Mg and Ni amounts (sample WPDD0012-15) and 3) high Ni montmorillonite with no Ni-Mg correlation (sample WPDD0012-16). Montmorillonites are characterized by an interlayer occupancy dominated by Ca (0.01 < Ca < 0.15 apfu/22, Fig. 5.8e). The Ni content of montmorillonites is negatively correlated to Al^{VI} (Fig. 5.8b), whereas it increases concurrently with Fe (Fig. 5.8d). In all the analyzed clays, Al^{VI} and Fe show a linear negative correlation, highlighting an almost continuous chemical variation between the Al- and Fe-rich end members (Fig. 5.8f). In the Si/Altot vs. Ni/Altot plot (Fig. 5.8g) an almost linear variation of this ratio is observed, with the exception of the above-mentioned Ni-rich montmorillonites of sample WPDD0012-16. The chemical weathering index $Si/\Sigma R$ molar ratio (R = Mg + Fe + Ni + Al; Fritsch et al., 2016) in montmorillonites varies between ~ 2 and ~ 3 (Fig. 5.8h), with the highest values reached in sample WPDD0012-16 (up to 3.15). However, no clear relationship between the Ni concentration and Si/ Σ R was observed. The R³⁺

vs. R^{2+} , as well as the 4Si-M⁺-3 R^{2+} (Figs. 5.8i, 5.9a) diagrams were used to distinguish tri- and dioctahedral phyllosilicates and to confirm the observation made on the RO patterns. In the R^{3+} vs. R^{2+} diagram, our data plot toward the R^{3+} (i.e. Al + Fe³⁺) field, whereas in the 4Si-M⁺-3 R^{2+} plot, they are close to the field of other dioctahedral montmorillonite (Eggleton, 1977). Other important features regarding the octahedral composition of montmorillonites are shown in the Mg-Ni-(Fe^{VI} + Al^{VI}) (Fig. 5.9b), where it can be seen that montmorillonites are close to the Al- and Fe-rich end members and overlap the compositional field of similar clay minerals measured by Kadir et al. (2015) in Turkish laterites. Moreover, the latter plot shows that starting from the bottom to the top of the local saprolite a general loss of Mg and enrichment of Fe occurred. In this frame, the highest Ni concentrations are shown by the montmorillonites from sample WPDD0012-16.



Fig. 5.8: Binary plots showing the mineral chemistry variations of montmorillonites occurring in the gabbro-derived saprolite (drillcore WPDD0012). All variables are expressed in apfu, with the exceptions of the Si/Al_{tot}, Ni/Al_{tot} and Si/ Σ R rations.

5.4.4.2 Chemical composition of serpentine from the serpentinite-derived saprolite (WPDD0019)

The mineral chemistry of serpentine is reported in Table 5.3 and in Fig. 5.10a–f. According to the mineral composition, we recognized two serpentine generations: serpentine I (srp I), which was mainly detected in the serpentinite bedrock, and serpentine II (srp II) that occurs in the uppermost saprolite section. Silicon in srp I almost fully occupies the tetrahedral site (1.89 < Si < 1.97 apfu/14; 0.04 < AIIV 0.11 apfu, Table 5.3 and Fig. 5.10a). The octahedral site composition of srp I (Fig. 5.10a–f) is poorly variable and is dominated by Mg (2.56 < Mg < 2.66 apfu/14) and AIVI (0.26 < AI^{VI} < 0.27 apfu/14), with minor Fe^{VI} (0.07 < Fe^{VI} < 0.12 apfu/14).



Fig. 5.9: a) $4\text{Si}-M^+-3R^{2+}$ chemiographic diagram and b) Mg-Ni-(Fe^{VI}+Al^{VI}) ternary plot showing the composition of phyllosilicates occurring in the gabbro-derived saprolite (drillcore WPDD0012). In both diagrams, a comparison of our data with those of literature is reported. Minerals abbreviations: Fe-m = Fe-montmorillonite (Eggleton, 1977).

The Ni content of srp I is negligible (0.00 < Ni < 0.01 apfu/14). Serpentine II is characterized by a chemical composition notably different in comparison with srp I. Serpentine II shows a more variable tetrahedral composition, being characterized by a decrease of the Si content toward the shallowest zone of the saprolite (1.96 < Si < 2.00 apfu/14 in WPDD0019-8

and 1.56 < Si < 1.65 apfu/14 in WPDD0019-5). Toward the top of the saprolite zone, srp II seems to show a Si deficiency not only counterbalanced by Al (0.08 < Al^{VI} < 0.17 apfu/14), but also by traces of Fe (0.13 < Fe^{IV} < 0.33 apfu/14). Moreover, the octahedral occupancy of srp II is also heterogeneous (Fig. 5.10a–f). In fact, in comparison with srp I, the second generation of serpentine is characterized by a significant Mg loss (1.75 < Mg < 2.51 apfu/14, Fig. 5.10b) and by enrichment in Ni (Fig. 5.10c and e) and Fe^{VI} (Fig. 5.10c) (0.06 < Ni < 0.13 apfu/14 and 0.41 < Fe^{VI} < 0.87 apfu/14, respectively). Another important chemical characteristic of the analyzed serpentines is the negative correlation between Mg and Ni, and a positive correlation between the Si/Al_{tot} and the Ni/Al_{tot} ratios, only recorded by srp II (Fig. 5.10b and 0). Both srp I and II have similar Si/ Σ R ratios (ranging between 0.61 and 0.78; Fig. 5.10e) and show a predominance of trioctahedral cations (Figs. 5.10f and 5.11).

5.4.4.3 Chemical composition of smectites from the serpentinite-derived saprolite (WPDD0019)

The mineral chemistry of smectites are reported in Table 5.4 and Figs. 10g-l and 13. The R^{3+} v.s. R^{2+} binary plot (Fig. 5.10g) and the 4Si-M⁺-3R²⁺ chemiographic diagram (Fig. 5.11) confirm that smectites from the serpentinite-derived saprolite belong both to the di- and trioctahedral types (nontronite- and saponite-like, respectively). The tetrahedral occupancy of dioctahedral smectites is homogenous with low Al^{IV} contents ranging from 0.00 to 0.15 apfu/22 (Fig. 5.10h). The octahedral composition of dioctahedral smectites is very variable but, in general, in comparison with montmorillonites from the gabbro-derived saprolite, these smectites are Al^{VI}-poor and Fe- and Mg-rich. However, in accordance with the octahedral occupancy, as well as with the interlayer composition, two dioctahedral smectite types (i.e. di-sme I and di-sme II) have been recognized. Dioctahedral smectite I occurs in the serpentinite bedrock (WPDD0019-11), whereas di-sme II has been detected in the upper saprolite (WPDD0019-4). Overall, di-sme I is characterized by relatively low AI^{VI} (0.01 < AI^{VI} < 0.25 apfu/22), Ni (0.02 < Ni < 0.05 apfu/22) and Ca (0.04 < Ca < 0.10 apfu/22)contents (Figs. 10h and 11j,) and by high Fe^{VI} (1.02 < Fe^{VI} < 1.29 apfu/22) and Mg (0.82 < Mg < 1.01 apfu/22) amounts (Fig. 5.10i). On the contrary, di-sme II shows Mg and Fe^{VI} depletion (0.44 < Mg < 0.95 apfu/22; 0.76 < $Fe^{VI} < 1.02$ apfu/22, Fig. 5.10i) and Al^{VI} (0.46 < $Al^{VI} < 0.59$ apfu/22, Fig.

5.10h) Ni and Ca (0.11 < Ni < 0.15 apfu/22; 0.08 < Ca < 0.15 apfu/22, Fig. 5.10j) gain. Trioctahedral smectites have a silicon content varying between 3.63 and 3.98 apfu/22 ($0.02 < Al^{IV} < 0.37$ apfu/22, Fig. 5.10h). As expected, the dominant octahedral cations are Mg and Fe^{VI}, with range values of 1.03–2.26 apfu/22 and 0.38–1.40 apfu/22 (Fig. 5.10i), respectively. The Ni content is very variable (Fig. 5.10j, 1) among the various generations but always<0.5 apfu/22.



Fig. 5.10: Binary plots showing the mineral chemistry variation of serpentines (a to f) and smectites (g to l) occurring in the serpentinite-derived saprolite (drillcore WPDD0019). All variables are expressed in apfu, with the exception of the Si/Al_{tot}, Ni/Al_{tot} and Si/ Σ R rations.




Fig. 5.11: a) $4\text{Si-M}^+-3\text{R}^{2+}$ chemiographic diagram and showing the composition of phyllosilicates occurring in the serpentinite-derived saprolite (drillcore WPDD0019). A comparison of our data with those of literature is reported. Minerals abbreviations: Non = nontronite (Deer et al., 1963); Sap = saponite (Cahoon, 1954); Fe-sap = Fe-rich saponite; Ste = stevensite (Faust et al., 1959); Mg-chl = Mg-rich chlorite (Foster, 1962); Liz = lizardite (Faust and Fahey, 1962).

In detail, here trioctahedral smectites can be distinguished. Trioctahedral smectite I (tri-sme I) was detected in the serpentinite bedrock (WPDD0019-11) and is characterized by a negligible Ni content (0.04 < Ni < 0.06 apfu/22). Trioctahedral smectite II (tri II) and III (tri III) was observed in the shallower sections of the saprolite (WPDD0019-5 and WPDD0019-8, respectively). Trioctahedral smectite II is characterized by a slight Ni gain (0.16 < Ni < 0.18 apfu/22) in comparison with tri-sme I, whereas the highest Ni concentrations were observed in tri-sme III (0.31 < Ni < 0.47 apfu/22) (Fig. 5.10l). In this framework, also the Fe^{VI} and Mg contents of the trioctahedral smectite types are heterogeneous. In fact, as shown by the crossplot in Fig. 5.10i, Mg and Fe^{VI} behave as antagonist octahedral cations, allowing to define two end members for the trioctahedral smectites: a Mg-rich (saponite-like) member, which is represented by tri-sme III and I. In this

context, the existence of the Ni-rich tri-sme III ensures a progressive chemical variability and continuity between the Mg- and Fe-rich end members of saponite. Other important clues on the composition of both diand tri-octahedral smectites are provided by the Si/Al_{tot} v.s. Ni/Al_{tot} crossplot in Fig. 5.10k, where some good linear positive relationships are displayed for trioctahedral smectite I and III. It must be noted that the regression lines have different angular coefficients in accordance with the smectite generations, which further highlights the different Ni, as well as Al_{tot}, concentrations in the analyzed clays. Tri- and dioctahedral smectite display also a significant difference in their Si/ Σ R ratio, which ranges between 1.07 and 1.52 in the tri-sme and between 2.29 and 2.97 in the disme (Fig. 5.10l).

5.4.4.4 Chemical composition of interstratified Ni-clays from the serpentinite-derived saprolite (WPDD0019)

The chemical composition and structural formulas of T/S and C/S are reported in Table 5.5 and Fig. 5.12a–g. In the 4Si-M⁺-3R²⁺ ternary plot (Fig. 5.12a), T/S and C/S are spread between the saponite-talc and the saponitechlorite nominal composition, thus confirming the observations obtained through XRPD analyses and one-dimensional modeling. Talc-smectite was observed in the shallower sections of the saprolite (WPDD0019-4 and WPDD0019-8) and shows a significant deficiency of the tetrahedral occupancy (Table 5.5), due to the low values of Al^{IV} (0.12 < AlIV < 0.56 apfu/22, Fig. 5.12b), which can be counterbalanced by the presence of tetrahedral Fe^{IV} (0.19 < Fe^{IV} < 0.81 apfu/22, Fig. 5.12c), similarly to that observed in similar T/S in other areas (Cuadros et al. 2008). In the octahedral site, Mg is the dominant cation (1.54 < Mg < 2.62 apfu/22, Fig.)5.12d), followed by Fe^{VI} (0.21–0.93 apfu/22, Fig. 5.12e). In this context, despite Ni occurring as a minor cation (0.23-0.46 apfu/22, Fig. 5.12e), T/S is characterized by a significant Ni concentration in comparison with saponite- and nontronite-like clays. The C/S interstratifications can be subdivided in two types, on the basis of their composition: C/S I and C/S II. Chlorite-smectite I shows low and Al^{IV} values, ranging between 0.67 and 0.97 apfu/50 (Fig. 5.12a), and trace amounts of Fe^{VI} (0.08 $< Fe^{IV} < 0.48$ apfu/50, Fig. 5.14c). The octahedral site composition is dominated by Mg (5.23 < Mg < 6.17 apfu/50, Fig. 5.12d), followed by variable Fe^{VI} and Ni (1.62–2.28 apfu Fe^{VI} and 0.75–1.02 apfu Ni, Fig. 5.12e). Chlorite-smectite

II is characterized by higher Al^{IV} contents (1.10 < Al^{IV} < 2.56 apfu/50, Fig. 5.12b) in comparison with C/S I, which results in the absence of trace amounts of tetrahedral Fe. The Mg and Ni contents in C/S II span in a wider range of values (3.22 < Mg < 7.15, 0.32 < Ni < 1.20 apfu, Fig. 5.12c), in comparison with C/S I. Moreover, C/S II has significantly lower Fe^{VI} (Fig. 5.12e) concentrations than C/S I. In the bivariate plots of Fig. 5.12e and f, it is clear visible that the Ni content of both T/S and C/S, as well as the Si/Altot and the Ni/Altot ratios, are characterized by a positive correlation.



Fig. 5.12: a) 4Si-M⁺-3R²⁺ chemiographic diagram showing the composition of T/S and C/S occurring in the serpentinite-derived saprolite (drillcore WPDD0019); b) to g) Binary plots showing the mineral chemistry variations of T/S and C/S occurring in the serpentinite-

derived saprolite (drillcore WPDD0019). All variables are expressed in apfu, with the exceptions of the Si/Al_{tot}, Ni/Al_{tot} and Si/ Σ R rations.

5.5 Discussion

5.5.1 Genesis of Ni-clays from the alteration of gabbro

The laterization of the mafic units in the Wingellina deposit resulted in the development of a secondary plasmic system, in which newly formed clay minerals (mainly Ni-montmorillonite and minor barren nontronite) totally obliterated the original rock texture. In laterite ores, the nature of the newformed Ni-clays is controlled by: (i) the mineralogy of the parent rock; (ii) the ratio of the water/rock interaction, and (iii) the activity and mobility of the components in solution (Golightly, 1981; Gaudin et al., 2004a; Velde and Meunier, 2008). In the specific case of the drillcore WPDD0012, the local magmatic bedrock is a gabbro containing forsteritic olivine, pyroxene (i.e. both cpx and opx), and Ca-plagioclase (i.e. anorthite). As expected, alteration started with the weathering of olivine, and developed through the formation of barren Fe/Mg-clays (i.e. nontronite) as a direct replacement of olivine and of Fe-oxy-hydroxides precipitation as fissure-fillings (Fig. 5.5d and c, respectively). During this first alteration step, Ni was not been enriched in the newly formed phases, neither the Fe/Mg-smectite nor the Feoxy-hydroxides (Table 5.2). This can be explained when considering the element availability during the lateritization process. In fact, even if olivine is generally the most Ni-enriched ferromagnesian mineral at Wingellina (0.38 wt% NiO, Table 5.2), it has be noticed that its chemistry is relatively consistent with that of barren smectite, which is Fe- and Mg-rich and has very low Al and Ni contents. The lack of Al and Ni in smectite from olivine weathering highlights the fact that early alteration of olivine develops as a nearly closed (micro)system (Velde and Meunier, 2008), where Al and Ni diffusion through migration from other adjacent magmatic minerals did not occur, thus favouring the formation of Fe/Mg-smectite. In the samples from the saprolite overlying the former assemblages, pyroxenes weather to Nimontmorillonite. The weathering of pyroxene to Ni-smectite has been described by Eggleton (1975), who observed that pyroxene alteration results in the loss of Ca, Mg and Si and the formation of dioctahedral Fe-bearing clays (nontronite). During this process, the clinopyroxene (hedenbergite) easily alters to nontronite via topotaxial growth along its cleavage planes. This process seems to be favoured by the similarity between the c parameter of the newly formed smectite and the *a* parameter of the pyroxene precursor, whose ratio is equal to ~1.5 in the case of the hedenbergite to nontronite transformation (Eggleton, 1975). At Wingellina, the mafic bedrock is characterized by the predominance of clinopyroxene (diopside, 45.65 vol %), while orthopyroxene occurs only in lower amounts (enstatite, 7.65 vol%). Therefore, the initial weathering of the pyroxenes resulted in the formation of Al-rich montmorillonites, which are found along the $\{1 \ 1 \ 0\}$ plane of diopside (Fig. 5.5e). From a crystallographic point of view, applying the same approach of Eggleton (1975), the diopside to montmorillonite alteration would be facilitated by the fact that the $c_{\rm sme}/a_{\rm px}$ ratio is equal to ~1. On the other hand, the $c_{\rm sme}/a_{\rm px}$ ratio between montmorillonite and enstatite is ~0.5, is evidence that, unlike the constant volume alteration of diopside, this mineral transformation can produce a significant decrease of the bulk volume. Another important aspect to consider for the formation of montmorillonite from pyroxene weathering is the significant amounts of Al and Ni required to develop this process, as at Wingellina pyroxenes are characterized by very low amounts of both elements (~1 wt% < Al₂O₃ < 4 wt%, NiO < d.l., Table 5.2). In fact, several studies (e.g. Gaudin et al., 2004a; Kadir et al., 2015) mention that montmorillonite formation in mafic to ultramafic lithologies requires the existence of an external sources of elements. For example, it was suggested that the Al supply required for montmorillonite precipitation in the deeply weathered ultramafic terrane of the Muratdaği region (Turkey), was provided by hydrothermal fluids circulating in aluminiferous country rocks (Kadir et al., 2015). Therefore, differently from the closed system occurred at the beginning of olivine weathering, also at Wingellina the alteration of pyroxenes to Al-and Ni-bearing dioctahedral smectites can only be explained by considering the existence of a completely open system, which allowed the Al and Ni addition from other phases occurring in the bedrock (i.e. pyroxene). Considering that plagioclases represent more than 30% vol. of the original mafic parent rock, it is likely that the dissolution of these minerals in the shallower section of the alteration profile, enriching the percolating waters of Ca, Si and Al, played a fundamental role for the formation of Al-bearing smectites in the deeper saprolite. Anorthitic plagioclases, such as those occurring in the Wingellina gabbroid rocks, are highly reactive during the interaction with acid solutions, and are weathered following a congruent dissolution process (Shotyk and Nesbitt, 1992). The

previously mentioned Ni enrichment was instead likely related to the effect of both the collapse of the local saprolite section and the potential dissolution/recrystallization of Fe-oxy-hydroxides in the upper part of the profile. The former process, recorded by the progressive Mg depletion toward the upper part of the local saprolite, likely accounted for the passive enrichment of immobile elements (including Ni) in relationship with leaching of the more soluble cation (Fig. 5.9b). The second process instead, i.e. the dissolution and recrystallization of Fe-oxy-hydroxides, likely enhanced the Ni recycling from to upper toward the lower part of the profile due to inverse relationship between the Ni-hosting capacity of goethite and its crystallinity degree (Dublet et al., 2015). The chemical composition of montmorillonite is quite variable in the studied samples, but the variations are also continuous: there is a negative correlation between AlVI and Fe (Fig. 5.8f), which suggests the existence of a linear and gapless solid solution in the Al- and Fe-montmorillonite series. In this context, despite the broad variation of the octahedral metals in the analyzed samples, Al^{VI} and Mg amounts in montmorillonites decrease upward in the profile, whereas Fe increase. Interestingly, the Mg depletion in montmorillonites in the uppermost saprolite, which is due to the high mobility of this element in the weathering zones (Gaudin et al., 2004a), occurs together with a decrease of the Ni grade in montmorillonite in uppermost zone of the profile (Fig. 5.8c). The observed Mg and Ni decrease in the montmorillonite occurring at the transition between the oxide-saprolite zones is consistent with the observations of Putzolu et al. (2019), which argued about the control exerted by the progressive decomposition of clays, marked by the local Mgdiscontinuity, on the bulk rock Ni geochemistry. However, variation in the amounts of the other octahedral elements in montmorillonites along the laterite profile are very helpful in defining the environmental condition governing the saprolitization. In particular, considering that the formation of Fe-dominated smectite requires the occurrence of "diluted" neutral circulating waters, while the genesis of Al-bearing smectites is attained when the soil solutions become more concentrated, more saline and thus more alkaline (Satyavathi et al., 2012), the early formation of Fe/Mg-clays (i.e. nontronite), followed by the formation of Al-clays (i.e. Nimontmorillonite) we observed in the Wingellina gabbro-derived saprolite likely indicate the shift from a dilute to a more saline (basic) environment favouring the montmorillonite stability. In the gabbro-derived smectite unit at Wingellina, kaolinite represents a minor phase in the uppermost section

of the saprolite profile. However, as shown by Putzolu et al. (2018, 2019), a more significant amount of kaolinite occurs in the mottled-clay zone which overlies the saprolite. This spatial variation is related to the montmorillonite to kaolinite transformation during chemical weathering and is widely considered an evidence of the transition from "immature" to "mature" soil systems caused by the upward increase of the leaching degrees (higher drainage, lower pH etc.; e.g. Karathanasis and Hajek, 1983). Another relevant aspect to consider is that the highest Ni concentrations were observed in the Al-poor and Fe-rich montmorillonite species (Fig. 5.8b, d and g), which from a metallurgical point of view, render the clay association from gabbro-derived laterite profile perfectly amenable to processing by the Caron method (Mano et al., 2019), according to importance of the coexistence of Fe and Ni in the lattice for the achievement of good grade recoveries.

5.5.2 Genesis of Ni-clays from the alteration of serpentinite

The mineralogical assemblage of the saprolite deriving from serpentinite weathering, which is characterized by saponite and nontronite as dominant clays, with minor amounts of talc and chlorite in interstratified clay minerals, is more complex than that developed on gabbro. The occurrence of this assemblage is directly dependent on the nature itself of the serpentinite bedrock, which derived from hydrothermal alteration of former ultramafic bodies, in particular peridotites (wehrlite) and olivine-spinel cumulates (Ballhaus and Glikson, 1989). In the studied serpentinite, primary magmatic minerals are totally pseudomorphosed by lizardite-1T (srp I), formed during a post magmatic hydration stage at a maximum temperature of 300 °C and at relatively low pressures (< 1.0 GPa) (Evans, 2004 and references therein). XRPD analyses and the modeling of the onedimensional XRPD patterns showed that in the Wingellina samples talc does not occur as discrete mineral, but it is interstratified with low percentages of smectite, and that chlorite has a regular structure (IIb polytype). There is no evidence of chlorite presence in the serpentinite bedrock. Chlorite-smectite random interstratifications mainly occur instead in the upper saprolite section, as a late stage mineral coating and/or overprinting smectite clays. These petrographic relationships suggest that the genesis of talc and chlorite at Wingellina is due to late stage authigenic processes rather than being inherited hydrothermal minerals from the

serpentinite bedrock. These mineral relationships allow to depict a paragenesis (Fig. 5.13), characterized by two supergene evolutionary stages: a laterization stage followed by post-laterization processes.

(i) Lateritization stage: during the initial stage of lateritic weathering, the main mineralogical changes detected in the serpentinite-derived saprolite are the precipitation of Fe-oxy-hydroxides/chalcedony microaggregates in the mesh cores, as well as the Ni gain in serpentine (e.g. srp II). During the transition from srp I (lizardite-1T) to srp II, serpentines released Mg, and incorporated significant amounts of Ni and Fe. This Ni enrichment in late serpentines (srp II) produced a slight chemical fluctuation between the Ni and Mg endmembers of the lizardite-nepouite isomorphous series (as also reported by Villanova-de-Benavent et al., 2014, Villanova-de-Benavent et al., 2017). In other cases mentioned in the literature of Al-depleted weathering systems, similar to the Wingellina serpentinite- derived saprolite, the formation of Ni-bearing serpentines at the expenses of their Mg counterparts is enhanced by increasing silica activity (Golightly, 1981; Soler et al., 2008; Galí et al., 2012). Considering this fact, the association between Fe/Ni-rich srp II and the Fe-oxy-hydroxides/quartz aggregates in the Wingellina laterite could have been produced in two combined ways:

A) During the alteration of serpentine I, a dissolution process occurring at the rims of the clay particles produces Mg and Si leaching, with Mg transported in solution as Mg^{2+} , and Si redeposited as chalcedony (e.g. Brindley, 1978; Bilbao et al., 2008). The occurrence of this process at Wingellina is not only testified by the presence of Fe-oxy-hydroxides/chalcedony aggregates, but also by a significant decrease of the R²⁺ content in srp II. A similar dissolution behavior was suggested for serpentine by Villanova-de-Benavent et al. (2017) in the Falcondo (Dominican Republic) and Moa Bay (Cuba) Ni-laterite deposits, where the formation of late stage Fe/Ni-rich serpentine phases in supergene settings (25 °C, 1 atm) is in equilibrium with both Fe-oxy-hydroxides and Fe²⁺ in aqueous solution;

B) During the initial stages of the ferralitic weathering affecting relicts of unserpentinized olivine grains, enveloped in the lizardite meshes, Fe-oxy-

hydroxides/chalcedony aggregates can form as a result of the impeded or limited drained regime.

The smectites occurring in the serpentinite-derived saprolite are mineralogically and chemically different from those of the gabbro-derived saprolite (i.e. montmorillonite), as they are represented by Mg-Fe-rich and Al-poor, tri- and dioctahedral types. As there is a clear evidence of clay forming directly at the expense of serpentine (e.g. Fig. 5.7c), the distinct nature of these smectites reflects the chemistry of the serpentinite bedrock. In several studies focused on the mineral transformation in mineralized Ni laterite deposits (e.g. Golightly, 1981, 2010; Gleeson et al., 2004), the serpentine to smectite transformation in supergene conditions is considered to be due to the dramatic increase of the serpentine solubility after a significant acidification of the soil system (pH ≤ -5) and is related to a dissolution-recrystallization mechanism, which decomposes the 1:1 phyllosilicates, providing elements for precipitation of the 2:1 clays (Lee et al., 2003).

Drillcore	Stage Mineralogy	Hydrothermal	Lateri Early	itization Late	Post-lateritization
Gabbro-derived saprolite	Nontronite Montmorillonite FeO/OH Kaolinite				?
erpentinite-derived saprolite	Serpentine I Serpentine II FeO/OH-qtz Saponite Nontronite C/S				
ഗ്	T/S				

Fig. 5.13: Proposed paragenesis of the alteration product observed in the studied Ni-saprolite sections showing the main alteration stages.

Consequently, the composition of newly formed smectite reflects that of the serpentine precursor. Considering the chemical composition of lizardite detected in the Wingellina serpentinite, it is reasonable to suppose that the first type of smectite to form at the expenses of serpentines was a Mg(Ni)-clay (saponite), rather than a Fe(Ni)-clay (nontronite), that instead forms

later. This two-stages smectite genesis has been already observed in other serpentinite-derived regoliths, where Fe-rich dioctahedral smectites are enriched in the uppermost section of the soil profiles, that are at the same time characterized by significantly reduced amounts of saponite (Nguyen-Thanh et al., 2017). At Wingellina, an important proxy of the trioctahedral to dioctahedral 2:1 clays conversion is provided by the variation of the Mg and Fe^{VI} composition of saponite (Fig. 5.10i). In fact, saponite is characterized by significant amounts of Fe^{VI} (up to 1.4 apfu/22 Fe^{VI}), whose variation is negatively correlated to the Mg amount, following a continuous and gapless Fe^{VI}-Mg trend, consistent with the existence of a solid solution between saponite- and ferro-saponite (Baldermann et al., 2014 and references therein). The Fe^{VI}-Mg compositions of the Fe-rich end member of trioctahedral smectite significantly overlap those of the dioctahedral smectite I clays (Fig. 5.10i), providing evidence that ferro-saponite would represent a transitional phase between Ni-saponite and Ni-nontronite. This transformation from saponite to nontronite can be related to: a) the high instability of ferro-saponite in oxidizing environments, and to its decomposition into the dioctahedral clay itself and Fe-oxy-hydroxides (Badaut et al., 1985); b) the impeded drainage occurring at depth in the profile, able to ensure a more effective retention of mobile cations as Mg (Golightly, 2010). Interestingly, the saponite to nontronite conversion produced a Ni loss, with saponite showing variably high Ni contents (up to 0.5 apfu/22), and the transitional saponite- to nontronite- like clays being characterized by significantly lower Ni amounts (di-sme I = 0.02-0.05apfu/22 Ni; di-sme II = 0.11 to 0.15 apfu/22 Ni). During this process, Ni was likely incorporated in the newly formed Fe-oxy-hydroxides (Badaut et al. 1985), which are able to act as metal scavengers (e.g. Freyssinet et al. 2005).

(ii) Post lateritization stage: as mentioned above, the formation of talcsmectite, and chlorite-smectite either as neoformed and precipitated phases in open spaces or as overprints of smectite (Fig. 5.6 and 5.7), suggests that they formed after the previously described smectites, which are genetically related to the lateritization process *sensu stricto*. Interestingly, the presence of T/S and C/S in Ni-laterite deposits is still poorly documented, whereas the chloritization of saponite, as well as the genesis of talc-smectite are widely described in several other environments. For example, randomly interstratified C/S is commonly formed during burial diagenesis or hydrothermal processes (Beaufort et al., 2015 and references therein). R0 T/S is instead a common interstratification formed through hydrothermal processes in oceanic spreading centre (e.g. Cuadros et al., 2008, 2013). Since the genesis of T/S does not properly fit with the low temperature environment in which laterites form (Thorne et al., 2012), the T/S occurrence in Greek Ni-laterites was considered to be related to syn- and/or post-lateritization hydrothermal processes (Christidis and Mitsis, 2006; Christidis and Skarpelis, 2010). Regarding the current case study, the Wingellina laterite profile occurs in an intracratonic tectonic setting, where there is no geologic evidence for post-weathering burial and/or hydrothermal processes. This suggests that the Wingellina T/S and C/S have a peculiar genesis, different from the other more common cases mentioned above. The geochemistry of the Wingellina laterite (see Putzolu et al., 2019), as well as the Rietveld refinement of bulk rock samples, show that significant amounts of Ca, Na, Mg and Si occur in the uppermost part of the saprolite (Table 5.1), in association with newly formed dolomite and quartz (i.e. calcrete-silcrete duricrust). This silica- and carbonates-rich assemblage was likely produced during post-lateritization processes, similarly to other Australian regoliths, where the post-lateritization enrichment of mobile elements was mainly related to the decrease in runoff that occurred during arid to semiarid climates, established in the central part of the continent from late Miocene-Pliocene (Tardy and Roquin, 1998; Anand and Paine, 2002). Under these conditions, the Wingellina laterite system experienced a dramatic change in the hydrochemical equilibria, consisting of increase in evaporation that led to an enrichment of the amounts of cations (e.g. Mg, Ca, Na, Si etc.) in solution. The resulting more saline-alkaline environment was able to trigger post-lateritization modifications within the laterite ore, allowing the precipitation of carbonates and chalcedony at the top of the profile (in the calcrete-silcrete duricrust) and to a lesser extent throughout the profile (Putzolu et al., 2019). Considering that associations of T/S and C/S, similar to those occurring at Wingellina have been extensively detected in modern continental evaporitic environments, where neutral to alkaline brines led to the authigenesis of clays, as well as of randomly interstratified phases, in association with calcrete, dolocrete and silcrete formation (Pozo and Calvo, 2018), it is likely that the Wingellina T/S and C/S formed during the onset of the arid to semiarid climates in Western Australia (Late Miocene to Pliocene). In light of the above discussed mineral paragenesis and the change in the pH conditions that characterize the evolution of the

serpentinite-derived saprolite ore, a comparison can be made between the evaporative precipitation of clays that occurred in the Wingellina laterite and the "per-descensum fluid flow model" that is widely accepted for the late precipitation of garnierite mineralization in laterite deposits on active convergent margins. The first significant difference is that at Wingellina there is no evidence of the contribution of active tectonics during the genesis and modification of the Ni-phyllosilicates assemblage such as in Nigarnierite endowed lateritic ores (e.g. Cluzel and Vigier, 2008; Villanovade-Benavent et al., 2014). Secondly, at Wingellina the Ni-smectites represent a significant component of the phyllosilicates association, both in terms of their genetic significance and in terms of their economic potential as their amounts within the saprolite ore is higher than in other hydrous Mg silicate-type deposits (e.g. Indonesia, Blancher et al., 2015; Dominican Republic, Tauler et al., 2017). The most significant analogy between the origin of Ni-clays in the saprolite zone of the Wingellina deposit and that of laterites evolved following the per descensum model is that both in the paragenetic sequences (lizardite \rightarrow smectite \rightarrow C/S and T/S, Wingellina, this study; lizardite-népouite \rightarrow kerolite-pimelite \rightarrow sepiolite-falcondoite \rightarrow barren sepiolite + quartz, hydrous Mg-silicate type, Galí et al., 2012) the terminal stages of the ore forming processes are marked by the precipitation of late-stage Ni-phyllosilicates as newly formed phases and not derived from the replacement of primary minerals (Villanova de-Benavent et al., 2014). In both the cases, these mineral sequences seem to be linked to a sharp change in the pH conditions within the profiles. In the case of garnierite ores, mineral succession is driven by an increase in the silica activity and the acidity of the solutions (Soler et al., 2008; Galí et al., 2012). On the contrary, the paragenesis observed at Wingellina suggests a more complex pathway in which the syn-lateritization acidity inferred from the serpentine-to-smectite transformation, while the higher evaporative and alkaline post-lateritization environment enhanced the neoformation of interstratified Ni-clay minerals. Therefore, the aridity-driven precipitation of clays that we observed in the Wingellina laterite can be seen as a new model for explaining the evolution of Ni-laterites in stable cratonic settings experiencing post-lateritization aridity, and can be seen as a counterpart of the "per-descensum fluid flow model" that instead describes the laterization process of serpentinites in active terrains. During the latter process, it seems that the montmorillonite developed over the gabbro bedrock did not experience any authigenic transformation (i.e. illitization process), which

was likely prevented by the paucity of K_2O in the local bedrock (Putzolu et al., 2019) and by the long term stability of montmorillonite in low leaching, saline and alkaline environments promoted by dry and arid climate (Satyavathi et al., 2012).

5.6 Conclusions

In the world-class Wingellina Ni-Co laterite deposit, Ni is contained not only in the Mn-oxy-hydroxides of the oxide zone, but also in several clay types occurring in both the saprolite and the oxide horizons. The lateritic evolution of the saprolite zone resulted in a clear differentiation of the clay types, based on the distinct protoliths outcropping in the area.

(i) In the gabbro-derived saprolite, the weathering of primary minerals resulted in the formation of Al- and Ni-rich montmorillonites and of minor nontronite. The main factor that controlled the Ni enrichment in the local saprolite was the existence of an open alterative system. A limited Ni enrichment in nontronite is due to the relatively closed alterative (micro)system that occurred during initial stages of the bedrock saprolitization (i.e. not serpentinized olivine). On the contrary, the Ni and Al enrichment in montmorillonite derived from alteration of pyroxene is explained through the onset of a more open system, in which the combined effects of the Al sourced from anorthite dissolution, saprolite collapse (loss of bulk volume after intense cation leaching), and element recycling from the upper part of the profile, accounted for the effective element redistribution and gaining in the saprolite ore. Local evolution of montmorillonite was characterized by a downward loss of Mg and Al, paired by a gain in both Fe and Ni. This reflects the progressive acidification of the solution, and thus the maturation of the regolith system, as also evidenced by the occurrence of kaolinite in the uppermost section of the saprolite.

(ii) The alteration of serpentinite (former peridotite unit) followed a multistage process. A Ni-enriched generation of supergene serpentine (srp II), associated with Fe-oxy-hydroxides and chalcedony, was one of the early phases to form. Differently from the gabbro-derived bedrock, alteration of both the widespread serpentine types (srp I and of srp II) resulted in the

genesis of tri- and di-octahedral smectite clays (i.e. saponite sensu lato and nontronite). Among the smectites, Ni-saponite was the first phase to form, being progressively modified to ferrosaponite and finally transformed into Ni-nontronite. During the saponite-to-nontronite transition, a significant amount of Ni was released from the saponite clays and likely incorporated into Fe-oxy-hydroxides.

(iii) During a further supergene evolution, interstratified Ni-clay minerals (C/S and T/S) formed, and overprinted the pre-existing smectites. The presence of these Ni-enriched interstratified clays suggests that the Wingellina saprolite experienced an incipient post-lateritization process under higher evaporative alkaline and saline conditions. The presence of these conditions was likely related to the onset of the climate aridity in central Australia during Late Miocene-Pliocene. In the case of montmorillonites formed on the gabbro-derived saprolite, an analogous evolution to illite did not occur because of the paucity of K in the system and of the long-term stability of montmorillonite in arid conditions.

Lithology/drill core ID	C	abbro-derive	d 012	Peridotite-derived saprolite/WPDD0019					
Sample ID	WPDD00 12-15	WPDD00 12-16	WPDD00 12-17	WPDD00 19-4	WPDD00 19-5	WPDD00 19-8	WPDD00 19-11		
Depth (m)	73	74	75	25	30	42.3	54		
Sme	87.8	94.3	98.6	43.8	58.1	60.8	67.8		
Kln	6.4	2.2	-	-	-	-	-		
Qtz	3.4	-	-	28.4	10.7	10.3	-		
Spl	2.5	3.4	1.4	0.7	2.4	3.0	0.3		
Gt	-	-	-	6.6	20.7	19.9	1.2		
Dol	-	-	-	2.9	-	-	24.7		
Tlc	-	-	-	17.6	-	-	-		
Srp	-	-	-	-	8.2	6.0	6.0		

Table 5.1: Quantitative mineralogical composition (%) of the Wingellina samples obtained by bulk XRPD analyses.;

Mineral abbreviations (mainly after Siivola and Schmid, 2007): Sme = smectite, Tlc = talc, Srp = serpentine; Gt = goethite, Kln = kaolinite, Qtz = quartz, Spl = spinel, Dol = dolomite. Notes: - = not detected or below the detection limit.

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Туре	Montmorillonite						Fe/Mg-smectite	Forsterite	Diopside	Enstatite	Anorthite					
wt%	W	PDD0012	2-5	WF	DD0012	-16	WF	PDD0012	-17				WPDD0012-18	8		
SiO ₂	54.27	52.55	51.40	53.02	52.82	52.31	58.80	50.34	50.95	52.96	52.24	51.14	39.03	51.63	55.37	42.48
Al_2O_3	9.55	11.39	9.91	10.23	13.24	10.01	18.71	18.57	18.08	12.90	12.63	0.11	0.12	4.31	1.62	38.67
FeO _t ^a	12.95	12.23	12.39	12.04	10.39	9.81	2.49	5.92	3.71	5.33	6.06	19.51	12.82	3.46	8.12	-
MgO	2.74	2.51	2.38	2.74	3.75	3.30	5.12	6.15	4.96	6.39	5.78	9.33	47.08	16.90	33.87	0.17
MnO	0.01	0.03	0.01	0.03	0.03	-	-	0.01	-	-	-	0.31	-	0.01	0.07	0.25
NiO	4.11	2.58	4.14	3.88	2.66	6.13	0.30	2.68	1.08	0.44	0.38	0.14	0.38	-	-	-
Cr_2O_3	1.16	1.20	1.23	2.46	2.20	2.26	0.58	1.23	0.66	0.82	0.48	-	-	0.02	-	0.36
TiO ₂	0.51	0.39	0.49	0.36	0.36	0.30	0.06	0.23	0.08	0.13	0.33	-	-	0.07	0.08	-
CoO	0.02	0.01	0.01	0.01	0.01	0.02	-	0.02	-	0.32	0.29	0.19	0.38	-	-	-
CaO	0.72	0.56	0.40	1.73	0.48	0.82	1.13	1.03	0.91	0.94	1.29	1.27	-	22.14	0.26	17.41
K_2O	0.05	0.05	0.07	0.07	0.05	0.05	0.04	0.05	0.05	0.01	0.10	0.54	-	0.01	0.05	0.16
Na ₂ O	0.04	0.05	0.03	0.17	0.06	0.14	0.05	0.02	0.02	0.04	0.23	0.13	-	0.56	-	1.01
Total	86.13	83.55	82.46	86.74	86.05	85.15	87.56	86.44	80.71	80.29	79.80	82.66	99.81	99.10	99.44	100.50
Si/ΣR	2.95	2.98	2.87	2.82	2.60	2.57	2.93	2.01	2.48	2.64	2.74	2.34	-	-	-	
apfu						01	n the basis o	f O ₁₀ (OH	$()_2$							
Si	3.97	3.92	3.93	3.88	3.82	3.90	3.96	3.58	3.78	3.96	3.95	4.00	0.98	1.90	1.94	1.95
Al ^{VI/Y}	0.03	0.08	0.07	0.12	0.18	0.10	0.04	0.42	0.22	0.04	0.05	-	-	0.10	0.06	0.05
Fe ^{VI/Y}	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Σ_{Tet}	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	0.98	2.00	2.00	2.00
Al ^{VI/Y}	0.79	0.92	0.82	0.76	0.94	0.78	1.44	1.14	1.36	1.10	1.07	0.01	-	0.08	0.01	2.05
Fe	0.71	0.69	0.71	0.66	0.56	0.55	0.13	0.32	0.21	0.30	0.34	1.15	0.27	0.11	0.24	-
Mg	0.30	0.28	0.27	0.30	0.40	0.37	0.51	0.65	0.55	0.71	0.65	1.09	1.76	0.93	1.77	0.01
Mn	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	-	-	0.02	-	-	-	0.01
Ni	0.24	0.15	0.25	0.23	0.15	0.37	0.02	0.15	0.06	0.03	0.02	0.01	0.01	-	-	0.00
Cr	0.07	0.07	0.07	0.14	0.13	0.13	0.03	0.07	0.04	0.05	0.03	-	-	-	-	0.01
Ti	0.03	0.02	0.03	0.02	0.02	0.02	0.00	0.01	0.00	0.01	0.02	-	-	-	-	-
Co	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.02	0.01	0.01	-	-	-
$\Sigma_{oct/Y}$	2.14	2.13	2.16	2.09	2.19	2.20	2.13	2.35	2.23	2.21	2.16	2.28	2.04	1.11	2.01	2.08
Ca	0.06	0.04	0.03	0.14	0.04	0.07	0.08	0.08	0.07	0.08	0.10	0.11	-	0.87	0.01	0.86
Κ	0.00	0.00	0.01	0.01	0.00	0.00	0.00	0.00	0.00	-	0.01	0.05	-	-	-	0.01
Na	0.01	0.01	0.00	0.02	0.01	0.02	0.01	0.00	0.00	0.01	0.03	0.02	-	0.04	-	0.09
$\Sigma_{int/X}$	0.07	0.06	0.04	0.17	0.05	0.09	0.09	0.09	0.08	0.08	0.15	0.18	-	0.91	0.01	0.96
\mathbb{R}^{3+b}	1.57	1.67	1.61	1.56	1.63	1.47	1.60	1.53	1.61	1.40	1.42	1.15	-	-	-	-
\mathbb{R}^{2+c}	0.54	0.44	0.53	0.53	0.56	0.74	0.53	0.81	0.61	0.74	0.67	1.12	-	-	-	-

Table 5.2: Selected EMPA analyses and structural formulas of smectite (i.e. montmorillonite and notronite) and of primary ferromagnesian minerals in drillcore WPDD0012.

Notes: a = total iron; b = sum of the trivalent octahedral cations; c = sum of the divalent octahedral cations; - not detected.

wt%	WP	DD0019-5 (sr	o II)	WP	DD0019-8 (sr	<u>p II)</u>	WPI	DD0019-11 (s	arp I)	
SiO ₂	36.77	36.15	32.81	38.26	39.07	39.22	40.60	40.05	38.14	
Al ₂ O ₃	1.74	1.62	1.97	0.35	1.03	0.36	2.62	2.52	3.05	
FeO _t ^a	11.67	11.14	15.19	13.23	11.53	13.40	6.16	6.48	5.62	
MgO	33.66	33.58	24.78	33.49	32.27	31.89	35.10	34.38	36.06	
MnO	0.16	0.16	0.43	0.05	0.06	0.06	0.09	0.09	0.07	
NiO	1.67	2.20	3.04	1.43	2.44	1.48	0.16	0.11	0.11	
Cr_2O_3	0.01	-	0.01	0.02	0.05	0.03	0.35	0.34	0.37	
TiO ₂	0.09	0.07	0.07	0.01	0.02	0.02	0.37	0.29	0.41	
CoO	0.03	0.03	0.03	0.02	0.01	0.02	0.02	0.02	0.02	
CaO	0.04	0.03	0.23	0.09	0.18	0.10	0.05	0.05	0.05	
K_2O	-	-	0.03	-	0.01	-	0.01	-	-	
Na ₂ O	0.02	-	0.03	0.03	0.03	0.04	-	-	0.01	
Total	85.86	84.98	78.62	86.98	86.70	86.62	85.53	84.32	83.91	
Si/SR	0.59	0.58	0.61	0.61	0.65	0.65	0.68	0.68	0.63	
apfu	on the basis of $O_{10}(OH)_2$									
Si	1.63	1.63	1.56	1.92	1.95	1.97	1.97	1.97	1.89	
Al ^{IV}	0.09	0.09	0.11	0.02	0.05	0.02	0.03	0.03	0.11	
Fe ^{IV}	0.28	0.28	0.33	0.06	-	0.01	-	-	-	
Σ_{Tet}	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	
Al^{VI}	-	-	-	-	0.01	-	0.25	0.27	0.23	
Fe ^{vi}	0.59	0.56	0.87	0.50	0.48	0.56	0.12	0.12	0.07	
Mg	2.23	2.26	1.75	2.51	2.40	2.39	2.53	2.52	2.66	
Mn	0.01	0.01	0.02	0.00	0.00	0.00	-	-	-	
Ni	0.06	0.08	0.12	0.06	0.10	0.06	-	-	-	
Cr	-	-	-	-	-	-	0.01	0.01	0.01	
Ti	-	-	-	-	-	-	0.01	0.01	0.02	
Co	-	-	-	-	-	-	-	-	-	
$\Sigma_{\rm Oct}$	2.88	2.90	2.76	3.06	3.00	3.01	2.94	2.94	3.00	
Ca	-	-	0.01	-	0.01	0.01	-	-	-	
K	-	-	-	-	-	-	-	-	-	
Na	-	-	-	-	-	-	-	-	-	
Σ_{Int}	-	-	0.02	0.01	0.01	0.01	-	-	-	
R3 ^{+b}	-	-	-	-	0.01	-	0.13	0.13	0.08	
R2 ^{+c}	2.88	2.90	2.76	3.06	2.99	3.01	2.79	2.80	2.90	

Table 5.3: Selected EMPA analyses and structural formulas of serpentines in the peridotite-derived saprolite (drillcore WPDD0019).

Notes: a = total iron, b = sum of the trivalent octahedral cations, c = sum of the divalent octahedral cations; -= not detected.

Туре		Dioctahed	Iral smectite		Trioctahedral smectite						
xx/t0/	WPDD	0019-4	WPDD(019-11	WPDD	0019-5	WPDD	0019-8	WPDD0	019-11	
wt 70	(di-sr	ne II)	(di-sr	ne I)	(tri-sı	me II)	(tri-sn	ne III)	(tri-sı	ne I)	
SiO_2	47.42	47.61	53.55	52.50	49.54	47.55	44.84	46.61	48.48	48.42	
Al_2O_3	6.79	5.53	2.44	2.49	3.48	3.44	3.67	2.22	2.75	2.80	
FeO _t ^a	13.38	12.28	18.51	19.04	7.02	8.27	11.14	13.69	17.97	17.67	
MgO	6.78	7.73	8.67	7.87	17.09	13.77	15.99	13.98	11.45	10.91	
MnO	0.07	0.09	0.02	0.01	0.04	0.05	0.04	-	0.02	0.01	
NiO	1.82	1.59	0.77	0.79	2.61	2.35	5.99	5.25	0.80	0.80	
Cr_2O_3	-	0.01	0.52	0.71	0.06	0.04	0.48	0.40	0.55	0.44	
TiO_2	0.01	0.00	0.11	0.11	0.02	0.08	0.04	0.01	0.12	0.07	
CoO	0.01	0.01	-	-	0.01	0.02	-	-	-	0.02	
CaO	1.54	1.34	0.45	0.71	0.17	0.94	0.65	0.69	0.66	0.73	
K_2O	0.12	0.12	0.12	0.14	0.12	0.14	0.16	0.12	0.10	0.15	
Na ₂ O	0.13	0.11	0.13	0.12	0.11	0.15	0.17	0.14	0.11	0.11	
Total	78.06	76.42	85.29	84.47	80.27	76.80	83.17	83.11	83.01	82.13	
$Si/\Sigma R$	2.29	2.29	2.42	2.47	1.39	1.51	1.11	1.23	1.40	1.44	
apfu					on the basis	of O ₁₀ (OH)	2				
Si	3.85	3.93	4.00	3.98	3.92	3.96	3.63	3.80	3.91	3.94	
Al ^{IV}	0.15	0.07	0.00	0.02	0.08	0.04	0.35	0.20	0.09	0.06	
Fe ^{IV}	-	-	-	-	-	-	0.02	-	-	-	
Σ_{Tet}	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	
$A1^{VI}$	0.50	0.46	0.21	0.20	0.24	0.30	-	0.01	0.17	0.21	
Fe ^{VI}	0.82	0.76	1.04	1.09	0.46	0.58	0.74	0.93	1.21	1.20	
Mg	0.82	0.95	0.97	0.89	2.01	1.71	1.93	1.70	1.38	1.32	
Mn	-	0.01	-	-	-	-	-	-	-	-	
Ni	0.12	0.11	0.05	0.05	0.17	0.16	0.39	0.34	0.05	0.05	
Cr	-	-	0.03	0.04	-	-	0.03	0.03	0.04	0.03	
Ti	-	-	0.01	0.01	-	0.01	-	-	0.01	-	
Co	-	-	-	-	-	-	-	-	-	-	
Σ_{Oct}	2.26	2.29	2.30	2.27	2.88	2.75	3.09	3.01	2.86	2.82	
Ca	0.13	0.12	0.04	0.06	0.01	0.08	0.06	0.06	0.06	0.06	
Κ	0.01	0.01	0.01	0.01	0.01	0.01	0.02	0.01	0.01	0.02	
Na	0.02	0.02	0.02	0.02	0.02	0.02	0.03	0.02	0.02	0.02	
Σ_{Int}	0.17	0.15	0.07	0.09	0.04	0.12	0.10	0.09	0.08	0.10	
$R3^{+b}$	1.32	1.23	1.29	1.33	0.24	0.30	0.03	0.03	0.21	0.24	
$R2^{+c}$	0.95	1.06	1.01	0.94	2.64	2.44	3.06	2.97	2.64	2.58	

Table 5.4: Selected EMPA analyses and structural formulas of smectites in the peridotite-derived saprolite (drillcore WPDD0019).

Notes: a = total iron, b = sum of the trivalent octahedral cations, c = sum of the divalent octahedral cations; -= not detected.

Phase		Talc/s	mectite		Chlorite/smectite					
wt%	WPDD	00019-4	WPDD	0019-8	WPDD001	19-4 (C/S I)	WPDD001	9-5 (C/S II)		
SiO ₂	38.40	39.24	42.29	40.48	36.05	36.27	35.67	36.79		
AI_2O_3	4.57	4.29	2.22	1.32	3.63	4.31	14.63	15.56		
FeO _t ^a	17.44	16.32	13.27	15.19	14.05	15.46	11.73	7.00		
MgO	16.64	16.96	19.01	19.82	21.44	18.44	18.27	23.40		
MnO	0.12	0.15	0.07	0.02	0.09	0.15	0.11	0.20		
NiO	6.82	6.70	4.68	4.00	5.97	6.29	8.52	5.21		
Cr_2O_3	0.01	0.01	0.51	0.35	0.01	0.01	0.06	-		
TiO ₂	0.02	0.01	0.18	0.11	0.02	0.01	-	0.01		
CoO	0.01	0.01	0.01	-	-	0.01	0.04	0.01		
CaO	0.22	0.23	0.42	0.56	0.10	0.11	0.24	0.96		
K ₂ O	0.04	0.02	0.04	0.08	-	0.02	0.05	0.03		
Na ₂ O	0.09	0.07	0.09	0.07	0.02	0.02	0.16	0.27		
Total	84.38	84.01	82.79	82.00	81.39	81.11	89.48	89.43		
Si/ΣR	0.97	0.99	1.09	1.03	0.81	0.88	0.75	0.72		
apfu		on the basis	s of O ₁₀ (OH) ₂		on the basis of $O_{20}(OH)_{10}$					
Si	3.12	3.18	3.39	3.31	6.86	6.95	6.14	6.15		
AI ^Ⅳ	0.44	0.41	0.21	0.13	0.81	0.97	1.86	1.85		
Fe ^{i∨}	0.44	0.41	0.40	0.56	0.33	0.08	-	-		
Σ_{Tet}	4.00	4.00	4.00	4.00	8.00	8.00	8.00	8.00		
Al ^{∨I}	-	-	-	-	-	-	1.11	1.22		
Fe ^{∨i}	0.62	0.59	0.40	0.37	1.68	2.15	1.52	0.88		
Mg	2.02	2.05	2.27	2.42	6.08	5.27	4.69	5.83		
Mn	0.01	0.01	-	-	0.01	0.02	0.02	0.03		
Ni	0.45	0.44	0.30	0.26	0.91	0.97	1.18	0.70		
Cr	-	-	0.03	0.02	-	-	0.01	-		
Ti	-	-	0.01	0.01	-	-	-	-		
Co	-	-	-	-	-	-	0.01	-		
∠Oct	3.10	3.09	3.03	3.08	8.70	8.42	8.53	8.00		
Ca	0.02	0.02	0.04	0.05	0.02	0.02	0.04	0.17		
К	-	-	-	0.01	-	0.01	0.01	0.01		
Na	0.01	0.01	0.01	0.01	0.01	0.01	0.05	0.09		
Σ _{Int}	0.04	0.03	0.05	0.07	0.03	0.04	0.11	0.27		
R3 ^{+b}	0.63	0.59	0.44	0.39	1.68	2.15	2.63	2.10		
R2 ^{+c}	2.47	2.50	2.58	2.68	7.01	6.26	5.89	6.56		

 Table 5.5:
 Selected EMPA analyses and structural formulas of talc/smectites and chlorite/smectite interstratified minerals in the peridotite-derived saprolite (drillcore WPDD0019).

Notes: a = total iron, b = sum of the trivalent octahedral cations, c = sum of the divalent octahedral cations; -= not detected.

Chapter 6:

Ni-bearing smectites in the Wingellina laterite deposit (Western Australia) at nanoscale: TEM-HRTEM evidences of the formation mechanisms

6.1 Introduction

In both clay- and garnierite-type deposits, although Ni-phyllosilicates play a significant role in determining the grade of the deposit and the Ni distribution within the laterite profile, these minerals also represent a challenging issue during the metallurgical treatment of the ore (e.g. Dalvi et al., 2004; Villanova-de-Benavent et al., 2014; Mano et al., 2019). Therefore, detailed mineralogical and chemical studies, aimed also to unravel the micro- to nanotextural features of the complex mineralogical assemblages occurring in saprolitic mineralizations, are beneficial to improve the processing strategies and the economic appraisal of these ore types. Up to date, there is a wide number of exhaustive papers dealing with the transmission electron microscopy (TEM) characterization of garnieritebearing saprolitic mineralizations (e.g. Soler et al., 2008; Tauler et al., 2009; Suárez et al., 2011; Villanova-de-Benavent et al., 2016). On the contrary, most of the studies carried out on smectite type Ni ores are traditionally performed through X-ray powder diffraction (XRPD) and electron probe microanalysis (EMPA) (e.g. Mano et al., 2014; Tauler et al., 2017). The number of contributions dealing with TEM investigation of smectite type ores is still limited (e.g. Gaudin et al., 2004b; Gaudin et al., 2005; Kadir et al., 2015), with most of them not providing high-resolution imaging and elemental mapping. Moreover, none of the above-mentioned studies used the ion-milling technique preparation, which is mandatory to preserve the mineral fabric of clays, and to obtain good textural data. This is mainly due to the time-consuming preparation procedure of the ion-milling technique, as well as to its very challenging application to soft smectite-bearing regolith specimens leading to the low probabilities of success. Therefore, in this part of the study, are presented a High-resolution Transmission Electron Microscopy (TEM-HRTEM) and Analytical Electron Microscopy (AEM) survey performed on the different smectite species previously identified by XRPD and EMPA in Chapter 5.

6.2 Sampling strategy, materials and analytical methods

6.2.1 Materials and previous work conducted on the studied samples

This study was conducted on four samples collected from saprolite sections developed on gabbro (Fig. 6.1a) and serpentinite (Fig. 6.1b,c) bedrocks (Putzolu et al., 2020). Sample WPDD0012–16 (hereafter "sample A"; Fig. 6.1d), was collected from the highest Ni-grade layer within the saprolite unit of drillcore WPDD0012. The latter drillcore was dug in a gabbro-derived laterite sector of the tenure. Samples WPDD0019–4 and WPDD0019–5 (hereafter "sample B" and "sample C", respectively; Fig. 6.1e,f), were collected from the Ni-rich portions of the upper saprolite zone of drillcore WPDD0019, intercepting a serpentine-derived profile.



Fig. 6.1: a) Drillcores of gabbro-derived saprolitic ore (ID: WPDD0012); b) and c) drillcores of serpentinite-derived saprolitic ore (ID: WPDD0019); d) to g) samples investigated in this study. Figures b), c) and e) are from Putzolu et al. (2020, modified).

Sample WPDD0019–8 (hereafter "sample D"; Fig. 6.1g), was collected from the lower saprolite horizon of drillcore WPDD0019. Bulk-rock Xray powder diffraction (XRPD) analysis coupled with Scanning Electron Microscopy (SEM) imaging (Appendices 6.1 and 6.2; Putzolu et al., 2020) highlighted that smectites, characterized by variably intense d_{001} reflections at ca. 15 Å, are a ubiquitous component of the mineralogical suite in the studied specimens. Moreover, 7 Å clay minerals (i.e. kaolinite in sample A and serpentine in samples C and D) were also extensively detected. The 10 Å clay species (i.e. talc-like) were solely revealed in sample B. Goethite was detected only in samples from the serpentinite-derived saprolite (i.e. B to D). Minor gangue phases (i.e. quartz, spinels and dolomite) were also observed. The saprolite samples from the gabbro-derived saprolite (drillcore WPDD0012) consist of dioctahedral smectite (montmorillonite and nontronite), with minor kaolinite, Fe-oxy-hydroxides and spinels (Table 6.1; Putzolu et al., 2020). Conversely, in the serpentinite derived saprolite (drillcore WPDD0019), the smectites belong to both the tri- and dioctahedral types (i.e. saponite, ferrosaponite and nontronite) (Table 6.1; Putzolu et al., 2020). Moreover, serpentine, interstratified clays, Fe-oxyhydroxides, carbonates and quartz also occur in this saprolite section.

6.2.2 Analytical methods

The textural characterization, as well as the micro- to nanoscale chemical investigation of Ni-phyllosilicates and of the associated clay mineral phases was conducted on ion-milled specimens by TEM and HRTEM, scanning transmission electron microscopy (STEM) and high-angle annular dark field (HAADF) at the Centro de Instrumentación Científica (CIC) of the Universidad de Granada (Spain). The copper rings were attached to selected areas of thin sections prepared with Canada balsam. These areas were detached through gentle heating, ion-thinned using a Fischione-1010 ion mill and further carbon coated. The ion milling was initially performed at 12°, 5 kV and 5 mA until the first hole opened, then the rings were treated at 8°, 4 kV and 5 mA. The last stage involved a treatment at 5°, 3 kV and 5 mA. The TEM-HRTEM study was conducted through a HAADF FEI TITAN G2 microscope, operating at 300 kV and with a point-to point resolution of 0.08 nm in the TEM mode and 0.2 nm in the STEM mode. The quantitative micro- to nano-chemical analyses, in STEM mode, were obtained by means of the AEM-EDX (energy dispersive X-ray microscopy), using the Super-X system. Compositional maps were obtained from the whole area of interest and the individual spectra of each pixel of homogeneous areas of the maps summed up to produce the average spectrum of all the area. In addition, scan windows including the entire analyzed particle were used for the chemical analyses. The K-factors used for the intensity ratio-to-concentration transformation were obtained by the use of albite, biotite, muscovite, spessartine, olivine, and titanite as standards, according to the procedure of Cliff and Lorimer (1975). It is

known that AEM is not an absolute-composition technique, but is based on the determination of chemical ratios that require a normalization to obtain structural formulae. The chemical compositions of smectites were calculated on the basis of 22 negative charges $[O_{10}(OH)_2]$ and expressed as atoms per formula unit (apfu). Following Newman and Newman and Brown (1987), Fe was considered bivalent in trioctahedral smectites (i.e. saponite and ferrosaponite) and trivalent in dioctahedral smectites (i.e. montmorillonite and nontronite). Electron diffraction patterns (selected area electron diffraction, SAED) were carried out, where possible, in the same areas investigated by TEM-AEM.

6.3 Results

6.3.1 Textural and SAED observations versus qualitative composition of Nibearing smectites and other phyllosilicates

The ion-milling technique preparation allowed the detection of a wide range of micro-textures of smectite clays in the Wingellina samples. In particular, smectite clays are commonly found either as variably compact clay packages (CCP) or as porous clay aggregates (PCA). The CCP in the Wingellina samples are irregularly flat, locally exhibiting a curved shape, with a length up to few thousands of nm and a thickness < 500 nm (Fig. 6.2a,b). Most of the PCA textures are observed in sample A, wherein Nismectites (i.e. montmorillonite) are closely associated with oxy-hydroxides, and have a flaky texture (Fig. 6.2c). Moreover, in the saprolite zone of drillcore WPDD0019, Ni-phyllosilicates were observed with other two common micro-textures: oriented clay aggregates (OCA; Fig. 6.2d,e) and polygonal serpentine (i.e. PS; Fig. 6.2f), which were detected in sample B and D, respectively. Ni-smectites occurring in sample A show diffractions with spacings at ca. 10 Å (Fig. 6.3a). This diffraction line can be ascribed to partially collapsed smectites, as a consequence of TEM vacuum and/or electron irradiation. In sample A, the PCA are also locally characterized by the occurrence of needle-shaped Co- and Ni-rich Mn-oxy-hydroxides (MnO/ OH), which at this scale appear as finely "intercalated" with smectite packets (Fig. 6.3b-f). HRTEM imaging (Fig. 6.3g,h), as well as fast Fourier transform (FFT; Fig. 6.3i) of the PCA ± MnO/OH shown lattice fringes at 10.5 Å and 4.4 Å to 4.5 Å, corresponding to the d_{khl} of smectite (collapsed

 d_{001}) and lithiophorite (d_{002}), respectively. The SAED, as well as HRTEM imaging, performed on the CCP in sample C revealed also minor reflections at ca. 14 Å and 7 Å, belonging to chlorite and serpentine clay species (Fig. 6.4a-d). Moreover, in sample C Ni-smectite is closely associated with chlorite and serpentine (Figs. 6.5 and 6.6).



Fig. 6.2: Microtextural images of smectite clays in the studied samples: a), b) CCP smectite textures in samples A and C; c) PCA associated with oxy-hydroxides in sample A; d), e) OCA locally replaced by oxy-hydroxides, in sample B; f) PS in sample D. Mineral identification was performed through SAED and STEM-EDX, and shown in following figures. Abbreviations: CCP = compact clay packages; PCA = porous clay aggregates; OCA = oriented clay aggregates; PS = polygonal serpentine.

Chemical mapping and EDX spectra of a chlorite- and smectite-rich area of sample C (Fig. 6.5a-g) highlighted that chlorite has a clinochlore-like composition, while the latter has a saponite-like composition. Polygonal serpentine is commonly barren (sample D; Fig. 6.6). Late-stage Ni-bearing phyllosilicates, detected solely in samples C and B, occur either as wavy clay packets overprinting CCP and massive clay aggregates (MCA) (Fig. 6.8) or as neo-formed OCA (Fig. 6.9). The HRTEM images obtained on the wavy clay packets overprinting the CCP and MCA (Fig. 6.7a-d), show a random interstratification of smectite and chlorite packets with basal

spacing of ca. 10 Å and 14 Å, respectively. The EDX spectra, as well as chemical mappings (Fig. 6.8), performed in the investigated area confirmed the occurrence of serpentine in MCA (Fig. 6.8b), which is Ni-richer in comparison with the polygonal serpentine generation (Fig. 6.6h). CCP smectite is Fe-rich (Fig. 6.8c-d). In this frame, EDX analysis carried out on the late stage overprints on CCP showed an intermediate composition between those usually detected for smectite and chlorite and higher Ni contents (Fig. 6.8e). The EDX mappings showed that most of the Ni in the selected areas is deported by late-stage clays and by MCA serpentine (Fig. 6.8f), while CCP smectite is Fe-rich (Fig. 6.8g). The OCA textures (sample B; Fig. 6.9a) were solely detected in the upper saprolite zone of drillcore WPDD0019. In this section of the ore, the Ni-clays assemblage is very homogenous and occurs as superimposed sets of layers with thickness up to ca. 500 nm, which are locally associated with oxy-hydroxides and quartz (Fig. 6.9a-b), with the former forming as pseudomorphic replacement of the clays assemblage. The SAED pattern performed on the OCA shows diffractions at 9.7 Å (Fig. 6.9c), due to the variable degree of turbostratic disorder of kerolite-like structural configurations, while HRTEM imaging highlighted the occurrence of talc-like (ca. 9 Å) and collapsed smectite (ca. 10 Å) lattice fringes (Fig. 6.9d). Important clues on the mineralogical and chemical nature of oriented Ni-clays aggregates is given by the elemental mapping reported in Fig. 6.10a-e, where significant Al and Na concentrations were detected in OCA. STEM-EDX spectra (Fig. 6.10f) performed on OCA showed an intermediate composition between talc and smectite end-members. Interestingly, the smectite-rich areas in the uppermost section of the saprolite ore show pseudo-annular SAED microdiffraction patterns (e.g. Fig. 6.3a), either due to the turbostratic disorder or to the occurrence of multiple randomly oriented crystals. On the contrary, the SAED patterns of chlorite and serpentine, with the former occurring as trace phase in the upper saprolite section and the latter representing the main phase in lowermost saprolite (samples C and D, respectively), show also discrete diffraction spots (Figs. 6.4b-c and 6.6b).

6.3.2 Chemical composition of Ni-bearing smectites inferred by AEM

Representative structural formulae of the detected Ni-bearing smectite species are reported in Tables 6.2 and 6.3, while Fig. 6.11a–f shows the chemical variations of smectites, comparing the AEM data collected in this

study with the EMPA data from Putzolu et al. (2020). The nanoscale (50–100 nm) AEM investigation of mineral grains showed that the CCP and PCA Ni-smectite clays of sample A (Figs. 6.2a and 6.3; Table 6.2) are solely composed of montmorillonite; this clay species is also commonly associated with Co- and Ni-bearing Mn-oxy-hydroxides, as already observed in Fig. 6.3b–i.



Fig. 6.3: Sample A: a) SAED pattern of partially collapsed smectites; b) Mn-oxyhydroxides intercalated with PCA montmorillonite; c) and d) STEM-EDX spectra of the area in the red frame in b); e) and f) EDX spectra of montmorillonite and Co-bearing Mnoxy-hydroxides (lithiophorite-like) g) and h) HRTEM imaging showing collapsed smectite (10 Å layers) and Mn-oxy-hydroxides with the typical d_{hkl} of ca 4.4 Å, respectively; i) FFT of Mn-oxy-hydroxides-rich area in Fig. h. Note that the structural formula of smectite (montmorillonite) of EDX spectra 1 is reported in Table 6.2.

The smectite-bearing CCP textures analyzed in samples C and D are characterized by a higher heterogeneity in comparison with those observed in sample A. Ni-nontronite, detected in samples C and D, is found in paragenetic association with late stage interstratified clays (i.e. chlorite-smectite; Fig. 6.7a), and with MCA serpentine (Fig. 6.6e, Fig. 6.7 and 6.8a). Among trioctahedral species, saponite was found texturally associated with discrete amounts of chlorite (Fig. 6.7), while ferrosaponite was detected in Fe-bearing CCP, where nontronite-like compositions were detected as well (Fig. 6.8a,c and d). Ni-bearing montmorillonite is characterized by a variable octahedral composition, which is due to the chemical fluctuation between montmorillonite *s.s.* and Fe-montmorillonite end-members (Fig. 6.11a).



Fig. 6.4: Sample C: a) Textural image of CCP; b) and c) SAED patterns showing the typical d_{001} of chlorite (14 Å) and the 7 Å periodicity of serpentine; d) HRTEM image showing a chlorite-serpentine intergrowth.

The AEM analyses presented in this study are coherent with EMPA dataset, confirming that the Ni-Al^{VI} anticorrelation and Ni-Fe^{VI} positive relationship are the main chemical trends observed in montmorillonite.



Fig. 6.5: Sample C: a) HAADF image of CCP; b) and c) EDX spectra of chlorite (clinochlore) and smectite (saponite), respectively; d) to g) STEM-EDX spectra of the investigated area. Note that the structural formula of chlorite (clinochlore) of EDX 1 is reported in Table 6.4, while that of smectite (saponite) of EDX spectra 2 is reported in

Table 6.3. In the STEM-EDX figures Al-and Mg-rich areas correspond to chlorite, while Si- and Ni-rich areas correspond to smectite.

However, some differences between EMPA and AEM were also observed. Firstly, the AEM results point to generalized higher concentrations of both Ni and Fe^{VI} (0.10–0.74 apfu Ni and 0.78–1.35 apfu Fe^{VI}; Fig. 6.11c,e-f and d, respectively), and to lower amounts of Al^{VI} (0–0.83 apfu Al; Fig. 6.11b). As regards to Ni-bearing nontronite, the AEM results show a more homogenous octahedral composition than EMPA (Fig. 6.11a), with Fe^{VI} and Mg being the main metals, and Ni occurring with the lowest concentration detected in this study (0.99-1.36 apfu Fe^{VI}, 0.59-0.87 apfu Mg and 0.16-0.29 apfu Ni; Table 6.3). Additionally, the microchemical data not only detected higher Ni concentrations (Fig. 6.11d) than the EMPA counterpart, but also showed clear relationships between the Ni contents and the concentrations of other octahedral cations (i.e. positive relationship with Mg and negative relationship with Fe^{VI}; Fig. 6.11c and d, respectively). The Nibearing saponite and ferrosaponite have similar chemical characteristics, with Ni contents between 0.47 and 0.73 apfu and 0.49-0.51 apfu, respectively (Table 6.3). The main chemical difference among those clay species resides in the measured relative amounts of Mg (Fig. 6.11c) and Fe^{VI} (Fig. 6.11d), which predominantly occupy the octahedral sites of saponite and ferrosaponite, respectively. It is worth noting that the AEM results show a deficiency of the interlayer occupancy if compared with EMPA (Fig. 6.11e), which is more pronounced in dioctahedral smectite species (Σ_{int} of montmorillonite = 0.01-0.06 apfu by AEM and 0.01-0.17 apfu by EMPA; Σ_{int} of nontronite = 0.08–0.14 apfu by AEM and 0.06–0.19 apfu by EMPA), while is less significant in trioctahedral smectites (Σ_{int} ferrosaponite = 0.09 apfu by AEM, Σ_{int} saponite by AEM = 0.06–0.12; Σ_{int} saponite and ferrosaponite = 0.01-0.14 apfu by EMPA; Fig. 11e). However, both AEM and EMPA data are characterized by a lower interlayer occupancy, if compared with the nominal smectite stoichiometry accepted by IMA (see Chapter 1). This could mean that smectite may potentially bear minor Mg amounts in the interlayer site, which would also explain the slightly higher octahedral occupancy systematically recorded by AEM (i.e. $\Sigma_{oct} = 2.14-2.38$ apfu in dioctahedral smectites, $\Sigma_{oct} = 3.17 - 3.23$ apfu in trioctahedral smectites; Tables 6.2 and 6.3). Although this qualitative evidence exists, since that AEM technique is not insightful in this discrimination, all the Mg detected is reported in the octahedral position following the accepted

stoichiometry of smectite (Newman and Brown, 1987). As regards to chlorite, AEM data show that this species bears significant Ni contents (0.35–1.21 apfu Ni) and has an octahedral composition dominated by Mg, followed by Fe and Al (2.80–3.43 apfu Mg, 0.80–1.16 apfu Fe^{VI} and 0.56–1-30 apfu Al^{VI}; Fig. 6.11 g to i).



Fig. 6.6: Sample D: a) Textural image of PS (i.e. polygonal serpentine; b) SAED showing the typical d_{00l} of serpentine (7 Å); c) HRTEM image showing the d_{00l} of serpentine; d) FFT of the investigated area in Fig. c) showing the basal reflection of serpentine; e) textural

image showing the paragenetic association between CCP smectite and MCA serpentine (modified from Putzolu et al., 2020); f) and g) SAED patterns showing the typical d_{00l} of serpentine (7 Å) and collapsed smectite (ca. 10 Å), respectively; h) EDX spectra of polygonal serpentine. Note that the structural formula of serpentine of EDX 1 is reported in Table 6.4.



Fig. 6.7: Sample C: a) textural image of CCP growing upon MCA (modified from Putzolu et al., 2020); b) HRTEM image showing the lattice fringe (7 Å) of serpentine; c) HRTEM image showing the lattice fringe (12 Å) of a partially collapsed smectite; d) HRTEM image showing the lattice fringe of R0 chlorite-smectite (modified from Putzolu et al., 2020).

The AEM data shown steep negative correlations between the Ni concentrations of chlorite and its Mg and Al^{VI} contents (Fig. 6.11 g and h). The analyses of Ni-rich chlorite are very close to those showing the chemical composition of smectite clays in terms of Al^{VI} (Fig. 6.11 h).

Conversely, no clear relationships are visible for the Ni – Fe^{VI} pair (Fig. 6.11i). Serpentine contains variable Ni concentrations (0.11–0.59 apfu Ni), which are anticorrelated with the observed Mg contents (1.72–2.67 apfu Mg; Fig. 6.11 g). Conversely, higher Ni concentrations are observed for the Fe-bearing (0.21–0.57 apfu Fe^{VI}) serpentine species (Fig. 6.11i). According to the stoichiometry data (Table 6.4), chlorite and serpentine phases have both a trioctahedral coordination and, similarly to smectite, a slight deficiency of the octahedral site, counterbalanced by trace amounts of Ca, K and Na.



Fig. 6.8: Sample C: a) textural image of CCP growing upon MCA; b) EDX spectra of serpentine; c) and d) EDX spectra of Fe-dominated smectite (nontronite- and ferrosaponite-like compositions, respectively); e) EDX spectra of chlorite-smectite; f) and g) STEM-EDX spectra of the area in the red frame in Fig. a). Note that the structural formula of serpentine

of EDX 1 is reported in Table 6.4, while the structural formulae of smectite of EDX spectra 2 and 3 (saponite and ferrosaponite, respectively) are reported in Table 6.3.



Fig. 6.9: Sample B: a) Textural image of OCA associated with oxy-hydroxides and quartz; b) textural image of oxy-hydroxides mimicking OCA; c) SAED pattern of turbostratic talc (see Fig. a for location); d) HRTEM image showing the lattice finger of talc-like (9 Å) and collapsed smectite packets (modified from Putzolu et al., 2020).

6.4 Discussion

6.4.1 Identification of Ni-bearing clays and Ni distribution in smectites

The micro- to nanoscale TEM-HRTEM data presented in this study provide additional insights about the complex Ni-bearing phyllosilicate assemblage occurring in the saprolitic ore of the Wingellina deposit. Preliminary results by Putzolu et al. (2020a) obtained by XRPD on oriented clay aggregates, NEWMOD® simulations and EMPA showed several peculiar clays associations, which are distributed within the profile following the control of the protolith and climatic regime.



Fig. 6.10: Sample B: a) HAADF image of OCA; b) to e) STEM-EDX spectra of the investigated area; f) EDX spectra of T/S.

Three groups were identified: a) montmorillonite + nontronite, developed from mafic rocks; b) serpentine (I), from the hydrothermal alteration of the ultramafic units; c) serpentine (II) + saponite + nontronite, developed from serpentine. The talc-smectite + chlorite-smectite assemblage overprints the assemblage c). Regarding the latter assemblage, Putzolu et al. (2020a) already highlighted the potential occurrence of the ferrosaponite-like smectite species, in paragenetic association together with saponite and nontronite. The TEM-HRTEM data not only confirmed the presence of the above phases but were also able to identify discrete trace amounts of Nibearing chlorite (i.e. clinochlore-like; Figs. 6.5 and 6.6). In general, the mismatches between XRPD- and TEM-based methods could either be due to the occurrence of phases below the limit of quantification of X-ray analysis (< 1%; i.e. Rietveld method) or to the poor to lacking crystallinity of the analyzed phases. However, ring-shaped SAED patterns were only

produced by smectite and kerolite-like clays (Figs. 6.3a and 6.9c). Instead, SAED patterns performed in chlorite-rich areas have produced regularly streaked reflections along the c* directions (e.g. Fig. 6.4b). This implies a certain degree of structural order of chlorite that is also consistent with the very few d_{hkl} of chlorite (belonging to the ordered IIb polytype) as supposed in previous studies conducted through XRPD methods (Putzolu et al., 2020). As a corollary, in the Wingellina samples the mismatch between XRPD and TEM is due to the very low concentrations of chlorite, rather than its lack of crystallinity. The diffractometric properties of chlorite provide also clues about its genesis as, in general, a high crystallinity is produced when specific environmental conditions, such as relatively high temperature and low water/rock ratio are attained (e.g. Velde and Meunier, 2008). This means that the detected chlorite would belong to the b) group and predates assemblages. The **TEM-HRTEM** the supergene clay nanoscale identification, combined with quantitative AEM data, allowed also to better constrain the Ni distribution in the Al-depleted smectite series (i.e. saponite \rightarrow ferrosaponite \rightarrow nontronite) occurring in the serpentinite-derived section of the Wingellina deposit (drillcore WPDD0019). The higher spatial resolution of AEM allowed a better underlining of the relationships occurring between the main octahedral cations. In particular, the chemical transition between ferrosaponite and nontronite is marked by a linear decrease of both Mg and Ni, which in turn confirmed the special affinity of Ni for entering the lattice of Mg-bearing trioctahedral species (saponite and ferrosaponite; Ni contents up to 0.73 and 0.51 apfu, respectively), rather than the Fe-dominated dioctahedral counterpart (i.e. nontronite; Ni content up to 0.29 apfu) (Fig. 6.11c). The progressive Ni-depletion observed for Mg-poor and Fe-rich smectites (Fig. 6.11c and d) of the saponite-nontronite series is consistent with the findings of previous studies on similar Nibearing smectite clays (Murrin Murrin deposit - Western Australia; Gaudin et al., 2004a), in which it is demonstrated that the Ni enrichment in smectite is closely related to the segregation of trioctahedral Ni clusters within the octahedral sheets of clay minerals. Therefore, the recorded loss of Ni during the saponite-to-nontronite transformation, either triggered by a decrease of pH or by an enhanced oxidation, can be due to a minor capability of dioctahedral smectite in hosting trioctahedral Ni clusters within the crystal lattice. Moreover, the microchemical AEM survey allowed the determination of significant Ni concentrations (0.35–1.21 apfu Ni) in the order IIb chlorite polytype. The anticorrelated relationships between the Ni

 $- Al^{VI}$ and Ni – Mg pairs (Fig. 6.11 g to h), as well as the slight octahedral deficiency coupled with the trace amounts of Na, K and Ca (Table 6.4), are the most significant geochemical features of chlorite.



Fig. 6.11: a) to f) Crossplots showing the chemical variations of Ni-smectites at Wingellina; g) to i) crossplots comparing the chemistry of smectites with those of serpentine and chlorite.

As discussed by Suárez et al. (2011), the occurrence of interlayer cations and the relatively low octahedral sum in II*b* chlorite might indicate the formation under oxidative environments of metastable and Ni-rich chloritelike clays. The latter may represent an intermediate stage typically ending
with the formation of smectite clays, which is consistent also with the close paragenetic relationship observed in this study between chlorite and smectite (Fig. 6.5). The most relevant aspect concerning the chemical composition of Ni-bearing serpentine is given by the correlation observed between the Ni and Fe^{VI} concentrations (Fig. 6.11i). The close Ni-Fe^{VI} association in serpentine species from the Wingellina deposit fits with the thermodynamic model proposed by Villanova-de-Benavent et al. (2017), which explained that the Ni endowment in serpentine under atmospheric conditions, as well as the stability of serpentine under oxidizing environment, is favoured the occurrence of significant Fe amounts in its crystal lattice. As regards to talc-like silicates, the detection of significant Al and Na concentrations are peculiarities of the 10 Å phases occurring at Wingellina, and do not fit with other kerolite-like phases observed in other typical study areas as the Dominican Republic (Villanova-de-Benavent et al., 2014; Villanova-de-Benavent et al., 2016; Tauler et al., 2017) and New Caledonia (Pelletier, 1983). This, as shown by the HRETM imaging (Fig. 6.9d), is due to the very low percentage of smectite-like packets occurring in R0 T/S, accounting for the tetrahedral $Si^{4+} \leftrightarrow Al^{3+}$ substitution, which is in turn balanced by the trace amounts of Na⁺ (Putzolu et al., 2020a).

6.4.2 Nanotextural imaging of Ni-bearing smectites: genetic clues

The use of ion milling technique for the TEM-HRTEM imaging allowed the detection of a range of clay textures (Fig. 6.12), with some of them, i.e. CCP and PCA as well as PS, already described in literature (Baronnet et al., 1994; Mondillo et al., 2015; Balassone et al., 2017). The OCA talc-smectite was described in detail in the present study. The Ni-smectite from Wingellina occurs solely with CCP and PCA textures (e.g. Fig. 6.2a-c). Mondillo et al. (2015) suggested that CCP form through overgrowing onto pre-existing oriented clays packets. This is consistent with our observations on CCP of (ferro)saponite, nontronite and chlorite-smectite, which often surround relict serpentine and chlorite (Figs. 6.5, 6.6e and 6.7a). Instead, as CCP montmorillonite occurs as isolated clays packets (Fig. 6.2a) this comparison cannot be drawn. As regards the PCA textures, in other supergene ores (i.e. Zn nonsulfides) their characteristics were ascribed to the neoformation process in cavities of clays directly precipitated from metalsrich solutions (Mondillo et al., 2015). However, in the laterite deposits the formation of phyllosilicates in discontinuities (e.g. faults and fractures) is a peculiarity of the *per descensum* model, which is effective in explaining the formation of garnierite-type ores (e.g. Cluzel and Vigier, 2008), while it cannot be applied to deposits like Wingellina that is located in cratonic areas. Therefore, to explain the formation of PCA at Wingellina, few additional key aspects need to be considered. Firstly, clays occurring in PCA are often associated at the microscale with a sort of "intercalations" of Mn-oxy-hydroxides (lithiophorite-like; Fig. 6.3b). As demonstrated by several authors (e.g. Nahon et al., 1989; Lambiv Dzemua et al., 2013; Dublet et al., 2017), in laterite systems the formation of Mn-oxy-hydroxides is an epigenetic process, which overprints the pre-existing mineralogical assemblage. Considering that Mn-oxy-hydroxides occurring in regolith systems very rarely have an isoriented needle-shaped texture (Dowding and Fey, 2007), the observed "intercalated" texture of Mn-oxy-hydroxides with PCA is likely inherited from montmorillonite after a direct-replacement process. Therefore, the above textural association indicates that oxyhydroxides post-date the formation of montmorillonite which, behaving as a template during the substitution process, gives the Mn-oxy-hydroxides a layered smectite-like (pseudomorph) structure. The montmorillonite-tolithiophorite transformation not only implies significant chemical changes (e.g. loss of Si and gain of Mn, Co, Fe, etc.), but also produces remarkable physical modifications. As a matter of fact, the volume of the montmorillonite crystal lattice is ca. 453 Å3 (Viani et al., 2002), while that of lithiophorite is ca. 207 Å3 (Post and Appleman, 1994). This means that the formation of Mn-oxyhydroxides as a replacement of clays leads to a significant bulk volume shrinkage, which would allow the formation of the porosity observed in PCA textures. Furthermore, the peculiar paragenetic association between montmorillonite and lithiophorite provides additional clues on the genesis of Co- and Ni-bearing oxy-hydroxides in laterite systems. In fact, earlier studies described the importance of aluminosilicate during the epigenetic formation of Co- and Ni-bearing oxy-hydroxides at the base of the oxide zones of a laterite profile (Nahon et al., 1989 and references therein; Putzolu et al., 2020a). In general, in laterite systems the initial formation stage of Mn-oxy-hydroxides was observed to develop as an epigenetic replacement of kaolinite (Nahon et al., 1989). Previous studies conducted on the oxide section of the Wingellina deposit confirmed the importance of the kaolinite-to-lithiophorite transformation (Putzolu et al., 2018), while the BSE imaging of the saprolite ore only shows that montmorillonite promoted the formation of Fe-oxyhydroxides (Putzolu et

al., 2020a). In this frame, the nanoscale TEM-HRTEM imaging presented in the present study (Fig. 6.3c–e) shows that montmorillonite behaves similarly to kaolinite, firstly because it offers a structural template for the epigenetic process and secondly because it supplies Al necessary to Mn-oxy-hydroxide crystallization.



Fig. 6.12: a) Summary of the observed and inferred parageneses of ore-bearing minerals occurring in the Wingellina saprolite zones; b) Sketch summarising the main clay textures detected in this study. Notes: * = information on the magmatic precursors from Putzolu et al. (2019, 2020), ** = Mg/Fe-smectite group comprehends the whole suite of Al-depleted smectite series (i.e. saponite, ferrosaponite, nontronite), *** =T/S clay species occurring as neoformed phase; Textures abbreviations: PS = polygonal serpentine; CCP = compact clay packages; MCA = massive clay aggregates; PCA = porous clays aggregates; OCA = oriented clay aggregates. Minerals abbreviations = Px = pyroxene; Ol = olivine; Pl = plagioclase; Srp = serpentine; Chl = chlorite; Mnt = montomorillonite; MnO/OH = Mn-

oxyhydroxide; Mg/Fe-sme = Mg- and Fe-rich smectite; Sap = saponite; Fe-sap = ferrosaponite; Non = nontronite; C/S = chlorite-smectite; T/S = talc-smectite.

Considering that in laterite systems, Co is never concentrated in clays but preferentially enriched in Mn-oxy-hydroxides, for its high geochemical affinity to Mn and for the high surface area of Mn-oxy-hydroxides capable to uptake Co³⁺ (McKenzie, 1989; Dowding and Fey, 2007), the detection of nanometric Mn-oxy-hydroxides disseminated within the smectites is a key for explaining the minor Co bulk-rock concentrations measured in the saprolitic zone of the Wingellina deposit, also useful for improving ore evaluation for metallurgical purposes. Moreover, the TEM-HRTEM imaging shown that the genesis of Ni-enriched smectite in samples from drillcore WPDD0019 (i.e. serpentinite-derived profile) is related with two distinct mechanisms: a) alteration of chlorite packets in the upper saprolite (sample B; Fig. 6.5); b) alteration of barren serpentine-bearing massive clay aggregates (MCA) in the lower saprolite (sample D; Fig. 6.6). The formation of smectite from serpentine is a common process in surficial settings and results from the relatively high solubility of serpentine when in contact with acid meteoric waters (pH \leq 5) (Lee et al., 2003). Despite this, the serpentine-to-smectite transformation, which we detected in the Wingellina deposit, has been rarely documented for Ni-laterite ores, with the only few cases corresponding to previous investigations dealing with the metallogenesis of the Murrin Murrin (Western Australia; Camuti and Gifford, 1997), Loma Ortega (Dominican Republic; Tauler et al., 2017) and of the Niquelândia (Brazil; Colin et al., 1990) laterite ores. As regards to the chlorite - smectite case, considering their distinct nature (i.e. hydrothermal for chlorite and supergene for smectite), the observed texture clearly indicates that trioctahedral chlorite (clinochlore-like; Fig. 6.5b) is relict and replaced by Ni-bearing trioctahedral smectite packets (saponite-like; Fig. 6.5c-g and Table 6.3). This peculiar association has been observed mostly in geological terranes where low-temperature retrograde alteration is superimposed on high-grade metamorphic assemblages (i.e. sub-greenschist facies), as a result of uplift and subsequent oxidation by phreatic waters (i.e. Nieto et al., 1994). Chlorite has been identified in the world-class smectiteendowed Ni-laterites of Niquelândia (Brazil; Colin et al., 1985) and Murrin Murrin deposits (Wells, 2003; Gaudin et al., 2005). However, since that previous mineralogical studies (Colin et al. 1985; Gaudin et al., 2005) relied either on XRPD- and SEM-based techniques or on TEM solely performed

on powders dispersed over carbon-coated copper grids, no attention has been devoted in defining the textural and paragenetic relationship between coexisting smectite and chlorite. As a result, it was believed that in lateritic ores the formation of Ni-bearing smectite clays was solely associated with the supergene alteration of ferromagnesian magmatic minerals (i.e. olivine and pyroxenes), and less with the alteration of serpentine (e.g. Nahon et al., 1982; Colin et al., 1990; Tauler et al., 2017; Putzolu et al., 2020a). Conversely, the nanoscale textural data presented in this study clearly evidenced that also chlorite acts as a template during the growth of saponite, which demonstrates that in laterite systems Ni-bearing smectites can also occur as alteration product of chlorite. This outcome is of importance in shedding new light on the minerogenesis of Ni-bearing smectites and could imply that ion milling-based TEM-HRTEM reanalysis of smectite-type deposits could be useful to better constrain the paragenetic pathway occurring during the ore-formation process.

6.5 Concluding remarks

The micro- to nanotextural TEM-HRTEM investigation from the Wingellina deposit confirmed that smectites, which correspond to a mixture of trioctahedral (saponite and ferrosaponite) and dioctahedral (nontronite and montmorillonite) species, are the main constituents of the Ni-bearing clays assemblage. The use of ion milling technique for the TEM-HRTEM imaging enabled to recognize two main smectite textural fabrics: an epigenetic fabric, inherited from pre-existing clay minerals (i.e. serpentine and chlorite; CCP textures) and a porous fabric (PCA texture) associated with late stage Co-bearing Mn-oxy-hydroxides. The epigenetic dioctahedral smectite (i.e. montmorillonite)-to-lithiophorite transformation, as well as the formation mechanisms of Ni-bearing saponite from primary chlorite, provide significant clues to improve the ore targeting in similar deposits worldwide and shed new light on the ore-formation processes occurring in Ni-laterite systems:

a) the detection of nanometric Co-bearing Mn-oxy-hydroxides substituting for PCA montmorillonite demonstrates that Ni- and Al-bearing smectite clays can act similarly to kaolinite during the epigenetic formation of lithiophorite-like phases. Moreover, the occurrence of Mn-oxy-hydroxides in the saprolite zone is also of importance to improve the Co targeting in similar laterite systems;

b) although the formation of smectite from chlorite has been recognized as a common process occurring in regions where the surficial alteration overprints metamorphic assemblages (i.e. sub-greenschist facies), before this study, this process was never described in Ni-laterite ores.

Drillcore ID	WPDD0012		WPDD0019	
Sample ID	Sample A	Sample B	Sample C	Sample D
Depth (m)	74	25	30	42.3
Sme	Х	Х	Х	Х
Kln	Х	-	-	-
Qtz	-	Х	Х	Х
Spl	Х	Х	Х	Х
Gt	-	Х	Х	Х
Dol	-	Х	-	-
T/S	-	Х	-	-
C/S	-	Х	Х	-
Srp	-	-	Х	Х

Table 6.1: Summary of the bulk rock mineralogical composition of the studied samples (modified from Putzolu et al., 2020a).

Mineral abbreviations (mainly after Siivola and Schmid, 2007): Sme = smectite, T/S= talc-smectite, C/S = chlorite-smectite; Srp = serpentine; Gt = goethite, Kln = kaolinite, Qtz = quartz, Spl = spinel, Dol = dolomite. Notes: X = detected; - = not detected or below the detection limit.

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Table 6.2: Structural formulas (apfu) of Ni-bearing montmorillonite from Wingellina, calculated on the basis on 22 negative charges [O ₁₀ (OH) ₂], obtained by AEM.																					
sample ID	А	А	А	А	А	А	А	А	А	А	А	А	А	А	А	А	А	А	А	А	А
EDX reference	-	Fig. 6.3: EDX 1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Si	3.10	3.54	3.74	3.61	3.59	3.59	3.68	3.74	3.63	3.60	3.56	3.51	3.74	3.32	3.35	3.37	3.42	3.36	3.22	3.23	3.23
Al ^{IV}	0.63	0.46	0.26	0.39	0.41	0.41	0.32	0.26	0.37	0.40	0.44	0.49	0.26	0.68	0.65	0.63	0.58	0.64	0.78	0.77	0.77
Fe ^{IV}	0.27	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
∑tet	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00
Al^{VI}	-	0.15	0.78	0.38	0.19	0.25	0.83	0.54	0.72	0.60	0.37	0.36	0.54	0.00	0.10	0.11	0.10	-	-	-	0.08
Fe ^{VI*}	1.19	1.35	0.83	1.15	1.15	0.87	0.78	1.06	0.85	0.90	1.14	1.10	1.06	1.25	1.16	1.15	1.18	1.31	1.14	1.16	1.13
Mg	0.48	0.34	0.52	0.37	0.40	0.40	0.48	0.41	0.45	0.43	0.36	0.41	0.41	0.34	0.42	0.44	0.44	0.48	0.40	0.39	0.38
Mn	0.01	0.04	-	0.01	0.01	0.01	-	0.01	-	0.01	-	-	0.01	0.01	0.01	-	-	0.02	0.01	0.02	-
Ni	0.51	0.38	0.10	0.33	0.51	0.71	0.15	0.26	0.17	0.20	0.28	0.27	0.26	0.54	0.49	0.52	0.46	0.41	0.74	0.58	0.53
Cr	0.03	-	-	-	-	-	-	-	0.05	0.07	0.06	0.07	-	0.06	0.05	0.03	0.05	0.03	0.03	0.07	0.08
Ti	0.03	-	-	-	-	-	-	-	0.01	0.03	0.04	0.03	-	0.04	0.04	0.02	0.03	0.05	0.03	0.04	0.04
Co	0.03	0.01	-	-	-	-	0.01	0.01	0.01	0.02	0.02	0.02	0.01	0.03	0.02	0.02	0.02	-	0.03	0.03	0.03
∑oct	2.28	2.27	2.24	2.24	2.26	2.24	2.25	2.29	2.26	2.26	2.26	2.25	2.29	2.26	2.28	2.29	2.27	2.30	2.38	2.28	2.27
Ca	0.02	0.03	0.06	0.06	0.04	0.06	0.04	0.01	0.03	0.04	0.03	0.04	0.01	0.04	0.02	0.01	0.03	0.01	0.02	0.02	0.03
К	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Na	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
\sum_{int}	0.02	0.03	0.06	0.06	0.04	0.06	0.04	0.01	0.03	0.04	0.03	0.04	0.01	0.04	0.02	0.01	0.03	0.01	0.02	0.02	0.03

Notes: * = all Fe was considered in the trivalent state; - = not detected.

Smectite group				Saponi	Ferrosa	Ferrosaponite					
sample ID	С	С	С	D	D	С	С	С	С	С	С
EDX reference	Fig. 6.8: EDX 2	-	-	-	-	Fig. 6.5: EDX2	-	-	-	Fig. 6.8: EDX 3	-
Si	3.57	3.62	3.62	3.54	3.54	2.78	3.07	2.98	3.35	3.57	3.65
Al ^{IV}	0.31	0.32	0.30	0.27	0.25	0.96	0.93	1.02	0.48	0.43	0.35
Fe ^{IV}	0.13	0.05	0.08	0.19	0.21	0.26	-	-	0.17	-	-
∑tet	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00
Al ^{VI}	-	-	-	-	-	-	0.01	0.08	-	0.04	0.18
Fe ^{VI*}	1.28	1.36	1.27	0.99	1.11	0.41	0.55	0.63	0.84	1.14	1.14
Mg	0.64	0.59	0.64	0.87	0.80	2.21	2.10	1.91	1.56	1.45	1.32
Mn	-	-	0.01	-	-	0.01	0.01	0.02	-	-	-
Ni	0.17	0.16	0.16	0.29	0.23	0.47	0.49	0.48	0.73	0.51	0.49
Cr	0.07	0.06	0.07	0.08	0.08	0.07	0.05	0.09	0.08	0.05	0.07
Ti	-	-	-	-	-	-	-	-	0.02	0.02	-
Co	-	-	-	-	-	-	-	-	-	-	-
\sum oct	2.16	2.17	2.14	2.22	2.22	3.17	3.21	3.21	3.23	3.21	3.20
Ca	0.09	0.08	0.10	0.07	0.07	0.01	-	0.02	0.05	0.07	0.07
Κ	0.05	0.05	0.03	0.01	0.02	-	-	-	0.01	0.02	0.02
Na	-	-	0.02	-	-	0.11	0.08	0.08	-	-	-
\sum int	0.14	0.13	0.16	0.08	0.08	0.12	0.08	0.10	0.06	0.09	0.09

Table 6.3: Structural formulae (apfu) of Ni-bearing nontronite, saponite and ferrosaponite from Wingellina, calculated on the basis of 22 negative charges $[O_{10}(OH)_2]$, obtained by AEM.

Notes: * = Fe was considered in the trivalent state for nontronite, whereas was considered in the bivalent form for saponite and ferrosaponite; - = not detected.

Clay group	•	Chlorit	te			Serpentine					
sample ID	С	С	С	С		С	С	С	D		
EDX	Fig. 6.5:						Fig. 6.8:		Fig. 6.6:		
reference	EDX 1	-	-	-			EDX 1	-	EDX 1		
Si	2.89	3.50	3.02	2.92		1.90	1.88	1.95	1.81		
Al ^{IV}	1.11	0.50	0.98	1.08		0.10	0.12	0.05	0.06		
Fe ^{IV}	-	-	-	-		-	-	-	0.14		
∑tet	4.00	4.00	4.00	4.00		2.00	2.00	2.00	2.00		
Al ^{VI}	1.08	1.29	1.01	0.83		0.11	0.07	0.18	-		
Fe ^{VI*}	0.92	1.04	0.86	1.07		0.57	0.51	0.51	0.38		
Mg	3.43	2.80	3.18	3.20		1.75	1.72	1.88	2.46		
Mn	0.02	0.02	0.02	0.02		0.01	-	-	-		
Ni	0.35	0.58	0.71	0.72		0.56	0.59	0.36	0.16		
Cr	0.05	0.12	0.11	0.08		0.01	0.04	0.03	-		
Ti	0.01	-	-	-		-	-	0.02	-		
Co	-	-	-	-		-	-	0.00	-		
\sum_{oct}	5.87	5.84	5.89	5.91		3.00	2.93	2.99	3.00		
Ca	0.02	0.01	0.02	0.01		-	-	0.01	-		
Κ	0.01	0.02	0.01	-		-	-	-	-		
Na	0.11	0.13	0.08	0.08		-	0.07	-	-		
\sum_{int}	0.13	0.16	0.11	0.09		-	0.07	0.01	-		

Table 6.4: Selected structural formulae (apfu) of Ni-bearing chlorite and serpentine from Wingellina, calculated on the basis on 28 $[O_{10}(OH)_8]$ and 14 negative $[O_5(OH)_4]$ charges, obtained by AEM.

Notes: * = Fe was considered in the bivalent form; - = not detected.



Appendix 6.1: XRPD patterns of the studied samples. Minerals abbreviations (mainly after Siivola and Schmid, 2007): Sme = smectite; Tlc = talc; Chl = chlorite; Srp = serpentine; Gt = goethite, Kln = kaolinite, Qtz = quartz; Spl = spinel, Dol = dolomite. N.B.: information about XRPD data acquisition in Putzolu et al. (2020).



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Appendix 6.2: Backscattered electron images of the studied samples. Minerals abbreviations (mainly after Siivola and Schmid, 2007): Sme = smectite; Srp = serpentine; Gt = goethite, Qtz = quartz; Spl = spinel. N.B.: information about SEM data acquisition in Putzolu et al. (2020).

Chapter 7:

Quantitative mineralogical evaluation of Ni-Co laterite ores through XRPD-QPA- and automated SEM-based approaches: the Wingellina (Western Australia) case study

7.1 Introduction

The quantitative mineralogical evaluation of Ni-Co laterite deposits and the determination of the metals distribution (i.e. their deportment) are critical for a reliable resource characterisation, for the identification of the ore types and for evaluation of the amenable processing methods (Crundwell et al., 2011; Dalvi et al., 2004). Most authors and mining companies have conducted routine study on Ni-Co laterites by conventional analytical methods, such as X-Ray Powder Diffraction (XRPD) followed by Quantitative Phase Analysis (QPA), Scanning Electron Microscopy-Back Scattered Electrons (SEM-BSE) and whole-rock geochemical assays. In the context of XRPD-related approaches, the Rietveld analysis (Rietveld, 1969) is one of the most widely applied. The Rietveld analysis allows the quantification of minerals in multiphase samples though the XRPD profile fitting method. The refinement is based on the crystallographic properties (e.g. cell parameters, atomic positions and Debye-Waller factors) of the compounds occurring in the sample. Moreover, by means of the internal standard approach, the Rietveld analysis also allows to evaluate the total amount of the non-crystalline components present in the analysed sample, or to assess the amount of crystalline phases not included in the refinement procedure, because their crystal structure is complex or not known (Bish and Howard, 1988). In the case of regolith ores, such as laterite and bauxite deposits, the most common issue related with the XRPD-QPA mineral quantification is the potential occurrence of amorphous or poorly-crystalline ore-bearing phases (e.g. Fe-oxy-hydroxides and silica-like phases, like chalcedony) and of poorly-crystalline minerals with not well-defined structures (i.e. smectite clays and certain Mn-oxy-hydroxides), which are only collectively quantified, but not distinguished (Negrão et al., 2018). SEM-based automated mineralogy techniques (e.g. QEMSCAN®, Mineral Liberation Analyser [MLA] and TESCAN Integrated Mineral Analyzer [TIMA-X]) have found widespread application in the quantitative mineralogical evaluation of laterite ores (Andersen et al., 2009; Blancher et al., 2015; Farrokhpay et al., 2019; Swierczek et al., 2011). However, the studies that have used automated SEM for the evaluation of Ni-Co laterites focused either on the quantification of Ni-bearing Fe-oxy-hydroxides in the oxide ore (Andersen et al., 2009), or on the mineralogical evaluation of the Ni-phyllosilicates and on the Ni deportment in the saprolite zone of the deposits (Blancher et al., 2015; Farrokhpay et al., 2019). These studies were focused on the mineral association and on Ni behaviour in specific ore zones of the laterite deposits, without considering the variability of Ni between the different facies of the regolith profile, or paying direct attention to the Co deportment. Based on the above quoted literature, also very little is known on the potential occurrence of poorly crystalline phases and on their role in Ni and Co deportment within the different ore zones of a typical laterite profile. Therefore, in this part of the study a comparison between XRPD-QPA and automated SEM is presented with the aim of unravel the challenges and benefits of these analytical methods during the mineralogical evaluation of Ni-Co laterite deposits. Special attention is also devoted to reach a more comprehensive knowledge of the relationship between the modal mineralogy and the deportment of both Ni and Co, and to determine to role of the poorly crystalline phases in the ore distribution. To pursue this goal, an extensive dataset of samples collected from the whole suite of mineralised facies (i.e. oxide and saprolite types) in the word-class Wingellina Ni-Co laterite deposit (Western Australia) will be described and discussed.

7.2 Materials and methods

7.2.1 Sampling strategy and sample preparation

Five samples from reverse circulation drill chips were used for this study (Table 7.1), each of them representing a homogenised sample over 2 m of drilled interval, therefore allowing a better understanding of the bulk profile properties. The sampling of the 2 m-interval of reverse circulation drillcores was performed following the representativeness guidelines provided by the JORC Code. Depending on lithological variations, the company yielded 40-50 kg of drill hole material, each one corresponding to a 2 m-interval, which underwent a cyclone cone splitting step, in order to obtain 2-3 kg of sample to be analysed as chemical assay. With this strategy, a representative assessment of the variable mineralised facies occurring within the laterite

profile was considered to be achieved. The five samples we used for this study were subsampled from the duplicate samples stored from the mining company, and re-assayed (Table 7.2) to avoid any mismatch deriving from the subsampling.



Fig. 7.1: a) and b) Representative laterite profiles of the Wingellina Ni-Co deposit (after Putzolu et al., 2018 modified); c) to f) Diamond drillcores showing the typical aspect of the ore types occurring at Wingellina (photos courtesy of Metals X Ltd).

Samples WCS04065 and WCS01936 (hereafter samples A and B) were taken from the FeO/OH-rich zones of the oxide ore, while sample WCS09603 (hereafter sample C) was collected from the MnO/OH-rich layers within the oxide ore (Fig. 7.1). Samples WCS01938 and W15803 (hereafter samples D and E, respectively), which represent the smectite and serpentine ore subtypes, respectively, were collected from the saprolite ore (Fig. 7.1). Sample preparation was carried out at the Dipartimento di Scienze della Terra, dell'Ambiente e delle Risorse (DiSTAR, University of Napoli, Federico II). The material from each sample was subdivided in two halves by coning and quartering. The first half (ca. 30 g) was used for whole-rock geochemical analyses and X-ray Powder Diffraction Analyses (XRPD). About 30 g of the other half were sieved to obtain 3 particle size subsamples for each specimen (ca. 1 g), to be analysed with automated, as well as with conventional SEM-EDS. The subsamples have a particle size from 0.17-021 mm (a), 0.3-0.42 mm (b) and 0.5-1 mm (c). This step was necessary to minimise the range of particle sizes in each sample, in order to make the measurement parameters more effective and to balance resolution versus time/costs (Santoro et al., 2015). One block for each subsample was prepared at the Core Research Laboratory of the Natural History Museum (NHM) in London (UK). The particles were englobed using bi-component epoxy resin (SpeciFix20) mixed with hardener. The particles were manually mixed while in suspension for about 6 min, in order to guarantee homogenization and to keep the air bubble formation low. The samples were then subjected to 2 bar pressure for 24 hours so to further reduce the air bubble formation during hardening and to polishing using an aluminium oxide (0.3 μ m) and diamond suspension (1 μ m), and finally carbon coated.

7.2.2 Analytical methods

7.2.2.1 Whole-rock geochemistry

Whole-rock geochemical analyses of major, minor and trace elements, were carried out at ALS Minerals, OMAC Laboratories Ltd (Co. Galway, Ireland). About 4 g of material were powdered and analysed by fused bead acid digestion. To obtain the major oxides composition multi-element Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) was used, while the multi-element ICP-MS was carried out to measure the Ni and Co grades as well as the trace elements.

7.2.2.2 X-ray Powder Diffraction

The XRPD analyses were conducted at the Natural History Museum in London (NHM) with a Panalytical X'Pert Pro MPD automated diffractometer, using a Co Ka. The operating conditions were of 40 kV and 40 mA, step scan size of 0.017° 2 θ , a measurement range of 4 °2 θ to 120°2 θ and counting time of 320s. The diffractometer operated with a soller slit of 0.02 rad, antiscatter slit 0.50° and divergence slit 0.25°. The "Mineral" identification was performed with the HighScore Plus software along with the PDF-2 database from ICDD (International Centre for Diffraction Data). The identification of the clay minerals occurring in the analysed samples was based on previous XRPD- and TEM-based studies conducted on the same mineralised laterite facies (Putzolu et al. 2020a and 2020b). The XRPD-QPA was carried out with the Topas software (academic version 4.1) by combining the Rietveld and the internal standard method, in order to calculate the amounts of poorly-crystalline phases, not directly quantifiable through the Rietveld profile fitting method. An amount of 10% of internal standard (corundum, Al₂O₃) was added to the powdered samples (Bish and Howard, 1988). To perform the Rietveld profile fitting method, the preferred orientation of crystallites was refined through the March function (Dollase, 1986), while the contribution from the instrument was modelled with a Lorentzian crystallite size, a strain component, and a 3rd or 4th order Chebyshev background (Cesarano et al., 2018). To assess the validity of the Rietveld refinement, we used the weighted profile R-factor (Rwp). Moreover, in order to ensure the accuracy of the results of the Rietveld analysis, the quantitative data of minerals recognized during the qualitative step and occurring in amounts <1w% were considered below the limit of quantification (LoQ; León-Reina et al., 2016 and references therein). Based on previous studies conducted on the oxide- and saprolite ores of the Wingellina deposit (Putzolu et al., 2018; 2020a), the main limits to the XRPD mineral quantification can be related with the occurrence of: 1) poorly to non-crystalline phases (e.g. oxy-hydroxides and silica), 2) structurally complex minerals (e.g. smectite clays), 3) phases with crystal structures not defined in the international mineralogical databases (e.g. asbolane). When referring in text to the comprehensive amount of all these phases not singularly evaluable via profile fitting, we used the term undistinguished poorly to non-crystalline phases (UPCP). When Rietveld analysis is carried out on samples containing UPCP, the amount of internal standard (X_{LS}) obtained with the profile fitting method, results bigger than the nominal amount initially added to the powder. At the same time, the

quantities of the other minerals (X_m) are also overestimated. The XRPD internal standard quantification method allows recalculating the true amounts of the diverse mineral phases occurring in the sample and used for the profile refinement, and to calculate by difference to 100 the total amount of UPCP. This is pursued by using the ratio between the nominal amount of internal standard initially added to the powder (in this case 10 wt.%) and the amount of internal standard (X_{IS}) resulting from the profile fitting method (Bish and Howard, 1988).

The true amounts of the diverse mineral phases (X_i) are recalculated as (equation 1):

(1)
$$X_i = X_m * 10 / X_{IS}$$

Where the X_m values represent the amounts of the diverse minerals obtained with the Rietveld profile fitting method. The total UPCP amount X_{UPCP} can be then calculated as (equation 2):

(2)
$$X_{UPCP} = 100 - \sum X_i - 10$$

For a correct view of the results, it is necessary to normalize the values X_i and X_{UPCP} to 100%, excluding the 10% of the internal standard. To determine and quantify each phase composing the UPCP, calculations were carried out on a chemical basis, comparing the whole-rock chemical compositions of the samples derived from ICP-MS analysis, and the bulk-rock chemistry calculated from the well-ordered crystalline phases identified through the XRPD; details on this procedure are reported in paragraph 3.3.

7.2.2.3 Scanning Electron Microscopy with Energy Dispersive Spectroscopy

SEM-EDS analyses were carried out at the DiSTAR using a Jeol JSM 5310 instrument. The analytical conditions were: 20 mm objective lens to specimen working distance, 15 kV accelerating voltage with a tilt angle of 0°. The EDS analyses were carried out with the INCA X-stream pulse processor and the 4.08 version Inca software (Oxford Instruments detector), interfaced with the Jeol JSM 5310.

7.2.2.4 Automated SEM

The automated SEM analyses were carried out at TESCAN Orsay Holdings (Brno, CZ), using the TIMA-X system equipped with 3 EDAX Element

silicon drift detectors and a TESCAN MIRA 3 Schottky field emission gun SEM. The data were collected using 5 µm pixel spacing and ca. 1000 total X-ray counts per spectrum. The analytical time was approximately 1 hour to 2 hours per block sample depending on the amounts of particles in each block. Standard instrument calibration (beam focusing, beam alignment, BSE and EDS) was performed prior to analyses. The analyses were operated at 25 kV and 10 nA at 15 mm WD. The analytical procedure used was the high resolution mapping (Hrstka et al., 2018) providing both the BSE image and EDX data collection simultaneously in order to have both the maps of the mineral phases distributions in the sample and a full dataset for each fraction analysed, i.e. modal mineralogy, element assays and element deportment. The modal mineralogy data are reported in wt% by known density of minerals and automatically calculated by the TIMA-X software from known mineral densities. The attribution of the density to the mineral entries has been made according to the following approach: (i) for entries consisting of minerals sensu strictu (e.g. goethite, serpentine etc.) we used the density data provided by the International Mineralogical Association (IMA); (ii) for mineral categories consisting of chemical or textural mixtures of different phases (e.g. lithiophorite-asbolane and goethitesmectite, respectively) we used an intermediate density between endmembers. For the data processing, a mineral list was defined a priori based on XRPD and SEM-EDS data. To improve the accuracy of the results, five different mineral lists (one for each sample) were created, due to the high variability of the mineral chemistry of the ore-bearing phases. The lists comprehend both minerals sensu stricto (i.e. IMA accepted), and materials identified by distinct chemical composition by the TIMA-X software after the analyses. The lists were then adjusted and re-processed after the data acquisition in off-line mode, in order to better constrain the mineralogy of the samples. Considering the large number of distinct minerals, it was necessary to group them into categories to facilitate the comprehension of the maps. The final mineral list and the average chemistry of each entry is displayed in Appendix 7.1. During the drafting of the mineral list, a special focus was devoted to the chemical classification of Mn-oxy-hydroxides and clay minerals. According to previous studies (Putzolu et al., 2018), Mn-oxyhydroxides mostly belong to the lithiophorite-asbolane group, which is characterized by a broad chemical fluctuation between the Al-rich (i.e. lithiophorite) and the Co- and Ni-rich (asbolane) end-members. Therefore, in this study we defined three main classes, based on the relative proportions

of Al, Co and Ni: a) lithiophorite (Al >10%, minor amounts of Ni and Co); b) lithiophorite-asbolane intermediates (Al 3-10%, Ni >10%, Co >2%); c) asbolane (Al <2%, Ni >10%, Co >2%). Regarding clay minerals, the classification was based on the Si/ Σ R ratio (Σ R = sum of the octahedral metals) of the mineral entries, which can be used as a chemical proxy of the nature of clays (Putzolu et al., 2020a). The Ni and Co contents of the entries in the mineral list were validated using the spectrum tool function (Hrstka et al., 2018). In order to improve the accuracy of the Ni and Co levels, only the spectra yielding more than 20,000 counts were quantified.

7.2.3 Approach to the data treatment

In order to obtain the mineralogical distribution (i.e. deportment) of Ni and Co, we relied on the principles adopted in previous studies (Frenzel et al., 2019; Goodall, 2008; Kern et al., 2018; Minz et al., 2015), where it has been proposed that the deportment of a *K* element having a C_K bulk-rock concentration in a sample consisting of *N* phases can be described by the following set of percentages (equation 3):

(3) Deportment of element
$$K = \left\{ \frac{C_i * x_i}{C_K} * 100 \right\}_{i=1,\dots,N}$$

where the c_i variable represents the concentration of the *K* element in the mineral *i*, and x_i is the abundance of mineral *i*. Since the bulk-rock concentration of the *K* element (C_K) is equal to (equation 4):

(4)
$$C_K = \sum_{i=1}^N c_i * x_i$$

the deportment of an element can be defined by knowing its concentrations within the phases occurring in the samples and the bulk-rock modal mineralogy. This method provides a useful tool to check the quality of deportment data by comparing the calculated bulk-rock concentration (C_{κ}) and the real assay data, obtained with an independent method (i.e. ICP-MS/AES). Specifically, it is possible to infer the difference between the calculated and the real assay, and thus the composition of the bulk UPCP, following the equation (5):

(5)
$$\Delta\% = \left\{ \left[\left(C_{K(XRPD-QPA/EDS)} - C_{K(ICP-MS/AES)} \right) / C_{K(ICP-MS/AES)} \right] * 100 \right\}$$

where, Δ % represents the percentage difference between the calculated and the real assay, $C_{K(XRPD-QPA/EDS)}$ parameter is the bulk-rock concentration of

the *K* element calculated by combining the XRPD-QPA and mineral chemistry data (see equation 2), while $C_{K(ICP-MS/AES)}$ is the real bulk-rock concentration of the *K* element observed through ICP-MS/AES. According to equation (5), if negative Δ % are observed, the chemical composition of the various phases enclosed in the UPCP can be deduced (e.g. a significant negative Δ % of Mn indicates the occurrence of non-crystalline Mn-oxy-hydroxides) and can by fitted with a trial and error approach, by using the following equation (6):

(6)
$$C_{K(XRPD-QPA/EDS)*} = \sum_{i=1+UPCP}^{N+UPCP} (c_i * x_i) + (c_{UPCP} * x_{UPCP})$$

In the above equation, C_{UPCP} is the concentration of the *K* element in the supposed phase of the UPCP, X_{UPCP} is the amount of phase in the bulk UPCP and $C_{K(XRPD-QPA/EDS)}$ * is the adjusted bulk-rock concentration of the K element. The outputs of TIMA-X (i.e. modal mineralogy [x_{class}], element deportment [c_{class}] and the calculated bulk element concentration in the sample [$C_{K(TIMA-X)}$]) for each subsample were combined automatically in order to give an estimated average of the features on the scale of the total sample. The modal mineralogy and the element deportment data obtained by automated SEM-BSE are combined through the software. The calculated element concentration in the sample ($C_{K(TIMA-X)}$) according to the equation (7):

(7)
$$C_{K(TIMA-X)} = \sum_{i=1}^{N} (c_{class} * x_{class})$$

For reliable geochemical reconciliation the $C_{K(XRPD-QPA/EDS)}$ * and $C_{K(TIMA-X)}$ values have to fit properly with the real chemistry obtained by independent direct methods, like ICP-MS/AES ($C_{K(ICP-MS/AES)}$).

7.3 Results

7.3.1 X-ray Powder Diffraction-Quantitative Phase Analysis (XRPD-QPA)

7.3.1.1 Qualitative observations

The XRPD patterns (Fig. 7.2) indicate that goethite is the most widespread phase as it has been detected in all ore types. In all the oxide ore specimens, as well as in the smectite ore, typical reflections allocated to MnO/OH have been also widely detected in the high *d*-spacing region of the patterns (at

approximately 10 Å to 4.5 Å). Among them, a distinct peak at 6.88 Å, visible in samples B and C, can be ascribed to the basal reflection (i.e. d_{001}) of the chalcophanite group MnO/OH.



Fig. 7.2: XRPD patterns of the different ore types. N.B.: the internal standard (i.e. corundum) peaks are highlighted in orange, while the mineral phases not modelled by Rietveld (i.e. MnO/OH and smectite) are indicated in red.

The peaks at ca. 9.50 Å and 4.60 Å fit relatively well both with lithiophorite and asbolane. However, considering the peak at around 9.50 Å, slight differences can be observed in the studied specimens. In sample C the 9.50 Å peak fits correctly with the lithiophorite d_{003} band, while in the samples A and B this peak is shifted to 9.58 Å, which might indicate the presence of partially crystalline asbolane. Clay minerals, such as smectite and serpentine, are very common in the saprolite ores (sample D and E). Following previous studies on clay minerals (Putzolu et al., 2020a and 2020b), dioctahedral smectites, characterized by a d_{060} reflection at 1.51 Å, are recognized in samples A, D and E, while trioctahedral smectites occur $(d_{060} = 1.53 \text{ Å})$ only in sample E. The serpentine occurring in sample E shows the typical d_{hkl} of lizardite-1*T* polytype (i.e., d_{201} at 2.50 Å and d_{202} at 2.14 Å). Among the other phases, quartz, kaolinite, gibbsite, spinel (picotite and hercynite) and magnetite have been detected both in the oxide and in the saprolite samples. In all the five studied samples the occurrence of very high backgrounds, together with the presence of relatively broad peaks (e.g. goethite peaks at ca. 4.20 Å and 2.40 Å), indicate a significant amount of poorly crystalline phases.

7.3.1.2 Quantitative mineralogy

The XRPD-QPA results are summarized in Fig. 7.3 and Table 7.3, while the Rietveld refinements are reported in Appendix 7.2.

Oxide zone: the mineral abundance of goethite varies largely among the studied oxide ore samples. In the FeO/OH-dominated samples (i.e. sample A and B) goethite (ca. 64 wt% and 38 wt%, respectively) is the major ore mineral, while trace amounts of lithiophorite and chalcophanite (ca. 3 wt% and <Limit of Quantification [LoQ], respectively) were detected only in sample B. Goethite is abundant also in the MnO/OH-rich oxide ore (ca. 20 wt%), where the highest amounts of lithiophorite (ca. 13 wt%) have been Moreover, in the MnO/OH-dominated ore, traces measured. of chalcophanite (<LoQ), were also detected. Spinel (ca. 2-3 wt%), magnetite (ca. 0-2 wt%), quartz (ca. 0-30 wt%) and kaolinite (ca. 0-8 wt%) are common in the FeO/OH-rich oxide ore samples, while gibbsite (ca. 17 wt%) has been detected only in the MnO/OH-rich ore type. Significant amounts of UPCP were calculated with the internal standard method both in the FeO/OH-rich oxide ore samples (ca. 23-27 wt%) and in the MnO/OH-rich ore type (ca. 50 wt%). In all samples from the oxide zone, relevant proportions of the UPCP comprise MnO/OH, not directly quantifiable for the lack of crystal structures. Similarly, smectite group minerals occur in the UPCP of sample A. The high background of sample B suggests the occurrence of amorphous phases s.s.

Saprolite zone: in the smectite ore the non-economic phases are kaolinite (ca. 16 wt%), quartz (ca. 9 wt%) and spinel (ca. 5 wt%). In the serpentinite subtype ore (sample E) serpentine (ca. 49 wt%) and goethite (20 wt%) are the main ore phases. In the smectite ore (sample D) goethite is the most abundant crystalline ore mineral (ca. 14 wt%). Moreover, traces of

lithiophorite have also been detected, although its concentration is <LoQ. In both the saprolite samples, the internal standard method allowed to calculate elevated contents of UPCP (i.e. ca. 25 wt% in the serpentinite ore and ca. 56 wt% in the smectite ore), which in both ore subtypes include smectite, while traces of MnO/OH only occur in the smectite ore.



Fig. 7.3: Pie charts showing the modal mineralogy of bulk samples obtained by XRPD-QPA and automated SEM (expressed in wt%). Abbreviations: * = undistinguished poorly to non-crystalline phases (calculated as difference to 100%); LoQ = Limit of Quantification of the XRPD-QPA method (i.e. <1wt%; León-Reina et al., 2016 and references therein);

Ght = goethite; Kln = kaolinite; Spl = spinel; Mgt = magnetite; FeO/OH = Fe-oxyhydroxides; MnO/OH = Mn-oxy-hydroxides; Sme = smectite; Lth = lithiophorite; Chp = chalcophanite; Qtz = quartz; Gbb = gibbsite; Srp = serpentine; Mnt = montmorillonite; Lth-Asb = lithiophorite-asbolane; Fe/Mg-sme = Fe-Mg smectite; Asb = asbolane; *Mnt-Ght = mixed montmorillonite-goethite; Mnt-Lth-Asb = mixed montmorillonite-goethite-asbolane; Asb-Ght = mixed asbolane-goethite; Ght-Qtz = mixed goethite-quartz; Mnt-Qtz = mixed montmorillonite-quartz; Ght-Sme = mixed goethite-smectite; Qtz-Clay = mixed quartzclay; Clay-Ght = mixed clay-goethite.* N.B. = abbreviation in italics represent mixed mineral classes detected by automated SEM.

7.3.2 Nature of the UPCP

In this section we report the results of calculated chemistry (C_K ; Table 7.4) based on amounts of mineral phases detected through XRPD-QPA (x_i ; Table 7.3) and their mineral chemistry by SEM-EDS (c_i ; Appendix 7.3) by following the equation 4 and we also show its difference to the real chemical assay (Δ %; equation 5). In addition, following the equation 6, the data obtained for chemical refinement of the UPCP are also reported (Table 7.3).

Oxide zone: in sample A by comparing the calculated bulk-rock concentration on crystalline minerals (C_K) and the real assay the most significant Δ % values are obtained for Co, Ni and Mn, while lower differences were detected for Si, Mg, Fe and Al. Considering the occurrence in the XRPD pattern of the typical reflection of MnO/OH and smectite groups minerals, the difference between the calculated and observed Fe amounts suggests that the UPCP is also composed of FeO/OH-like phases together with MnO/OH and smectite (x_{UPCP} approximately 10 wt%, 7 wt% and 6 wt%, respectively). In sample B the most significant Δ % are displayed by Mn, Fe, Ni, Al, Cr and Si, suggesting that UPCP might be represented by FeO/OH-, MnO/OH- and silica-like poorly crystalline compounds (x_{UPCP} approximately 17 wt%, 1 wt% and 8 wt%, respectively). The remarkable Δ % values for Ni, Co, Mn and Mg, observed in sample C confirm that the bulk of the UPCP is represented by a MnO/OH-like phase (x_{UPCP} approximately 50 wt%).

Saprolite zone: in the smectite ore (sample D), the most underestimated elements of the C_K assay are Ni and Mg, followed by Co, Cr, Si, Fe and Mn. Similarly to sample A, the chemical calculation allowed to confirm that UPCP are only represented by smectite and MnO/OH (x_{UPCP} approximately of 55 wt% and 1 wt%). In the serpentinite ore (sample E), Al and Ni,

followed by Si are the most underestimated elements in the calculated C_K assay, confirming that a smectite-like phase represents the bulk of UPCP (x_{UPCP} approximately of 25 wt%).

7.3.3 Automated SEM analyses

7.3.3.1 Modal Mineralogy

The average modal mineralogy (x_{class}) automatically calculated by means of the TIMA-X software is shown in Fig. 7.3 and Table 7.5.

Oxide zone: in the FeO/OH-dominated samples, goethite is the dominant phase with concentrations (76.46 wt% in sample A and 53.30 wt% in sample B) comparable to XRPD-QPA results. Similarly, the quantification of MnO/OH conducted by automated SEM led to outcomes close to those of XRPD-QPA, although improving the classification scheme by adding more specific mineralogical (and chemical) classes as lithiophorite-asbolane (3.02 wt% in sample A and 3.70 wt% in sample B) and asbolane (2.14 wt% in sample A). The modal analysis conducted by automated SEM reclassified the lithiophorite amounts detected by XRPD-QPA in sample B (ca. 3 wt%) as lithiophorite-asbolane. In sample A, montmorillonite concentration was slightly lower (3.44 wt%) in comparison to the smectite amounts measured by XRPD-QPA. However, the balance is represented by montmorillonite occurring in a few mineral classes consisting of mixtures of distinct minerals (i.e. grains composed by distinct minerals), specifically 5.14 wt% of mixed montmorillonite-goethite and ca. 1.49 wt% of mixed montmorillonite-asbolane. In both FeO/OH-dominated samples, the main non-economic minerals have been quantified, with modal values slightly different to those produced by XRPD-QPA. In MnO/OH-dominated oxide ore, the data obtained by automated SEM show an overestimation of the goethite amount (28.5 wt%), and an underestimation of lithiophorite (3.46 wt%) in comparison with XRPD-QPA. The lithiophorite-asbolane and the gibbsite concentrations (49.45 wt% and ca. 15.92 wt%) fit properly with the XRPD-QPA data. Minor amounts of asbolane (0.76 wt%) were also detected.

Saprolite zone: in the smectite ore subtype montmorillonite, spinel (including hercynite and chromite) and MnO/OH amounts (57.42 wt%, 6.54% and 1.47 wt%, respectively) match those of XRPD-QPA. Similar to oxide ores, the automated SEM analysis classified the lithiophorite and the

poorly-crystalline MnO/OH measured by XRPD-QPA as lithiophoriteasbolane intermediates. Goethite and quartz amounts detected through automated mineralogy (11.49 wt% and 4.96 wt%, respectively) are slightly lower in comparison with the XRPD-QPA data, due to the detection of minor amounts of mineral classes as mixed goethite-smectite and mixed quartz-goethite. However, the significant amounts of kaolinite that were observed through analysis by XRPD-QPA were not observed in the analysis carried out with the automated SEM method. The serpentine and smectite amounts (42.27 wt% and 19.69 wt%, respectively) in the serpentinite ore subtype were slightly underestimated in comparison with XRPD-QPA, due to the occurrence of significant amounts of mixed classes comprising clay minerals (e.g. mixed clay-goethite and mixed quartz-clay). Moreover, trace amounts of MnO/OH (i.e. lithiophorite-asbolane; 0.43 wt%), were also detected.

7.3.3.2 Ni-Co deportment

Oxide zone: in FeO/OH-dominated oxide samples, significant amounts of Ni and Co (c_{class}) are contained in goethite (55.72% Ni in sample A and ca. 52.07% Ni in sample B; 6.52% Co in sample A and 25.18% Co in sample B; Table 7.6). Despite the abundance of goethite, the Ni and Co deportments are defined by MnO/OH. Sample A is the most extreme case following the previous rule: although MnO/OH species represent a minor component of the mineralogical assemblage in the sample, they carry almost half of the total Ni amount (24.40% in lithiophorite-asbolane and 15.62% in asbolane), and about 85% of bulk Co (64.09% in lithiophorite-asbolane and 19.03% in asbolane). A similar situation is observed in sample B, where Ni and Co are hosted in Ni-chalcophanite (16.27% and 6.60%, respectively) and in lithiophorite-asbolane (29.83% and 67.87%, respectively). Another aspect highlighted by the ore deportment in samples B and C is that Ni and Co follow a peculiar speciation that is not controlled by the modal abundances of the MnO/OH classes detected through automated SEM. In sample B Nichalcophanite plays a primary role in controlling both the Ni and Co distribution, despite its modal abundance being very low (1.82 wt% by automated mineralogy). Conversely, in sample C the lithiophorite control on the Ni-Co distribution is negligible (0.45% Ni and 0.31% Co), although its detection by XRPD-QPA and by automated SEM in significant amounts. In the MnO/OH-dominated oxide ore, Ni and Co are almost totally carried in lithiophorite-asbolane (91.64% and 94.77%, respectively), while minor

portions of the ore metals are carried in asbolane (4.70% Ni and 1% Co) and goethite (2.30% Ni and 3.82% Co).

Saprolite zone: in smectite ore, most of the Ni is associated with montmorillonite (71.80%). However, a significant portion of Ni is also hosted in goethite (8.18%) and in lithiophorite-asbolane (8.82%), as well as in the goethite-smectite mixed class (10.16%). Iron- and MnO/OH are the major Co sinks also in the clay-dominated ore (76.13% in lithiophorite-asbolane and 23.83% in goethite). In the serpentinite ore, most Ni is associated with the goethite-clay mixed class (40.65%) and to Fe/Mg-smectite (36.07%), while serpentine and goethite account less of the Ni content (18.89% and 3.75%, respectively). The Co deportment is very similar to that observed in the smectite ore, with lithiophorite-asbolane and 18.66% in goethite).

7.3.4 Quality control: bulk geochemistry (ICP-MS/AES) vs. XRPD-QPA and automated SEM calculated chemistry

The data obtained from automated SEM and from XRPD-OPA are commonly affected by errors like mis-classification of phases. Therefore, the key quality control step is crucial for studies that aim to assess the modal mineralogy and the ore deportment by means of these techniques (e.g. Kern et al., 2018). To this end, the bulk geochemistry obtained by ICP-MS and ICP-AES analyses ($C_{K(ICP-MS/AES)}$)), (Table 7.2) has been used to help to validate the results obtained by both XRPD-QPA ($C_{K(XRPD-QPA/EDS)}$ *) and automated SEM ($C_{K(TIMA-X)}$). For data validation, we have selected Mg, Al, Si, Cr, Mn, Fe, Ni and Co as they represent the major elements occurring in the Wingellina ore-carriers and gangue minerals. Agreement between the observed data $(C_{K(ICP-MS/AES)})$ and the calculated geochemistry $(C_{K(XRPD-QPA/EDS)} * \text{ and } C_{K(TIMA-X)})$ is represented by means of the coefficient of determination R^2 , where a perfect geochemical reconciliation is achieved when $R^2 = 1$. The results of the quality control step are reported in Fig. 7.4 and Tables 7.7 and 7.8. Overall, the best fits between the bulkrock geochemical data and the calculated chemistry are observed for Mg and Si. For these elements both the XRPD-QPA and automated SEM produced a very coherent reconciliation with $R^2 = 0.99$. Regarding Al, few differences can be observed both between the $C_{K(ICP-MS/AES)}$ data and the XRPD-QPA- and automated SEM-derived assays. In particular, the largest deviation is found for the smectite ore (sample D), where the XRPD-QPA overestimated the $C_{K(ICP-MS/AES)}$ data by +1.65%, whereas the automated SEM produced an underestimation of -0.68%. Moreover, both XRPD-QPA and automated SEM slightly underestimated the bulk Al composition of -0.81% and -1.15%, respectively.



Fig. 7.4: Comparison between the calculated assays (from automated SEM and XRPD-QPA) vs. the whole-rock geochemistry from ICP-MS/AES.

The data observed between the measured and calculated Cr composition show that automated SEM ($R^2 = 0.97$) was more effective than XRPD-QPA (R2 = 0.89). Despite this, the calculated Cr compositions are characterized by significant discrepancies compared to the $C_{K(ICP-MS/AES)}$ data. In particular, the automated SEM data show a Cr overestimation of +1.56%, while XRPD-QPA underestimated the Cr concentration of -0.42%. The Mn geochemistry was effectively calculated by both automated SEM and XRPD-QPA methods ($R^2 = 0.99$). However, XRPD-QPA overestimated Mn (+6.90%) in the MnO/OH-dominated oxide ore (sample C) that was not found in the automated SEM computation. Iron concentration of all studied

ore types is well fitted by the XRPD-QPA calculation ($R^2 = 0.99$), while the automated SEM quantification yields a significant overestimation in both the MnO/OH-dominated (sample C, +6.70%) and smectite (sample D, +4.11%), showing a lower correlation coefficient ($R^2 = 0.94$). Both XRPD-QPA and automated SEM produced reliable calculations of the Ni and Co grades of the studied samples. Regarding the Ni grades, this study indicates that both techniques were effective in modelling the ore content in the FeO/OH- and MnO/OH dominated ores, while significant misfits are observed for the saprolitic ores. In this context, few differences between the applied techniques are still observed mainly in the Ni reconciliation, where XRPD-QPA led to a better fit ($R^2 = 0.97$) as compared to the automated SEM ($R^2 = 0.90$). The poorer Ni reconciliation obtained by automated SEM is mainly due to its slight overestimation for serpentinite ore (+0.45%). Moreover, both XRPD-QPA and automated SEM underestimated the Ni content in the smectite ore (-0.45% and -0.32%, respectively). The Co grade was accurately calculated both by automated SEM and by XRPD-QPA; however, the automated SEM-derived modelling led to better fits (R^2 = 0.98) as compared to the XRPD-QPA method ($R^2 = 0.97$). The slight difference is mainly due to errors in the FeO/OH- and MnO/OH-dominated samples A and C and in the smectite ore (sample D). In particular, the XRPD-OPA modelling of sample A and D led to an overestimation of the Co grades (+0.30% and +0.11%), while in sample C the Co grade was underestimated by -0.17%.

7.4 Discussion

The complex mineralogy of the ore types occurring in the Wingellina Ni-Co laterite deposit has been quantitatively characterized using both XRPD-QPA (with a combination of the Rietveld and the internal standard methods) and automated SEM analysis techniques. The XRPD-QPA analysis allowed the quantification of both the potentially major ore-carriers and of the noneconomic minerals. Moreover, with the addition of the internal standard, it was also possible to quantify the amount of UPCP, which were also chemically classified (Table 7.4), on the basis of the whole-rock geochemistry and of the mineral chemistry (ICP-MS/AES and SEM-EDS analyses). The automated SEM data not only provided an alternative method to assess the modal mineralogy of the Wingellina mineralised facies, but also added significant information about the textural relationships between the main and minor components of the ore (Fig. 7.5 and 7.6) as well as the Ni and Co distribution within the economic phases (Table 7.6), a fact that is not directly achievable by XRPD-QPA. Our study highlights that automated SEM techniques provide distinct benefits, notwithstanding the difficulties related to the evaluation of complex ores, such as Ni-Co laterite deposits. The challenges include conflicting phase quantification and mismatches between the XRPD-QPA- and automated SEM-derived bulk geochemistry (Fig. 7.4; Tables 7.7 and 7.8).



Fig. 7.5: Backscattered electron (BSE) photomicrographs and relative false colour image of selected particles from the oxide ore (FeO/OH- and MnO/O-dominated ores). Yellow circles report the position of representative EDS analyses listed in Appendix 7.4.

However, as discussed previously (e.g. Anderson et al., 2014; Boni et al., 2013; Mondillo et al., 2011; Rahfeld et al., 2018; Santoro et al., 2014), when comparing data obtained from XRPD-QPA and from automated SEM, it must be recognised that a number of differences exist between those techniques, which can constitute a limitation/issue for data comparison:

- The XRPD-QPA identifies and quantifies the minerals on the basis of their structural properties, while the phase evaluation conducted by automated SEM avails of the chemistry and density of the selected mineral candidates. This means that the XRPD-QPA methods might be limited by the absence of well-defined crystal structures in the database, while the quantitative data of automated SEM techniques can be affected by errors deriving from a less accurate assessment of the average chemistry of the mineral entries;



Fig. 7.6: Backscattered electron (BSE) photomicrographs and relative false colour image of selected particles from the saprolite zone (smectite and serpentinite ores). Yellow circles report the position of representative EDS analyses listed in Appendix 7.4.

- As the mineral quantification by XRPD-QPA is based on bulk sample powders, the representativity issues are lower when compared with those of automated SEM analysis performed on 2D surfaces. Despite the use of reverse circulation material for automated SEM analyses allows a better understanding of the downhole properties of the cored interval, the chip samples have a heterogeneous original grain size. This make compulsory a sieving pre-treatment of the samples with the aim of producing homogenous size fractions to ensure the effectiveness of the measurement parameters. However, the flaws of the sieving procedure are the potential loss of some part of the fine-grained sample fraction and the densimetric classification of grains, which might produce discrepancies between the ICP-MS assay and the automated SEM calculated data;

- Automated SEM techniques commonly have detection limits lower than those of XRPD-QPA and are able to detect trace minerals that are hardly quantified by the Rietveld method when applied to samples consisting of a large number of phases.

The main limitations encountered during the XRPD-QPA characterization of the Wingellina ore facies are due to the mineralogical discrimination between lithiophorite and asbolane and to the occurrence of non-crystalline phases sensu stricto (i.e. amorphous silica and FeO/OH) and of phases with poorly defined and/or complex structures (i.e. MnO/OH such as asbolanelike phases and smectite clays). Therefore, the most important advantages of the application of automated SEM on the evaluation of the Wingellina ore facies were: (1) the classification and quantification of the phases that in the XRPD-QPA resulted undistinguished due to their poorly-crystalline nature; (2) the chemical classification of complex MnO/OH, which cannot be discriminated on the basis of their crystal structure; (3) the chemical classification of Ni-bearing clays (i.e. smectite), again not classifiable on their structure alone. By comparing the results obtained using the two techniques (Tables 7.3 and 7.5), it is possible to observe that the total FeO/OH content directly and indirectly measured by XRPD-QPA (i.e. crystalline goethite and amorphous FeO/OH) is very similar to the goethite amounts measured by automated SEM (Fig. 7.5a to 6d), with the highest difference occurring in the MnO/OH-dominated ore (Fig. 7.5e,f), where automated SEM overestimated the goethite content by ca. 9%. Similarly, a good fit of data can be also observed in the quantification of the total amount of SiO₂ phases (i.e. crystalline guartz and amorphous silica [sample B]) and in the quantification and classification of Ni-bearing clays such as smectite and serpentine (samples A, D and E). In respect to the MnO/OH phase, a more complex scenario is observed, with good fits of the quantitative data for the FeO/OH-dominated oxide ore (samples A and B) and for the smectite ore (sample D), whilst in the MnO/OH-dominated oxide ore (sample C), the automated SEM underestimated the total content of MnO/OH by ca. 10%. Remarkable agreement is observed between the portion of the UPCP calculated as the contribution by smectite clays, and the amount of both montmorillonite (samples A and D) and Fe/Mg-smectite

that automated SEM detected in the studied specimens. This confirms the ability of automated SEM technique to mitigate the issues when notclassifiable poorly-crystalline phases are present. The chemical discrimination of the MnO/OH phase is one of the most relevant outcomes obtained through automated SEM, since MnO/OH constitute the major Co and Ni carriers in many word-class oxide type deposits (e.g. Butt and Cluzel, 2013), and their downhole quantification by using XRPD-QPA methods is always challenging, due their poor crystallinity. Furthermore, as shown by several authors (Burlet and Vanbrabant, 2015; Chuckhrov et al., 1982; Post and Appleman, 1994) even in the most favourable scenario, in which both asbolane and lithiophorite are characterized by a degree of structural order that can produce peaks during the XRPD analysis, their major diffraction lines are either overlapped or decoupled by only 0.1-0.2 Å. Moreover, it must be considered that the XRPD-QPA quantification of asbolane-like phases is also not possible, due to the absence of defined structures in the ICDD crystal structure databases. In the present study, the occurring MnO/OH can be subdivided in phases that were detected by XRPD-QPA (i.e. Ni-chalcophanite), and in others whose detection and quantification by XRPD was limited (i.e. lithiophorite, lithiophoriteasbolane intermediates and asbolane [i.e. Al-free MnO/OH]). In this regard, automated SEM analysis was effective in the quantification and in the differentiation of: a) lithiophorite (Al >10%, Ni <0.5%, Co <0.5%, Fe <0.5% and Mn 30-40%), b) lithiophorite-asbolane (Al 3-10%, Ni >10%, Co >2%, Fe <10% and Mn 25-40%) and c) asbolane (Al <2%, Ni >10%; Co >2%). The importance of such classification is clear when comparing the quantitative data obtained by XRPD-QPA and automated SEM and considering the metal deportment within MnO/OH. The XRPD-QPA analysis presented in this study was only able to directly quantify minor amounts of lithiophorite (oxide samples B and C). Looking at the lithiophorite amounts detected by XRPD-QPA in samples B (ca. 3 wt%; Table 7.3), they are very similar to the lithiophorite-asbolane detected by automated SEM (Table 7.5), with a difference of ca. 1%. Such good agreement of the quantitative data is a significant result and was achieved by using an assumed intermediate density for the lithiophorite-asbolane class between the nominal end member densities for the processing of the automated SEM data. Another striking result that validates the quality of our chemical approach during the classification of complex MnO/OH is the metal deportment observed in such mineral classes (Table 7.6). For instance,

in sample C even though lithiophorite occurs in the MnO/OH assemblage, it does not contribute to the metal deportment (0.45% Ni and 0.31% Co; Table 7.6). On the contrary, although the amount of asbolane in sample C is negligible (0.76%, Table 7.5), it deports for a significant amount of Co and Ni (1% Co and 4.70% Ni; Table 7.6).

However, the lower effectiveness of XRPD-QPA in evaluating the amounts of trace minerals in the studied samples is well represented by the cases of chalcophanite and lithiophorite in FeO/OH-dominated oxide ore (sample B) and smectite ores (sample D), respectively. In these ore types, even though these minerals were detected during the qualitative step of the XRPD analysis (Fig. 7.2), their concentrations were below the limits of quantification (<LoQ) of XRPD-QPA, thus limiting the reliability of the results (Table 7.3). This issue resulted in the underestimation of phases that play an important role in defining the modal mineralogy, as well as the Ni-Co deportment. In this frame, automated SEM showed that ca. 2 wt% of chalcophanite occurs in sample B, while ca. 1% lithiophorite-asbolane in sample D. In the FeO/OH-dominated ore (sample B), automated SEM revealed that despite the Ni-chalcophanite amount is very low, it accounts for a significant portion of the bulk Ni and Co budget (ca. 16% Ni and 7% Co; Table 7.6). Similarly, in the smectite ore, automated SEM not only allowed to classify the lithiophorite detected by XRPD-QPA as lithiophorite-asbolane, but also revealed that it contributes in defining the ore deportment (ca. 9% Ni and 76% Co; Table 7.6) in the smectite mineralisation. Another important point is that automated SEM analyses were successful in discriminating complex Ni-bearing phyllosilicates occurring both as major ore phases in the smectite and serpentinite ores and as minor components in the FeO/OH oxide ore (sample A). During the evaluation of Ni-phyllosilicates-, the automated SEM was able to bypass the very similar X-ray spectra of such phases based on their Si/ Σ R ratio (Σ R = sum of the octahedral metals; Putzolu et al., 2020a). At Wingellina a progressive increase of the Si/SR ratio can be observed starting from serpentine (ca. 0.70), to Fe/Mg-smectite (nontronite-saponite smectite series; ca. 0.90-1) up to montmorillonite (ca. 0.90-1.50). Whilst the Ni-clays represent here a subordinate component of the whole deposit, the classification approach based on the Si/2R ratio can be useful in the characterization through automated SEM of other laterite ores thatalmost completely consist of phyllosilicates (i.e. clay type deposits), where their

chemical and mineralogical properties critically affect the Ni recovery (e.g. Mano et al., 2019). As already mentioned by other authors (e.g. Anderson et al., 2014; Boni et al., 2013; Mondillo et al., 2011; Santoro et al., 2014), the biggest issue affecting automated SEM analysis was also in this case, the occurrence of mineral phases characterized by fine-grained textures and by complex mineral intergrowths, which at Wingellina are typically 1-5 µm (Fig. 7.5 and 7.6). These complex mineral aggregates led to the classification of a large suite of mixed mineral classes (samples A, B, D and E). This issue produced several discrepancies between the quantitative mineralogical data obtained by XRPD-QPA and the results of automated SEM, as well as to mismatches between the bulk-rock geochemistry (ICP-MS/AES) and the assays calculated through the automated SEM. Kaolinite is one of the phases that was affected by this issue, resulting in underestimates in the automated SEM both for the FeO/OH-dominated oxide ore (sample A) and for the smectite ore types. At Wingellina, as shown by BSE images, kaolinite forms very complex intergrowths with FeO/OH and other clay minerals, and has been thus modelled by automated SEM as a series of mixed classes (e.g mixed kaolinite-montmorillonite, Fig. 7.6d to g). Moreover, another possible process leading to the underestimation of kaolinite may be due to its impure composition (e.g. Fekaolinite) that is very common in residual ores (Boni et al., 2013). The presence of impure phases produces atypical spectra, which would not be identified as a single mineral phase during data processing. This critical issue has been recorded also by SEM analyses, which commonly detected fine-grained smectite-kaolinite aggregates resulting in mixed EDS spectra (Fig. 7.6g). Other significant examples of issues related to the presence of impure phases have been recorded in the MnO/OH-dominated ore, as well as in the smectite and serpentinite ore types. In the first example, i.e. in the MnO/OH-dominated ore, (sample C), Mn and Fe show reverse issues when comparing the bulk rock geochemical data with the calculated chemistry (Fig. 7.4). The Fe amount calculated by the XRPD-QPA mineralogy remarkably fits with that of the bulk geochemistry, whilst Mn is overestimated. Conversely, automated SEM overestimates the bulk Fe (as well as the goethite modal amount, Table 7.5), whereas the Mn values are in good agreement with the bulk rock geochemistry. The poor Fe and Mn reconciliations (leading to an overestimation of FeO/OH and to an underestimation of lithiophorite, Table 7.5) obtained by automated SEM in the MnO/OH-dominated oxide ore, can be explained by considering the

texture of FeO/OH in this ore facies: according to the BSE observations (Fig. 7.5g to i), FeO/OH are locally characterized by a skeletal to microacicular shape forming fine intergrowths (size $<5 \mu m$) with MnO/OH. Comparing the BSE image with the false colour map obtained by automated SEM, it can be observed that such complex intergrowths have been misidentified by automated SEM and were evaluated as goethite. A similar issue was observed in the smectite and serpentine ores, where complex intergrowths between Ni-clays (i.e. montmorillonite, serpentine and Fe/Mgsmectite, Fig. 7.6) and FeO/OH were not effectively detected by automated SEM and were therefore identified as mixed classes. At the same time, the occurrence of fine-grained mineral aggregates did not affect the ore modelling obtained by automated SEM in the MnO/OH-dominated ore (Sample C, Fig. 7.4). In fact, since MnO/OH has a primary role in defining the ore distribution in the high-grade MnO/OH-rich oxide facies (Table 7.6), their underestimation would be expected to lead to an underestimation of the Ni and Co grades. However, this was not the case for the Wingellina highgrade MnO/OH-rich ore. The good fitting reconciliation in the MnO/OHdominated ore can be explained by comparing the quantitative data obtained by XRPD-QPA and by automated SEM (Tables 7.3 and 7.5). The total amount of MnO/OH evaluated by XRPD-QPA is ca. 63 wt%, of which ca. 13 wt% corresponds to lithiophorite and ca. 50% to the undistinguished poorly-crystalline MnO/OH component. Automated SEM measured ca. 52 wt% of MnO/OH, corresponding to 3 wt% of lithiophorite and 49 wt% of lithiophorite-asbolane. Therefore, the underestimation of lithiophorite obtained by automated SEM, together with the negligible role played by this phase in defining the Ni and Co deportment in sample C (Table 7.6), suggests that part of the missing lithiophorite corresponds to the MnO/OH portion occurring in the fine-grained Fe-MnO/OH intergrowths. In contrast, the occurrence of fine mineral intergrowths was found to be a critical issue during the assessment of the Ni deportment in the smectite and serpentinite ores, where significant amounts of Ni occur in mixed goethite-smectite (ca. 10%) and in mixed clay-goethite, (ca. 41% Ni), respectively. The high Ni amounts detected in mixed classes led in turn to a relatively poor modelling of the Ni grades in the saprolite facies, where slight misfits between the measured and calculated assays were observed. This issue is likely related to the assignment of a fixed value of the Ni content to the mixed classes containing Ni-clays and FeO/OH. In fact, as shown by previous studies (Putzolu et al., 2018 and 2020a), as well as by new EDS microanalyses
(Appendix 7.3), not only FeO/OH and Ni-clays have very different Ni amounts, but Ni-clays are also characterized by very variable Ni concentrations. The occurrence of erratic ore grades in the serpentinite samples implies that the assignment of a representative Ni content for mixed mineral classes, where relative proportions between the clay and the oxyhydroxides are variable, can be very challenging. This critical issue may be resolved by using an increased analytical resolution (<5 µm). However, since mixed mineral classes were proved to have a negligible contribution to the overall results in the studied oxide-dominated samples, and given the higher analytical costs and the longer acquisition times, the use of higher instrument resolution is not suggested for samples of oxide-type laterites like Wingellina. On the contrary, based on the results obtained on the claydominated facies, such an approach would be recommended for assessing the modal mineralogy and grade distribution in saprolitic laterites (i.e. smectite- and hydrous Mg-silicate types). At last, it is important to mention that, the discrepancies between the automated SEM-derived results and the data obtained by traditional XRPD-QPA and ICP-MS/AES analyses could be caused by densiometric sorting during block sample preparation (Santoro et al.,2013). In particular, this issue might potentially explain the mismatches observed in sample D (i.e. serpentinite ore subtype; Fig. 7.4 and Table 7.8), where the geochemical reconciliations show a slight overestimation of Cr, normally carried by spinels having high density and the underestimation of Ni, Al and Co, commonly carried by lighter mineral phases (Fe- and Mn-oxy-hydroxides and phyllosilicates). However, the accuracy of steps followed during block sample preparation and the consistency of the automated SEM results for the three subsamples of specimen D, in addition with the fact that this issue was not observed in the other specimens, strongly exclude this option.

7.5 Conclusions

The mineralogical evaluation of Ni-Co laterite ores through XRPD-QPA is affected by several limitations derived from the high mineralogical complexity of the ore assemblage. These limitations can be mitigated by the additional use of automated SEM systems. For this study, automated SEM-BSE analyses were beneficial both in defining the nature of the undistinguished poorly to non-crystalline component of the ore assemblage in the mineralised facies of the Wingellina Ni-Co deposit, and in the chemical classification of the major Co(Ni)-bearing MnO/OH occurring in the specimens analysed. The effectiveness of automated SEM in discriminating barren Al-rich lithiophorite from Ni-Co-bearing types and relatively Al-depleted lithiophorite-asbolane intermediates is of great help for the mineralogical evaluation of MnO/OH-rich oxide-type laterites also applied to metallurgical purposes. The MnO/OH underestimation and errors of classification using XRPD-QPA alone, together with the ability of automated SEM to improve the knowledge about the chemical properties of Ni-Co laterite (i.e. Al, Fe, Mn contents and ore distribution) must be carefully considered during the evaluation of these ores, as both the mineralogy and chemistry of MnO/OH could lead to poor processing decisions. Nevertheless, the use of automated SEM analysis seems to be limited when applied to the clay-dominated facies of the Wingellina Ni-Co deposit (i.e. smectite and serpentinite ores), where the occurrence of finegrained minerals intergrowths results in the detection of mixed compounds and misleading phases. For the above reason, a quality control of automated SEM data through geochemical reconciliation based on whole-rock geochemistry- and XRPD-QPA-related data is highly advised.

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Table 7.1: Samples descr	Table 7.1: Samples description and provenance						
Sample ID	Drillcore ID	Particle size (mm)	Unit	Subtype	Depth (m)		
Sample A (WCS04065)	WPRC0141	(A) 0.17-0.21 (B) 0.3-0.42 (C) 0.5-1	Oxide ore	FeO/OH-dominated	20-22		
Sample B (WCS01936)	WPRC0111	(A) 0.17-0.21 (B) 0.3-0.42 (C) 0.5-1 (A) 0.17 0.21	Oxide ore	FeO/OH-dominated	32-34		
Sample C (WCS09603)	WPRC0287	(A) 0.17-0.21 (B) 0.3-0.42 (C) 0.5-1	Oxide ore	MnO/OH- dominated	20-22		
Sample D (WCS01938)	WPRC0111	(A)0.17-0.21 (B) 0.3-0.42 (C) 0.5-1	Saprolite ore	Smectite ore	36-38		
Sample E (W15803)	WPRC0481	(A) 0.17-0.21 (B) 0.3-0.42 (C) 0.5-1	Saprolite ore	Serpentinite ore	56-58		

Table 7.2: Whole-rock geochemistry [$C_{K(ICP-MS/AES)}$ variable] of the major, minor elements and of the Ni and Co grades.

Sample ID	Sample A	Sample B	Sample C	Sample D	Sample E
Unit		Oxide ore		Sapr	olite ore
Subtype	FeO/OH-dominated		MnO/OH-dominated	Smectite ore	Serpentinite ore
wt%					
SiO_2	10.7	42.5	4.13	40.5	43.1
Al_2O_3	6.41	2.89	27.2	11.6	1.17
Fe ₂ O ₃	61.9	39.9	18.55	20	18
CaO	0.04	1.00	0.3	0.27	0.06
MgO	0.96	0.56	1.18	4.21	21.6
Na ₂ O	0.26	0.08	0.1	0.22	0.09
K ₂ O	0.02	0.03	0.05	0.06	< 0.01
Cr ₂ O ₃	0.311	0.602	0.52	2.55	0.425
TiO_2	0.18	0.05	0.12	0.44	0.06
MnO	3.69	2.74	19.05	0.39	0.24
P_2O_5	0.02	0.02	0.01	0.01	0.02
BaO	0.09	0.03	0.09	< 0.01	< 0.01
LOI	14.95	9.35	22.3	17.95	15.45
Total	99.53	99.75	93.6	98.2	100.22
wt%					
Ni	1.1	1.24	1.43	2.64	1.265
Со	0.447	0.409	2.42	0.208	0.0337

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Sample ID		Sample A	Sample B	Sample C	Sample D	Sample E	
Unit			Oxide	ore	Saprolite ore		
Subtype	Crystal structure file (.cif)	FeO/OH-	dominated	MnO/OH-dominated	Smectite ore	Serpentinite ore	
Lithiophorite	Post and Appleman (1994)	-	2.78	13.14	<loq< td=""><td>-</td></loq<>	-	
Chalcophanite	Post and Appleman (1988)	-	<loq< td=""><td><loq< td=""><td>-</td><td>-</td></loq<></td></loq<>	<loq< td=""><td>-</td><td>-</td></loq<>	-	-	
Goethite	Gualtieri and Venturelli (1999)	64.37	37.63	20.32	14.07	19.96	
Lizardite	Guggenheim and Zhan (1998)	-	-	-	-	48.70	
Gibbsite	Balan et al. (2006)	-	-	16.90	-	-	
Hercynite	Harrison et al. (1998)	3.11	2.27	-	5.39	<loq< td=""></loq<>	
Magnetite	O'Neill and Dollase (1994)	2.25	-	-	-	-	
Quartz	Rosa et al. (2005)	-	30.72	-	8.90	5.93	
Kaolinite	Bish and Von Dreele (1989)	7.64	-	-	15.95	-	
UPCP	N/A	22.63	26.47	49.51	55.45	24.62	
Total		100	100	100	100	100	
Smectite*	N/A	5.63	-	-	54.50	24.62	
MnO/OH*	N/A	7.00	1.70	49.51	0.95	-	
FeO/OH*	N/A	10.00	16.77	-	-	-	
Silica*	N/A	-	8.00	-	-	-	
Rwp		1.78	2.61	3.59	4.14	8.69	

Table 7.3: Rietveld quantitative phase analysis reported as wt.% (x_{UPCP} and x_i variables).

Notes: * =Composition of the undistinguished poorly to non-crystalline phases (UPCP), determined on the basis of the SEM-EDS and whole rock chemical analyses (see section 3.2); - = not detected; LoQ = Limit of Quantification; N/A = not applicable.

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Sample ID	Sample A Sample B					S	ample C		S	ample D	e D Sample E				
Unit				O	xide ore							Saproli	te ore		
Subtype	FeO/0	OH-dominated		FeO/O	H-dominated		MnO/C	OH-dominated		Sm	nectite ore		Serp	entinite ore	
	Assay[C _{K(ICP-} MS/AES)]	C _{K(XRPD-} QPA/EDS)*	Δ%	Assay[C _{K(ICP-} MS/AES)]	C _{K(XRPD-} QPA/EDS)*	$\Delta\%$	Assay[C _{K(ICP-} MS/AES)]	C _{K(XRPD-} QPA/EDS)*	Δ%	Assay[C _{K(ICP-} MS/AES)]	C _{K(XRPD-} QPA/EDS)*	Δ%	Assay[C _{K(ICP-} MS/AES)]	C _{K(XRPD-} QPA/EDS)*	Δ%
Mg	0.58	0.43	-26.07	0.34	0.31	-9.14	0.71	0.01	-98.19	2.54	0.51	-80.01	13.03	10.61	-18.55
Al	3.39	3.25	-4.06	1.53	1.22	-20.54	14.40	8.95	-37.80	6.14	4.99	-18.78	0.62	0.06	-90.41
Si	5.00	3.01	-39.78	19.87	15.53	-21.82	1.93	1.77	-8.25	18.93	8.19	-56.73	20.15	13.96	-30.70
Cr	0.21	0.44	109.01	0.41	0.33	-20.17	0.36	0.10	-71.03	1.74	0.74	-57.75	0.29	0.02	-93.05
Mn	2.86	0.46	-83.91	2.12	1.44	-32.19	14.75	5.01	-66.04	0.30	0.15	-49.39	0.19	0.13	-28.23
Fe	44.79	37.57	-16.12	28.87	19.86	-31.23	13.42	10.82	-19.40	14.47	7.28	-49.68	13.02	11.30	-13.25
Co	0.45	0.16	-63.35	0.41	0.44	8.21	2.42	0.09	-96.10	0.20	0.08	-63.29	0.03	0.04	27.24
Ni	1.10	0.42	-61.61	1.24	0.85	-31.27	1.43	0.06	-95.67	2.64	0.28	-89.49	1.27	0.63	-50.48
Total UPCP amount by XRPD- QPA (wt%)		22.63			26.47			49.51			55.45			24.62	

Table 7.4: Comparison between the real assay [CKICP-MSAES] and the XRPD-QPA-calculated chemistry [CKIXRPD-QPAEDS]] based solely on crystalline phases (expressed as wt%)

Notes: * = chemical composition based solely on the abundance and mineral chemistry (xi and ci variables) of crystalline phases.

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Table 7.5: Modal mineralogy resu	ults by TIMA-X	$X(x_{class} \text{ variable})$), reported as wt.%.		
Sample ID	Sample A	Sample B	Sample C	Sample D	Sample E
Unit		Oxid	e ore	Sapı	rolite ore
Subtype	FeO/OH-	dominated	MnO/OH-dominated	Smectite ore	Serpentinite ore
Ore-bearing oxy-hydroxides					
Ni-chalcophanite	-	1.82	0.13	-	-
Lithiophorite	-	0.05	3.46	-	-
Lithiophorite-asbolane	3.02	3.7	49.45	1.47	0.43
Asbolane	2.14	-	0.76	-	-
Goethite	76.46	53.3	28.5	11.49	5.17
Ore-bearing phyllosilicates					
Fe/Mg-smectite	-	-	-	0.15	19.69
Serpentine	-	0.07	-	-	42.27
Montmorillonite	3.44	-	-	57.42	-
Gangue					
Carbonates	0.04	0.02	0.71	0.06	0.05
Gibbsite	0.13	0.01	15.92	-	0.24
Spinel	3.08	2.58	0.03	6.54	0.38
Kaolinite	2.65	0.22	0.09	0.2	-
Quartz	0.08	33.5	-	4.96	7.66
Mixed/not defined					
Asbolane-goethite	1.45	1.41	-	-	-
Goethite-kaolinite	-	0.14	-	-	-
Goethite-quartz	-	2.09	-	4.68	1.47
Goethite-clay	-	-	-	-	18.92
Quartz-clay	-	-	-	-	1.55
Quartz-Fe/Mg-smectite	-	-	-	0.15	-
Goethite-smectite	-	-	-	8.79	-
Kaolinite-montmorillonite	-	-	-	0.37	-
Montmorillonite-quartz	-	-	-	1.69	-
Montmorillonite-asbolane	1.49	-	-	-	-
Montmorillonite-goethite	5.14	-	-	-	-
Kaolinite-goethite	-	-	-	-	-
Unclassified	0.88	1.01	0.95	2.03	2.17
Total	100	99.92	100	100	100

Notes: - = not detected.

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Sample ID	Sample A	Sample B	Sample C	Sample D	Sample E		
Unit		Oxide	e ore	Saprolite ore			
Subtype	FeO/OH-	dominated	MnO/OH-dominated	Smectite ore	Serpentinite ore		
			Nickel deport	nent			
Ore-bearing oxy-hydroxides							
Ni-chalcophanite	-	16.27	0.91	-	-		
Lithiophorite	-	-	0.45		-		
Lithiophorite-asbolane	24.40	29.93	91.64	8.82	-		
Asbolane	15.62	-	4.70	-	-		
Goethite	55.72	52.07	2.30	8.18	3.75		
Ore-bearing phyllosilicates							
Fe/Mg-smectite	-	-	-	-	36.07		
Serpentine	-	-	-	-	18.59		
Montmorillonite	-	-	-	71.80			
Mixed							
Goethite-smectite	-	-	-	10.16			
Goethite-quartz	-	1.63	-	-	-		
Montmorillonite-asbolane-goethite	3.77		-	-	-		
Goethite-clay	-	-	-	-	40.65		
Phases <1%	0.49	0.10	1.36	1.04	0.95		
Total	100.00	100.00	100.00	100.00	100.00		
			Cobalt deports	nent			
Ore-bearing oxy-hydroxides	-						
Ni-chalcophanite	-	6.60	0.10	-	-		
Birnessite	-	-		-	-		
Lithiophorite	-	0.25	0.31	-	-		
Lithiophorite-asbolane	64.09	67.97	94.77	76.13	81.34		
Asbolane	19.03	-	1.00	-	-		
Goethite	6.52	25.18	3.82	23.87	18.66		
Ore-bearing phyllosilicates							
Fe/Mg-smectite	-	-	-	-	-		
Lizardite	-	-	-	-	-		
Montmorillonite	-	-	-	-	-		
Mixed							
Montmorillonite-asbolane	8.19	-	-	-	-		
Asbolane-goethite	2.17	-	-	-	-		
Total	100.00	100.00	100.00	100.00	100.00		

Notes: - = not detected.

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Table 7.7: Whole-rock geochemist	ry of oxide ores (samp	les A to C) by ICP-MS/AES	CK(ICP-MS/AES)], XRPD-OPA	$[C_{K(XRPD-OPA/EDS)^*}]$ and TIMA-X $[C_{K(TIMA-X)}]$.
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Sample ID			Sample A					Sample B					Sample C			
Unit								Oxide ore								
Subtype			FeO/OH-domina	ated				FeO/OH-domin	ated				MnO/OH-domin	ated		
	C _{K(ICP-} MS/AES) ^a	$\Sigma C_{K(TIMA-X)}^{b}$	$\Sigma C_{K(XRPD-QPA/EDS)}$	$\frac{\Delta [CK_{(ICP-MS/AES)^{-}}}{\sum_{CK(TIMA-X)}]^{d}}$	$\Delta [CK_{(ICP-MS/AES)^{-}} \sum_{CK(XRPD-QPA/EDS)^{*}}]^{e}$	C _{K(ICP-} MS/AES) ^a	$\Sigma C_{K(TIMA-X)}^{b}$	$\Sigma C_{K(XRPD-QPA/EDS)*^{c}}$	$\frac{\Delta [CK_{(ICP-MS/AES)^{-}}}{\sum_{CK(TIMA-X)}]^{d}}$	$\Delta[CK_{(ICP-}]^{MS/AES]^{-}}$ $\Sigma_{CK(XRPD-}]^{e}$ $QPA/EDS)^{*}]^{e}$	$C_{K(ICP-MS/AES)}^{a}$	$\Sigma C_{K(TIMA-X)}^{b}$	$\Sigma C_{K(XRPD-QPA/EDS)*^{c}}$	$\frac{\Delta [CK_{(ICP-MS/AES)^{-}}}{\sum_{CK(TIMA-X)}]^{d}}$	$\Delta [CK_{(ICP-MS/AES)^{-}} \sum_{CK(XRPD-QPA/EDS)^{*}}]^{e}$	
Mg	0.58	0.97	0.64	0.39	0.07	0.34	0.16	0.36	-0.18	0.02	0.71	0.10	0.07	-0.61	-0.64	
Al	3.39	4.35	4.23	0.96	0.83	1.53	1.35	1.48	-0.18	-0.05	14.40	13.25	13.58	-1.15	-0.81	
Si	5.00	3.81	4.44	-1.19	-0.56	19.87	17.94	19.76	-1.93	-0.11	1.93	1.52	0.76	-0.41	-1.17	
Cr	0.21	0.52	0.46	0.31	0.25	0.41	0.44	0.35	0.03	-0.06	0.36	0.31	0.20	-0.05	-0.16	
Mn	2.86	2.86	2.68	0.00	-0.18	2.12	2.50	2.17	0.38	0.05	14.75	15.56	21.65	0.81	6.90	
Fe	44.79	41.69	44.86	-3.10	0.07	28.87	29.00	28.97	0.13	0.10	13.42	20.12	14.09	6.70	0.66	
Co	0.45	0.37	0.75	-0.08	0.30	0.41	0.63	0.67	0.22	0.26	2.42	2.48	2.26	0.06	-0.17	
Ni	1.10	1.35	1.26	0.25	0.16	1.24	1.43	1.25	0.19	0.01	1.43	1.53	1.49	0.10	0.06	

Notes: a = Whole rock geochemistry on the basis of ICP-MS/AES analyses (see Table 7.2); b = elements mass by TIMA-X calculated on the basis of the modal mineralogy; c = elements mass calculated on the basis of the mineral proportions detected through XRPD-QPA (Rietveld method) and on the mineral chemistry (EDS); d= difference between ICP-MS/AES and TIMA-X; e = difference between ICP-MS/AES and QPA/EDS.

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Table 7.8: Whole-rock geochemistr	v of saprolite ores (samples D and E) by	VICP-MS/AES [CK/ICP-MS/AES], XRPD-OPA [CK/XRPD-OPA/EDS)*] and TIMA-X [CK	TIMA. YIL
	, at any attack at a (attack a the b) o)		

Sample ID				Sample D		Sample E				
Unit					Saproli	ite ore				
Subtype				Smectite ore					Serpentinite ore	
	$C_{K(ICP-MS/AES)^a}$	$\Sigma C_{K(TIMA-X)}^{b}$	$\Sigma C_{K(XRPD-QPA/EDS)*^{c}}$	$\Delta [CK_{(ICP-MS/AES)} - \Sigma_{CK(TIMA-X)}]^d$	$\Delta [CK_{(ICP-MS/AES)} - \Sigma_{CK(XRPD-QPA/EDS)^{\circ}}]^{c}$	C _{K(ICP-} MS/AES) ^a	$\Sigma C_{K(TIMA-X)}^{b}$	$\Sigma C_{K(XRPD-QPA/EDS)*^{c}}$	$\Delta [CK_{(ICP-MS/AES)}-\Sigma_{CK(TIMA-X)}]^d$	$\Delta [CK_{(ICP-MS/AES)} - \Sigma_{CK(XRPD-QPA/EDS)^*}]^{e}$
Mg	2.54	2.75	1.79	0.21	-0.75	13.03	12.19	12.45	-0.84	-0.58
Al	6.14	5.46	7.79	-0.68	1.65	0.62	0.64	0.61	0.02	-0.01
Si	18.93	18.47	19.97	-0.46	1.04	20.15	19.99	18.96	-0.16	-1.19
Cr	1.74	3.30	1.32	1.56	-0.42	0.29	0.28	0.10	-0.01	-0.19
Mn	0.30	0.36	0.42	0.06	0.12	0.19	0.12	0.14	-0.07	-0.05
Fe	14.47	18.58	13.87	4.11	-0.61	13.02	12.62	13.64	-0.40	0.61
Co	0.20	0.16	0.32	-0.04	0.11	0.03	0.03	0.04	0.00	0.01
Ni	2.64	2.32	2.19	-0.32	-0.45	1.27	1.72	1.40	0.45	0.14

Notes: a = Whole rock geochemistry on the basis of ICP-MS/AES analyses (see Table 8.2); b = elements mass by TIMA-X calculated on the basis of the modal mineralogy; c = elements mass calculated on the basis of the mineral proportions detected through XRPD-QPA (Rietveld method) and on the mineral chemistry (EDS); d = difference between ICP-MS/AES and TIMA-X; e = difference between ICP-MS/AES and QPA/EDS.

Appendix 7.1: Explanation of Mineral Classed detected by TIMA.

Mineral class	Description
Ore-bearing oxy- hydroxides	
Ni-chalcophanite	Any phase with Mn (45-55%), Ni (>10%) and Co (<3%); may contain trace amounts of Al (<2%), Fe and K (<0.5%)
Lithiophorite Lithiophorite-	Any phase with Mn (30-40%) and Al (>10%); may contain minor amounts of Ni (<0.5%), Co (<0.5%), Fe (<0.5%) and Si.
asbolane	Any phase with Mn (25-40%), Ni (>10%), Co (>2%), Al (3-10%) and Fe (<10%); may contain trace amounts of Na, Mg, Si and Ca Any phase with Mn (45-50%), Ni (<10%) and Co (>2%); may contain trace amounts of Al (<2%), Fe and Ca and may be mixed with other Al-free $M = O(O(1/4))$.
Asbolane	MIC/OH (i.e. as bounded such as manganite, romanecinite etc.) A rescalator with Eq. (450), more containing an experiment of A1 (20), Si (450). Ni (4150) and C2 (4150), as well as traces of C2 and M2 (410).
Goethite	Any phase with Fe (>45%); may contain minor amounts of AI (<5%), SI (<5%), NI (<1.5%) and Co (<1.5%), as well as traces of Cr and Min (<1%)
Ore-bearing phyllosilicates	
Fe/Mg-smectite	Any phase with Si (20-22%), Fe (10-15%), Mg (5-10%) and Ni; may contain minor to trace amounts of Al (<2%), Ca and Cr. Smectite clays belonging to the nontronite-saponite series.
Lizardite	Any phase with Si (20-22%), Fe (<10%), Mg (>15%); contains minor amounts of Ni
Montmorillonite	Any phase with Si (19-22%), Fe, Mg and Al (>5%); contains minor to trace amounts of Cr and Ni
Gangue	
Carbonates	Any phase with Ca and Mg; includes calcite, dolomite and magnesite
Gibbsite	Any phase with AI (>30%)
Spinel	Any phase with Cr, Fe, Al and Mg; includes hercynite, picotite and chromite
Kaolinite	Any phase with Si (20-25%) and Al (20-25%)
Quartz	Any phase with Si (>45%)
Mixed/not defined	
Asbolane-goethite	Any phase with Fe (10-40%) and Mn (1-20%); may contain minor amounts of Ni, Co and Al
Goethite-kaolinite	Any phase with Si, Fe, Al; may contains minor amounts of Ni
Goethite-quartz	Any phase with Si (>10%) and Fe (<40%); may contain minor amounts of Ni
Goethite-clay	Any phase with Fe, Si (10-15%), Mg (>10%) and Ni
Spinel-quartz	Any phase with Si (>5%), Cr, Fe, Al and Mg
Quartz-clay Quartz-Mg/Fe-	Any phase with Si (>30%), Mg and Ni; may contain minor to trace amounts of Al (<2%)
smectite	Any phase with Si (>22%), Fe, Mg and Ni; may contain minor to trace amounts of Al, Ca and Cr
Goethite-smectite	Any phase with Mg, Si, Fe (>20%) and Ni
Kaolinite- montmorillonite Montmorillonite-	Any phase with Si (20-22%), Fe (5-15%), Mg (<5%), Al (5-15%) and Ni; contains minor to trace amounts of Ca, Na, Cr and Mn (<0.5%)
quartz Montmorillonite-	Any phase with Si (>22%), Fe, Mg and Al; contains minor to trace amounts of Cr and Ni
asbolane Montmorillonite-	Any phase with Si (<19%), Mn (>1%), Fe, Mg and Al (>5%); contains minor to trace amounts of Cr and Ni
goethite	Any phase with Si (<19%), Fe (>20%), Mg and Al (>5%); contains minor to trace amounts of Cr and Ni
Kaolinite-goethite	Any phase with Si (20-25%), Al (10-20%) and Fe (>5%)
Background	All resin related/edge effects





Appendix 7.2: Rietveld refinements of the studied samples. Notes: black line = XRPD pattern; red line = modelled pattern; grey line = difference.

	FeOt	SiO ₂	Al ₂ O ₃	NiO	MnO	CoO	Cr ₂ O ₃	MgO	K ₂ O	CaO	Na ₂ O		
Mineral	1001	5102	1 112003	1110	wt%	000	0.203		1120	euo	11420		
E	1.40\8				WC/0								
Fe-oxy-hydroxides (n =	= 149)"												
Mean	71.37	5.16	2.54	1.25	1.05	0.33	0.25	-	-	-	-		
Stand. Dev	4.81	1.54	1.07	0.84	1.63	0.29	0.46	-	-	-	-		
Maximum	91.57	9.73	6.39	7.05	11.12	2.96	3.83	-	-	-	-		
Minimum	50.34	0.15	0.21	0.14	0.00	0.00	0.00	-	-	-	-		
Median 71.56 5.37 2.57 1.16 0.52 0.31 0.13													
Ernienickelite (n = 10)													
Mean	0.83	-	2.66	13.87	61.36	2.16	-	0.43	0.33	-	-		
Stand. Dev	0.39	-	3.18	1.02	4.52	1.79	-	0.31	0.25	-	-		
Maximum	1.52	-	8.90	15.49	69.74	5.09	-	1.11	0.84	-	-		
Minimum	0.50	-	0.30	11.89	55.80	0.27	-	0.08	0.11	-	-		
Median	0.60	-	1.04	13.81	62.27	1.67	-	0.34	0.23	-	-		
Lithiophorite (n = 16)													
Mean	2.57	2.10	22.70	2.65	45.37	5.19	-	0.08	-	-	-		
Stand. Dev	2.10	1.90	1.26	1.44	5.87	2.93	-	0.08	-	-	-		
Maximum	7.22	6.33	25.60	4.95	57.28	8.89	-	0.28	-	-	-		
Minimum	0.30	0.04	21.11	0.14	37.43	0.15	-	0.00	-	-	-		
Median	1.93	1.39	22.45	2.62	44.09	5.56	-	0.05	-	-	-		
Lithiophorite - asbolane (n = 33) ^b													
Mean	8.44	2.13	11.65	10.54	38.28	7.98	-	1.57	-	-	-		
Stand. Dev	3.52	2.58	5.69	5.56	5.32	2.96	-	1.01	-	-	-		
Maximum	15.64	9.41	20.52	19.53	50.16	13.08	-	2.82	-	-	-		
Minimum	1.46	0.24	5.84	1.68	23.97	1.20	-	0.10	-	-	-		
Median	8.08	1.09	8.71	12.80	39.29	8.34	-	1.59	-	-	-		
Asbolane $(n = 6)^b$													
Mean	Mean $4.14 = 0.74 = 3.19 = 16.63 = 38.77 = 13.78 = -1.32 =$												
Stand, Dev	2.26	0.40	0.37	2.98	5.03	1.02	-	0.26	-	-	-		
Maximum	6.88	1.16	3.57	18.92	48.80	15.19	-	1.77	-	-	-		
Minimum	0.70	0.11	2.59	11.27	35.23	12.64	-	1.13	-	-	-		
Median	4.61	0.78	3.21	17.84	37.03	13.73	-	1.21	-	-	-		
Fe-Mg smectite $(n = 4)^{c^{*}}$													
Moon	0.16	52 62	1 22	0.73			0.24	15 22		0.24	0.24		
Stord Day	9.10	10.22	1.55	0.75	-	-	0.24	6.06	-	0.34	0.34		
Maximum	18.07	67.42	2.67	0.07	-	-	0.24	25.24		0.34	0.34		
Minimum	0.23	44.93	0.06	0.62			0.40	0.12		0.72	0.00		
Median	8.72	51.06	1.30	0.00	_	_	0.23	13.45		0.32	0.32		
Serpentine $(n = 22)$	0.12	51.00	1.50	0.70			0.25	10.10		0.52	0.52		
Mean	7.15	35.43	0.24	1.48	0.05	-	-	26.86	-	-	-		
Stand. Dev	2.77	4.05	0.24	0.91	0.05	-	-	4.03	-	-	-		
Maximum	16.90	45.46	1.19	3.12	0.19	-	-	33.08	-	-	-		
Minimum	4.79	30.57	0.06	0.38	0.00	-	-	20.10	-	-	-		
Median	6.56	34.23	0.16	1.23	0.05	-	-	25.71	-	-	-		
Montmorillonite (n = 46)													
Mean 15.25 49.29 10.98 4.08 1.63 4.04 - 0.44 0.37													
Stand. Dev	4.63	6.52	2.51	2.09	-	-	0.91	1.19	-	0.23	0.19		
Maximum	23.87	59.33	20.12	9.94	-	-	3.45	7.30	-	1.37	0.79		
Minimum	4.76	31.28	6.80	0.08	-	-	0.00	1.69	-	0.15	0.00		
Median	15.71	50.01	10.65	3.98	-	-	1.41	3.72	-	0.42	0.39		

	Appendix 7.3: Mineral chemistry	y of the ore-bearing phases (ci and CUPCP variables	s) by SEM-EDS.
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Notes: - = not determined/below detection limit; ^a = composition used for the appraisal of the FeO/OH-like component of the amorphous; ^b = composition used for the appraisal of the MnO/OH-like component of the amorphous; ^c = composition used for the appraisal of the smectite-like component of the amorphous; * = data from Putzolu et al. (2020a).

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Sample ID	Sample A	Sample A	Sample A	Sample B	Sample C	Sample C	Sample D	Sample D	Sample D	Sample E	Sample E	Sample E				
Unit	Oxide ore								Saprolite ore							
Subtype	FeO/OH-dominated			MnO/OH-dominated					Smectite ore			Serpentinite ore				
Reference point	1.00	2.00	3.00	4.00	5.00	6.00	7.00	8.00	9.00	10.00	11.00	12.00	13.00	12.00	13.00	14.00
Mineral class	L-A	L-A	Asb	L-A	Lth	Lth	Lth	L-A	Lth	L-A	Mnt	Mnt	L-A	Fe/Mg-Sme	Fe/Mg-Sme	Srp
MgO	3.36	3.56	1.44	2.29	0.18	0.16	0.04	0.09	0.05	0.00	5.17	4.39	1.43	14.23	9.12	31.07
Al ₂ O ₃	7.24	7.07	2.71	4.75	23.21	22.54	23.26	20.05	20.08	18.29	15.60	15.52	8.31	2.41	2.67	0.19
SiO ₂	1.24	0.50	0.15	0.27	-	9.59	-	0.62	0.02	0.56	52.71	51.91	0.94	44.93	46.53	40.22
CaO	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	0.43	0.23	n.d	0.52	0.72	0.04
Cr ₂ O3	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	0.37	0.26	n.d	0.48	0.41	0.01
MnO	35.78	36.27	45.80	39.47	44.63	39.69	44.71	34.90	37.68	33.51	0.18	0.00	35.84	-	-	-
FeOt	4.08	3.76	1.71	0.22	0.48	0.14	0.28	-	-	0.00	5.18	5.86	7.53	16.57	18.97	7.91
CoO	9.06	10.71	3.23	9.61	0.63	1.17	1.51	8.36	-	10.45	n.d	n.d	11.51	-	-	-
NiO	6.13	5.98	10.84	11.42	0.00	1.04	0.78	2.85	0.15	2.04	1.16	0.60	14.86	0.82	0.68	2.38
Al/(Ni+Co)*	0.32	0.29	0.13	0.15	24.73	6.86	6.85	1.20	90.92	0.99	n.d	n.d	0.21	n.d	n.d	n.d
Si/ΣR*a	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	1.47	1.51	n.d	0.89	0.97	0.70

Appendix 7.4: Selected EDS analyses (expressed as wt%) of ore-bearing MnO/OH and clay minerals in the Wingellina mineralized facies.

Notes: * = expressed as elemental ratios; a = ratios between silicon and octahedral metals; - = not detected; n.d. = not determined.

Chapter 8:

The influence of the magmatic to post-magmatic evolution of the parent rock on the Co deportment in lateritic systems: the example of the Santa Fe' Ni-Co deposit (Brazil)

8.1 Introduction

The Santa Fe' Ni-Co laterite deposit (Fig. 8.1a-b) is one of the largest unexploited deposits of the South Goiás alkaline Province (GAP, Brod et al., 2005), with an indicated resource of 35.7 Mt, grading 1.14% Ni and 0.083% Co and inferred resources of 104.3 Mt, grading 1.03% Ni and 0.054% Co (Dreisinger et al., 2008). Although the ore potential of the Santa Fe' deposit is relatively high, the specific mineralogical and geochemical features of the deposit are still poorly known. Therefore, one of the aims of this chapter is to shed new light on the genesis, the nature of the main orecarrier phases, and on the Ni and Co deportment within the deposit. Furthermore, several studies have highlighted the fact that the original features of the magmatic bedrock can exert a primary role in defining the Ni mineralogy and fertility in laterite ores. For example, the alteration of olivine-rich cumulates (i.e. dunite) generally produces oxy-hydroxidesdominated ores, whereas the alteration of pyroxene-rich bedrocks (i.e. peridotite and pyroxenite) gives rise to laterites containing well-developed Ni-enriched clay zones (e.g. Freyssinet et al., 2005 and references therein). Furthermore, Lambiv Dzemua and Gleeson (2012) showed that the variable mineralogy of the Ni-carriers in the ultramafic parental rocks, and in particular the differential weathering rate of Ni-bearing phases, can play a primary role in defining the Ni fertility of laterites deposits. Another significant aspect to consider is that many laterite ores can experience postformation diagenetic-metadiagenetic stages that can enhance the ore redistribution. For example, in some Greek laterites, it was shown that Co and other transition metals (i.e. Mn and Zn) can be concentrated in chromite grains, due to the onset of a more reducing environment after the main supergene event (Economou-Eliopoulos, 2003). Therefore, in this part of the study a particular focus will be on how the original geochemistry and nature of the magmatic parent rock and its alteration history acted on the Co deportment during supergene alteration and thus on the metal recovery.



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Fig. 8.1: a) Geological map of the south Goiás region showing the location of Goiás Alkaline Province (modified after Lacerda et al., 2000); b) Simplified geological map of the Santa Fe' ultramafic massif (modified after Golightly, 2010) with the drill hole grid. The drill holes used in this work are shown in colours: red circles indicate the location of the drillcores used for the geochemical survey, while the dark green circles show the location of the drillcores sampled for the mineralogical study

To pursue this aim an extensive geochemical dataset has been treated through a multivariate statistical approach based on Principal Component Analysis (PCA) and Factor Analysis (FA). Moreover, the statistical outputs will be also discussed on the light of the mineralogical and petrographic features of the laterite units and of the bedrock evaluated by XRPD, EMPA and EDX mapping and by also considering the results of the metallurgical testworks conducted on the deposit.

8.2 Materials and analytical methods

8.2.1 Mineralogical and petrographic analyses (XRPD, EMPA and EDX mapping)

Mineralogical and petrographic characterization was carried out on 29 samples of the regolith profile collected from selected drillcores (i.e. FDSF-01, SFDD-003, SFDD-017, SFDD-041, SFDD-308; Fig. 8.1b and Appendices 8.1 to 8.6). The identification of major minerals was carried out using X-ray Powder Diffraction (XRPD) analyses, performed with a Panalytical X'Pert PRO MPD diffractometer equipped with an X'celerator PSD 2.1° detector at the Natural History Museum (NHM) in London (UK). The instrument was operated using a Co Ka radiation at 40 kV, and 40 mA° with a Fe filter and a 1/4° divergence slit. The XRPD patterns were collected between an incident angle of 5 and 100° 2 θ at a step size of 0.02° 2θ . The run time per step was of 75s. The analyses were interpreted with the "High Score Plus" software, using the PDF-4 database from 'The International Centre for Diffraction Data (ICDD)'. Mineral chemistry of the ore-bearing phases occurring on selected specimens was performed using Scanning Electron Microscopy equipped with Energy Dispersive X-ray Spectroscopy (SEM-EDS) and then refined by Electron Microprobe Analysis (EMPA). SEM-EDS analyses have been carried out at the NHM with a ZEISS EVO LS 15 operating with a working distance of 8.5 mm, an accelerating voltage of 20 kV and a current of 3 nA. Energy Dispersive Xray Spectroscopy microanalyses were obtained with an X-Max detector. Electron probe microanalyses (EPMA) were performed at the NHM using a Cameca SX100 Electron Microprobe Analyse equipped with five Wavelength Dispersive Spectrometry (WDS) Bragg spectrometers. Peak overlaps corrections were performed prior to matrix correction for the following elements: V (overlapping element: Ti; used standard: RUT STD082), Cr (overlapping element: V; used standard: VAN STDIC), Mn (overlapping element: Cr; used standard: CRO₂ STDIC), Fe (overlapping element: Mn; used standard: MNT STDIC). A beam current of 20 nA, an accelerating voltage of 20 keV and a spot size of 1 µm to quantify the following elements: Al (TAP, Ka), Mg (TAP, Ka), P (TAP, Ka), K (PET, Kα), Ca (PET, Kα), Fe (LIF, Kα), Mn (LIF, Kα), Ti (PET, Kα), Co (LIF, Kα), Ni (LIF, Kα), V (LIF, Kα), Cr (PET, Kα), Na (TAP, Kα), Si (TAP, K α), Cl (PET, K α) and Zn (PET, K α). High-resolution elemental maps were obtained using a FEI Quanta 650 FEG SEM at the NHM. The instrument was equipped with a Bruker Flat Quad 5060F energy dispersive X-Ray detector (EDS) for hyperspectral mapping. The maps were acquired at a HV mode and the instrument operated at 15 Kv, with 28 mm working distance and 8 μ m pixel time.

8.2.2 Geochemical and statistical analyses

The whole-rock geochemical data was treated using multivariate statistical analyses, i.e. principal components analysis (PCA) and factor analysis (FA), in order to evaluate the associations between the major and minor elements in the laterite profile, and to assess the Ni and Co distributions in the different facies of the ore. Combining PCA and FA methods was chosen in order to ensure a much more robust quantitative analysis of geochemical interdependencies (Toffolo et al., 2020). The advantage of PCA is that the number of components is not dependent on the operator's decision, and it is thus effective as an explorative analytical tool. As regards to FA, although the factors produced by this statistical method may be controlled by the user, this will not significantly distort the variance of the dataset entirely, resulting in a more reliable result (Reimann et al., 2002 and 2011). Therefore, during FA, the approach to the factor extraction was based on: i) the selection of factors with eigenvalues > = 1; ii) the reduction of the data dimensionality performed by previous PCA (Reimann et al., 2011). The statistical analyses of the whole-rock geochemical data were conducted on 9509 samples from ca. 617 drillholes, provided by Mineradora INVI Ltda. Prior to analysis, each sample was dried at 105°C for 12 h and then crushed to 2 mm. Afterwards, a fraction of about 300 g was pulverized in a ring pulverizer to 150 mesh, from which an 10 g portion was selected for wholerock assays. Major oxides and trace elements were analysed by SGS Geosol Laboratories Ltd. in Belo Horizonte (Brazil), using X-ray Fluorescence (XRF). The statistical analyses were performed with the R software. The data were normalized using the isometric logratio transformation, in order to favour the opening of the data. This transformation requires a matrix of data with no zero. The concentrations below the detection limits (dl) have been represented as a multiplication between the dl and 0.65 (Martín-Fernández et al., 2003). In order to quantify and to visualize the enrichment of immobile elements (i.e. Fe and Al), as well as the leaching of the mobile components (i.e. Si and Mg) during the weathering process, bulk rock concentrations were also used for the calculation of the Ultramafic Index of Alteration (UMIA), according to the equation proposed by Babechuk et al. (2014 and references therein):

$$UMIA = 100 \text{ x } [Al_2O_3 + Fe_2O_{3(T)})/(SiO_2 + MgO + Al_2O_3 + Fe_2O_{3(T)})]$$

Following the procedure of Aiglsperger et al. (2016 and references therein), the UMIA index was calculated with molar ratios, by converting into moles the bulk rock elemental concentrations (wt%).

8.3 Results

8.3.1 Geochemistry of the laterite profile

8.3.1.1 Whole-rock geochemistry

The average chemical composition of the Santa Fe' profile's regolith is reported in Figure 8.2. The dominant oxide in the laterite profile is Fe_2O_3 , (mean ca. 43.9 wt%), followed by SiO₂ (mean ca. 27.1 wt%) and MgO (mean ca. 9.7 wt%). The Fe₂O₃ content increases progressively from the saprock (mean ca. 10.9 wt%) to the uppermost regolith units (i.e. R6 to R1), where it reaches mean concentrations always at or above 50 wt%. SiO₂ and MgO shows a significant depletion towards the surficial zone of the profile, from a mean of 43.5 wt% SiO2 and 30.7 wt% MgO in the saprock to values around 1.4 wt% SiO₂ and 14.5 MgO in the pisolitic soil. Al₂O₃, Cr₂O₃ and TiO₂ have similar concentrations (~ 3.5 wt%, 2.96 wt% and 2.0 wt%, respectively), while CaO, MnO and P₂O₅ are very low (~ 0.83 wt%, 0.75 wt% and 0.11 wt%, respectively). As regards to MgO, a significant drop in its concentration was observed at the transition between green and ferruginous saprolite. A slight increase in the MnO concentration is observed at the transition between the green saprolite ($\sim 0.29 \text{ wt\%}$) and the uppermost section of the ore zone (i.e. R6 to R1, mean > ca. 0.60), with the highest MnO concentration occurring in the lateritic crust (~ 1.43 wt%). In the regolith profile, Ni and Co have mean concentrations ~ 0.84 wt% and 0.08 wt%, respectively, with the highest Ni grades occurring in the ferruginous and the ochre saprolite horizons (mean 1.3 wt% and 1.4 wt%, respectively). The Co grade is negligible in the saprock and in the green saprolite (mean < 0.05 wt%), while it is higher in the surficial regolith (ranging between 0.06-0.12 wt%). The dominant oxide in the silcrete unit is SiO₂ (~ 64.6 wt%), followed by MgO and Fe₂O₃ (mean ~ 16.5 wt% and 11.4 wt%, respectively).



Fig. 8.2: Schematic section of the Santa Fe' laterite profile, based on the considered drillcores and geochemical logs, showing the average chemical composition of each regolith unit.

The Ni and Co grades measured in the silcrete are significantly lower (~ 0.3 wt% and 0.04 wt%, respectively), in comparison with the other regolith

units (Table 8.1). The saprock and the green saprolite units have the lowest Ultramafic Index of Alteration (Fig. 8.2, 8.3 and Table 8.1) (~ 4.9 and 11.4, respectively), whereas the samples from the ferruginous saprolite to the pisolitic topsoil (R6 to R1) show a significant increase in the UMIA (up to 63.9 in the R1 unit), due to the Al_2O_3 and Fe_2O_3 enrichment in the uppermost zones of the profile.



Fig. 8.3: MgO-SiO₂-(Al₂O₃+Fe₂O₃) molar ternary plot, showing the geochemical variations in the Santa Fe' deposit during chemical weathering. The UMIA index has been calculated following the equations of Babechuk et al. (2014) and Aiglsperger et al. (2016).

As expected, the silcrete unit has a low UMIA (5.5), characterized by a progressive trend towards elevated SiO_2 content. Despite the general rise of the UMIA in the oxy-hydroxides-dominated zones of the orebody (R6 to R1), the Fe₂O₃ and Al₂O₃ increase in these zones is not accompanied by a total MgO loss. In fact, some compositions measured in the R6, R5 and R3 are displaced toward more MgO-rich compositions in comparison with the typical in situ lateritization trend observed in other deposits (e.g. Wingellina, Putzolu et al., 2019; Moa Bay, Aiglsperger et al., 2016). The UMIA index does not show any relationship with the Ni grades, while a

slight covariance between Co and UMIA is observed in samples from the ferruginous saprolite to the pisolitic topsoil (Fig. 8.4). However, the highest Co concentrations (>0.20 wt% Co) fall outside the correlation trends giving rise to outliers.



Fig. 8.4: Binary plots showing the relationship between the metals grades and the UMIA index.

8.3.1.2 Principal component analysis

To visualize the interelemental relationships, a PCA has been carried out on the bulk rock chemical assays, firstly taking into account all the major and minor oxides, together with Ni and Co (Fig. 8.5a), and secondly selecting only MnO, Cr_2O_3 , Fe_2O_3 , SiO_2 , Ni and Co (Fig. 8.5b-e). In the first PCA (Fig. 8.5a and Appendix 8.7), the first two components explain ca. 71% of the total variance (52.3% PC1 and 19.3% PC2) of the geochemical dataset. Along the PC1 axis, the MgO and the SiO₂ eigenvectors show a positive correlation toward negative PC1 values.



Fig. 8.5: a) PC1 vs. PC2 bi-plot showing the association between the major and minor oxides in the Santa Fe' geochemical dataset; b) c), d) and e) PC1 vs. PCn bi-plot showing the association of Ni and Co with MnO, Cr_2O_3 and Fe_2O_3 and SiO_2 .

They form an anticorrelated group with Fe₂O₃-MnO and are relatively less anticorrelated with TiO₂-Al₂O₃-Co-Cr₂O₃-Ni, which have variably positive

and negative PC2 values. However, PC1 was able to discriminate the (phyllo)silicate- and oxide-dominated sections of the orebody (bedrock samples to ochre saprolite and silcrete; ferruginous saprolite to pisolitic topsoil, respectively). Along the PC2 axis, Al_2O_3 and TiO_2 show a good correlation in the R6 to R1 units, while CaO and P2O5 are significantly displaced toward higher PC2 values and are correlated within the lower section of the profile (U to R7). The MnO, Co, Cr₂O₃ and Ni eigenvectors display a progressive displacement towards negative PC2 values and are mostly distributed within oxide-dominated sections of the ore. The PCA of the full dataset highlighted a complex Co deportment, which is associated with a relatively wide group of elements (mostly Cr₂O₃-Mn, and less Ni-Fe₂O₃). Therefore, the second PCA was conducted on selected variables to better constrain the Co behaviour (Fig. 8.5c-e, Appendix 8.9). In this PCA, PC1 explains ca. 67% of the total variance, PC2 accounts for 14%, and the components that are subsequent to PC2 account for significant proportions of the bulk variance. In the PC1 vs. PC2 plot (Fig. 8.5b) Co is closely associated with MnO and Cr₂O₃ (R1, R2, R3 and R5 units), while Ni (R6 unit) and Fe₂O₃ (R1 unit) are displaced toward negative and positive PC2 values, respectively. The Co-Cr₂O₃-Mn group is dominant also in the PC1 vs. PC3 plot (Fig. 8.5c), but here Co is slightly decoupled toward positive PC3 values. In addition, Ni and Fe₂O₃ are strongly correlated with negative PC3 values. The PC1 vs. PC4 plot shows a similar scenario, with a correlation between Co and Fe₂O₃ along positive PC4 values and a strong association between MnO, Ni and Cr₂O₃. Lastly, the PC1 vs. PC5 (Fig. 8.5e) plot is the only computation where Cr_2O_3 is decoupled from the other variables, which form the Fe₂O₃-Ni-Co-MnO group characterized by low to moderately positive PC5 values.

8.3.1.2 Factor analysis

A factor analysis (after Varimax rotation) has been performed on each regolith unit and on the magmatic bedrock (Appendices 8.10 to 8.12). The MnO-Fe₂O₃-Co-Cr₂O₃ group, showing positive weightings, is widespread in almost the whole dataset (i.e. in the magmatic bedrock and in the R8, R7, R5, R4, and R3 units), and occurs in the in the first factor in association with the SiO₂ and MgO pair, which is instead characterized by negative loadings. These groups collectively account for 20 to 34% of the explained variance. The association between MnO-Fe₂O₃-Co-Cr₂O₃ becomes more

complex in the lateritic crust, in the pisolitic topsoil, and to a lesser extent in the ochre saprolite horizons. In the former, Fe₂O₃ shows a positive weighting in association with negative weightings of SiO₂ and MgO in F1, while MnO and Co are positively correlated with Al and Ni in F2. In this context, Cr is geochemically decoupled and shows a positive weighting in F3. In the pisolitic topsoil, Fe₂O₃ occurs in F1, while the F4 and F5 factors highlight the Mn-Ni-Co and Cr-Co associations, respectively. Although the Cr-Co association occurs in the last factor (F5), it accounts for 9% of the explained variance. The Cr-Co association, accounting for 10% of the total variance, has been detected also in the F3 of ochre saprolite unit. Other important associations are the Al₂O₃-TiO₂-CaO-P₂O₅ group, occurring throughout the profile, and Ni-Mg (and locally TiO₂-Al₂O₃-Fe₂O₃), which have been detected from the ferruginous and ochre saprolites and in the pisolitic topsoil.

8.3.2 Mineralogy and textures

XRPD (Fig. 8.6) shows that the saprock unit consists of remnant magmatic olivine and pyroxene, of layered silicates (i.e. chlorite, serpentine and vermiculite), together with spinel group minerals. The mineralogy of the green saprolite is similar to that of the saprock, except that it also contains smectite. In the uppermost units of the laterite profile (R6 to R1), goethite, hematite and magnetite are the dominant oxy-hydroxides, while chlorite is the only phyllosilicate. Mn-oxy-hydroxides have been also detected and occur as minor constituents of the ore. In the saprock, olivine is crosscut by several generations of serpentine with typical mesh-like textures (Fig. 8.7a), while pyroxenes are cut by veinlets of serpentine and/or cryptocrystalline quartz (Fig. 8.7b-c). In the green saprolite, newly formed serpentine has totally obliterated the magmatic texture; it occurs in two generations: massive (srp I) and vein-filling (srp II) serpentine (Fig. 8.7d). Chlorite occurs extensively in the saprock and green saprolite units, either as filling of cavities in cryptocrystalline silica (Fig. 8.7e), or as replacement of spinels (Fig. 8.7f). Smectite clays only occur as alteration rims around olivine in the phyllosilicate-dominated section of the profile (Fig. 8.7f). Remnants of perovskite and apatite occur extensively mostly in the lowermost section of the profile (Fig. 8.7h-i), with the former commonly exhibiting Al-bearing Ti-oxides alteration rims (Ti/Al-oxide I, Fig. 8.7h). Hypogene Cr-Fe-oxides





Fig. 8.6: Representative XRPD patterns of the regolith units in the Santa Fe' laterite. Mineral abbreviations: verm = vermiculite; am = amphibole; qtz = quartz; en = enstatite; chl = chlorite; srp = serpentine; fo = forsterite = chr = chromite; sme = smectite; ght = goethite; spl = spinel; MnO/OH = Mn-oxy-hydroxide; gbb = gibbsite; hem = hematite; ant = anatase; ilm = ilmenite.

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Based on its texture, two types of magnetite were detected: coarse grained magnetite I (mt I) (Fig. 8.8a), which commonly shows either hematite lamellae (hem I, martitization, Fig. 8.8b) or ilmenite exsolutions (Fig. 8.8c); magnetite II (mt II), which mainly occurs in the saprock and in the green saprolite as tiny rims around serpentine (Fig. 8.7a-d). Chromite commonly shows porous/spongy alteration zones that are locally spread toward the grain core, thus indicating a pervasive alteration of the Cr-spinel (Fig. 8.8d). Two ferritchromite (Fe-chr) generations were also recognized, with Fe-chr I occurring as massive grains, which host amphibole- and Ni-Fe(Co)-sulfide inclusions (Fig. 8.8e).



Fig. 8.7: Backscattered electron photomicrographs showing the typical textures of the magmatic minerals and of the newly formed phyllosilicates: a) serpentine and magnetite II enveloping olivine grains (saprock); b) mesh of serpentine replacing pyroxene grains (saprock); c) cryptocrystalline quartz cementing pyroxene (saprock); d) mesh serpentine II crosscutting pseudomorph serpentine I (green saprolite); e) layered chlorite within cryptocrystalline silica; f) newly formed chlorite replacing a spinel grain (green saprolite); g) pelitomorphic smectite replacing olivine; h) primary perovskite grains crosscut by Ti/Aloxide I (transition zone); i) apatite and pyroxene grains cemented by cryptocrystalline silica (saprock). Mineral abbreviations: ol = olivine; px = pyroxene; mt = magnetite; chl =

chlorite; srp = serpentine; sme = smectite; ap = apatite; prv = perovskite; Ti/Al-ox = Ti/Al-oxide.



Fig. 8.8: Backscattered electron photomicrographs showing the typical textures of the spinels: a) coarse magnetite I grain associated with partially altered perovskite; b) magnetite I grain exhibiting hematite exsolutions (hem I; martitization) (transition zone); c) magnetite I with trellis-type ilmenite exsolutions (ferruginous saprolite); d) chromite grain with pervasive alteration rim (transition zone); e) ferritchromite I enclosing amphibole and Ni-Fe(Co)-sulfide inclusions (transition zone); f) ferritchromite II replacing ferritchromite I (ferruginous saprolite). Minerals abbreviations: pev = perovskite; mt = magnetite; hem = hematite; chr = chromite; ilm = ilmenite; Fe-chr = ferritchromite; am = amphibole.

Furthermore, a late generation of zoned ferritchromite (Fe-chr II) was observed partially replacing Fe-chr I (Fig. 8.8f). Among newly formed Fe-oxy-hydroxides, a first type of goethite (ght I) occurs as skeletal aggregates in the lowermost section of the profile (i.e. saprock and green saprolite, Fig. 8.9a).



Fig. 8.9: Backscattered electron photomicrographs showing the typical textures of supergene oxy-hydroxides: a) skeletal goethite enveloped in serpentine mesh (saprock); b) oolitic Fe-oxy-hydroxides (ferruginous saprolite); c) detrital chlorite and pyroxene in a goethite-rich matrix (ferruginous saprolite); d) massive hematite crust (lateritic crust); e) neoformed Ti/Al-oxide (Ti/Al-ox II) in goethite matrix (ferruginous saprolite); f) gibbsite crosscutting hematite (lateritic crust); g) Mn-hydroxides vein crosscutting chlorite (saprock); h) Mn-oxy-hydroxides replacing chlorite (saprock); i) layered Mn-oxy-hydroxides encrustation (lateritic crust). Mineral abbreviations: gt = goethite; srp = serpentine; MnO/OH = Mn-oxy-hydroxide; chl = chlorite; hem = hematite; gbb = gibbsite; Ti/Al-ox = Ti/Al-oxide; px = pyroxene.

The textures of the more surficial ferruginous saprolite show a certain degree of reworking, with ubiquitous composite Fe-oxy-hydroxides-rich oolites (Fig. 8.9b) and detrital chlorite (Fig. 8.9c). Supergene hematite (hem II) is commonly found in the core of the ooids, while goethite (ght) occurs at

their external rims (Fig. 8.9b). Hematite locally occurs also as massive crusts (Fig. 8.9d). Late generations of Ti- and Al-oxy-hydroxides have been extensively detected: a second generation of Ti/Al-oxide (Ti/Al-oxide II) was observed as globular and concentric aggregates (Fig. 8.9e). Veinlets of gibbsite cutting the hematite/goethite ooids have been observed (Fig. 8.9f). Mn-hydroxides occur in the lowermost section of the profile as replacement of chlorite (Fig. 8.9g-h), while in the oxide-dominated units they form massive to layered encrustations (Fig. 8.9i).

8.3.3 Mineral chemistry

Selected microprobe analyses of ore-bearing and gangue minerals are reported in Tables 8.2 to 8.7, while box and whisker plots, showing the full dataset in chemical variance of the pre-lateritic, as well as of the supergene phases are reported in Appendices 8.13 and 8.14, respectively.

Ferromagnesian minerals: Forsteritic olivine (Fo# mean = 87.56) has average Ni and Co contents of 0.35 wt% NiO and 0.03 CoO wt%, respectively. Clinopyroxene (diopside) and amphibole (K-bearing ferropargasite) have very low Co (mean CoO = 0.03 wt% and below detection limit, respectively) and Ni grade contents (mean NiO = 0.17 wt% and below detection limit, respectively).

Pre-lateritic Fe-Cr-oxides: Chromite displays significant amounts of Cr, Fe^{2+} , Al, Mg and Ti (mean = 50.61 wt% Cr₂O₃, 19.69 wt% FeO, 7.99 wt% Al₂O₃, 7.49 wt% MgO and 2.88 wt% TiO₂). In a limited group of analyses, chromite grains are also enriched in Fe^{3+} (up to 14.36 wt% Fe_2O_3), transformation to Fe³⁺-bearing chromite indicating an incipient (ferritchromite). In ferritchromite I, Fe is the dominant element, while the Cr amounts are relatively low (mean = 39.82 wt% Fe₂O₃, 26.05 wt% FeO, and 23.91 wt% Cr₂O₃). Minor concentrations of Ti, Al, Mg and Zn have been also detected (mean = 3.62 wt% TiO₂, 1.08 wt% Al₂O₃ and 4.10 wt % MgO, 1.54 ZnO). In comparison with ferritchromite I, ferritchromite II displays higher Al, Cr and Zn concentrations (mean = 5.57 wt% Al₂O₃, 39.51 wt% Cr₂O3 and 12.16 wt% ZnO, respectively) and lower Fe³⁺ concentrations (mean = 6.21 wt% Fe₂O₃). Iron is the main cation in magnetite (mean = 69.83 wt% Fe₂O₃ and 34.74 wt% FeO), which locally

exhibits relatively high Ti and Al amounts (up to 8.56 wt% TiO₂ and 3.25 wt% Al₂O₃). Moreover, the Fe-Cr-oxides contain traces of Ni, Co and Mn. There are significant amounts of Co in the chromite grains (up to 0.53 wt% CoO), whereas their Ni content is lower (<0.20 wt% NiO) and is similar to that of ferromagnesian minerals. High Ni and Co contents were measured in ferritchromite. Ferritchromite I has Ni and Co concentrations up to 1.94 wt% NiO and 1.63 wt% CoO, while in ferritchromite II the Ni and Co grades reach values up to 2.29 wt% NiO and 1.23 wt% CoO. Manganese occurs as minor element mainly in chromite and ferritchromite I (up to 1.73 wt% and 1.41 wt% MnO). Other significant chemical features of Fe-Cr oxides can be observed on the Al-Cr-Fe³⁺ projection of the spinel prism (Fig. 8.10). In particular, the analyzed minerals are characterized by a progressive chemical evolution between the chromite and magnetite endmembers, following an increase of Fe³⁺ (Fig. 8.10a). Interestingly, in the Al-Cr-Fe³⁺ system (Fig. 8.10b) the analyzed primary chromite plots within the very low-grade metamorphic field (i.e. greenschists facies), while most of the ferritchromite data are spread within the metamorphic field ranging from lower to upper amphibolite facies. This is also confirmed by the data distribution in the crossplot of Figure 8.10c, where ferritchromites (I and II), as well as a few chromite analyses, show Cr and Mg numbers (i.e. and $Mg/[Mg+Fe^{2+}]$, respectively) different from Cr/[Cr+Al]the conventional mantle spinels, being instead located in the high temperature compositional field of altered spinels observed in other ultramafic suites (Arai and Akizawa, 2014 and reference therein). Another relevant aspect is shown by the geochemical transect performed in a residual chromite grain, which exhibits a well-developed reaction rim (Fig. 8.10d). The main chemical variations between the fresh chromite core and the altered rim are the decrease of the Cr, Mg and Al concentrations and the increase of the total Fe content (Fe^{2+} and Fe^{3+}).

Mg-Ni phyllosilicates: The chemistry of mesh-like (srp I) and vein-filling (srp II) serpentine is characterized by very similar Mg contents (mean = 34.38 wt% and 32.49 wt% MgO respectively), while Ni, Fe and Al differ significantly among the two serpentine generations. In srp I Al, Fe and Ni are relatively low (mean = 0.49 wt% NiO, 7.80 wt% FeOt and 0.17 wt% Al₂O₃), while in srp II Al (mean = 0.74 wt% Al₂O₃), as well as Ni and Fe are significantly increased (1.64 wt% NiO and 11.08 wt% FeOt). In smectite clays the octahedral site is characterized by high Mg and Fe contents (mean

= 16.89 wt% MgO and 12.16 wt% FeO_t), while Al and Ni occur as minor cations (mean = 1.88 wt% Al₂O₃ and 1.54 wt% NiO). Chlorite contains variable amounts of Ni (0-11.50 wt% Ni, mean = 3.04 wt% Ni).



Fig. 8.10: a) and b) ternary plots showing the mineralogy and chemistry of spinels, respectively; c) Mg# vs. Cr# binary plot showing the chemical variation between chromite and ferritchromite (I and II) (adapted from Akizawa and Arai, 2009); d) geochemical transect in an altered chromite grain. Compositional and metamorphic fields of Figs. a and b are from Barnes and Roeder (2001) and Evans and Frost (1976), respectively.

Overall, Mg is the dominant octahedral cation (mean = 23.61 wt% MgO), followed by Al and Fe (mean = 9.06 wt% Al₂O₃ and 7.35 FeO_t). Furthermore, chlorite contains variable amounts of Ti and Cr, which can reach concentrations up to ca. 5 wt% TiO₂ and 1 wt% Cr₂O₃.

Secondary oxy-hydroxides: Among Mn-oxy-hydroxides, three mineral species have been identified at Santa Fe': romanèchite, asbolane and lithiophorite-asbolane intermediates. Overall, Co is almost equally distributed within Mn-oxy-hydroxides, with romanechite showing a slight enrichment (mean = 3.62 wt% CoO), in comparison with asbolane and lithiophorite-asbolane (mean = 2.58 wt% and 2.35 wt% CoO, respectively). Nickel is enriched in asbolane (mean = 20.20 wt% NiO), and to a lesser extent in romanèchite and lithiophorite-asbolane (13.16 wt% and 12.43 wt% NiO, respectively). Barium is a major constituent of romanèchite (mean = BaO), whereas lithiophorite-asbolane shows high Al 5.13 wt% concentrations (12.32 wt% Al₂O₃). In the Al-Ni-Co system (Fig. 8.11), the chemistry of Mn-oxy-hydroxides from Santa Fe' is significantly different from those of other world-class Co-bearing laterite deposits such as Wingellina (Western Australia; Putzolu et al., 2018) and Nkamouna (SE Cameroon; Lambiv Dzeuma et al., 2013). In particular, despite the observation that Mn-oxy-hydroxides have high Ni concentrations, the Co grades are significantly lower in comparison with the above-mentioned deposits. Hematite has average Ni and Co contents of 0.80 wt% NiO and 0.23 wt% CoO, while goethite is more Ni-enriched (mean = 0.97 wt% NiO) and a lower Co grade (mean = 0.18 wt% CoO). To better constrain the elements deportment in Fe- and Mn-oxy-hydroxide-bearing zones of the ore, EDX high-resolution maps were carried out on selected hydroxide-rich regions of the ferruginous saprolite (R6; Fig. 8.12), where relict skeletal goethite is coated by Mn-oxy-hydroxides encrustations, while spinels grains are enclosed in a Fe-oxy-hydroxide-rich matrix. As expected, Fe is distributed in Fe-oxy-hydroxides and spinels (Fig. 8.12b). Manganese and Cr are mostly concentrated in Mn-oxy-hydroxides (Fig. 8.12c) and spinels (Fig. 8.12d), respectively. Moreover, lower Mn amounts were also detected in spinels grains. Interestingly, Mn-oxy-hydroxides exert a strong control on the Ni distribution (Fig. 8.12e). Conversely, Co is found to be equally distributed among Fe- and Mn-oxy-hydroxides and is highly concentrated in spinels grains (Fig. 8.12f).





Fig. 8.11: Co-Ni-Al ternary plot (cationic composition wt%) displaying the mineral chemistry of Mn-oxy-hydroxides from Santa Fe', and comparing their composition to those from Wingellina, Western Australia (Putzolu et al., 2018) and Nkamouna, SE Cameroon (Lambiv Dzemua et al., 2013).

8.4 Discussion

8.4.1 Genesis and evolution of the Santa Fe' deposit: from an alkaline ultramafic intrusion to an oxide-dominated laterite

The mineral paragenesis of the Santa Fe' laterite is shown in Figure 8.13. Ferromagnesian minerals (olivine and pyroxene), apatite and primary Fe-Cr (chromite, ferritchromite I and II, magnetite I and hematite I) and Ti oxides (perovskite, ilmenite and Ti/Al-oxide I), represent the earliest formed

minerals. Olivine and pyroxene represent remnants of parent rocks preserved in the saprock horizon, while Fe-Cr oxides, as well as apatite and Ti/Al-oxides occur also in the upper zones of the profile.



Fig. 8.12: EDX high-resolution maps of Fe- and Mn-oxy-hydroxides region in the ferruginous saprolite (R6).

Although ilmenite and Ti/Al-oxide are found as exsolution lamellae in magnetite I and perovskite respectively, their formation from alkaline melts is generally related to very different stages of the evolution of the orthomagmatic system. Such trellis-type ilmenite exsolution commonly indicates an oxy-exsolution process occurring at magmatic temperatures (T > 600 °C; Tan et al., 2016), whilst Ti/Al-oxides rich exsolution in perovskite mainly form at lower temperatures (T < 350 °C; Chakhmouradian and Mitchell, 2000), typical of later hydrothermal

alteration stages. The olivine and pyroxene replacement by serpentine I is also related to a hydrothermal alteration stage that occurred prior to lateritization. Mineralogical characteristics serpentinites are related to both the original mineralogy of the protolith and to the hydrothermal fluid oxidation state (e.g. Mével, 2003; Lambiv Dzemua et al., 2012; Evans et al., 2013, and references therein).

Stage	(i) Magmatic	(ii) Hydrothermal	(iii) Silicification	(iv) Early Lateritization	(v) Late Lateritization
Mineralogy					
Olivine Pyroxene Magnetite I Chromite Perovskite Apatite Ilmenite					
Ti/Al-oxide I Serpentine I Magnetite II Silica Ferritchromite I Ferritchromite II Chlorite Amphibole Fe-Ni(Co)-sulfide					
Serpentine II Smectite Mn-oxy-hydroxides Goethite I Hematite II Goethite II Gibbsite Ti/Fe-Al-oxide II					
	Late Cretaceous	? E St	ocene to Oligocen <i>Il-Americano</i> cyc	e Miocene-Plioc le Velha	ene to present (?) s cycle

Fig. 8.13: Mineral paragenesis in the Santa Fe' laterite deposit.

Hydrothermal alteration of olivine-pyroxene-dominated cumulates produces a serpentine-brucite-magnetite assemblage (e.g. Mével, 2003), whereas high silica activity allows formation of cryptocrystalline quartz, as observed at Santa Fe'. Ferritchromite is one of the main minerals in the saprock and green saprolite, widespread in the oxy-hydroxide section of the weathering profile. Ferritchromite did not form directly from the crystallization of the magma, but as an alteration product of Al-spinel and chromite (e.g. Merlini et al., 2009; Lambiv Dzemua et al., 2012). Mellini et al. (2005) showed that chromite alteration to ferritchromite and/or Cr-magnetite is common during late stages of regional serpentinization of spinel-bearing dunites, accompanied by chlorite precipitation. Moreover, as shown by Colás et al. (2017) showed that SiO₂-rich hydrothermal fluids during low temperature serpentinization of ferromagnesian minerals enhance the metamorphism of primary chromite, leading to a Fe³⁺-rich spinel+chlorite assemblage. At Santa Fe' this process is visible in the early paragenetic evolution of chromite-to-ferritchromite I. Late chromite alteration to ferritchromite supplied high amounts of Cr, Mg and Al to the system (Fig. 8.10d), which in presence of high-SiO₂, triggered chlorite formation. This explains the close paragenetic association observed between chlorite-ferritchromite (Fig. 8.7f) and chlorite with cryptocrystalline quartz (Fig. 8.7e). High Cr and low Mg numbers of ferritchromite (Fig. 8.10c), and the occurrence of ferropargasite inclusions in spinels (Fig. 8.8h) indicate a high temperature alteration process, under retrograde amphibolite facies metamorphism (Barnes and Roeder, 2001; Mellini et al., 2005; Arai et al., 2006; Arai and Akizawa, 2014). Early supergene processes were likely related to the Sul-Americano weathering cycle (Eocene to Oligocene, Braun, 1971), largely recorded by silcrete layers. Silica-rich sections within the weathering profiles have been reported in many Ni-laterite deposits, as in Australia (e.g. Mt. Keith and Wingellina, Butt and Nickel, 1981; Putzolu et al., 2018, 2019), in the Mediterranean area (e.g. Çaldağ, Thorne et al., 2009) and in Brazil (de Oliveira et al., 1992), and are a common feature of laterites derived from olivine-dominated cumulates (i.e. dunite; Butt and Cluzel, 2013 and references therein). Silica precipitation occurs by evapotranspirative oversaturation of silicic acid formed either during the olivine hydrolysis or due to serpentine decomposition (e.g. Thorne et al., 2009). However, it is widely accepted that silicification is an alteration process mainly developed during arid to semi-arid climatic stages, rather than during tropical weathering sensu stricto (e.g. Golightly, 2010 and references therein). Lateritic weathering sensu stricto likely started with the onset of the Velhas Cycle (Braun, 1971). Evidence for this comprise formation of Ni-enriched serpentine (srp II), skeletal goethite (ght I), smectite clays and Mn-oxy-hydroxides. Serpentine II was developed directly from serpentine I, whereas both goethite I and smectite formed from olivine. Nevertheless, as shown by Golightly (2010 and references therein), genesis of smectite at Santa Fe' was controlled by alteration of pyroxene. Given that minor smectite and Mn-hydroxides are found in the lowermost section of the
profile (i.e. saprock), while in situ goethite I occurs in the green saprolite unit in the mesh cores, less acidic conditions and a lower degree of leaching have enhanced the stability of clays and of Mn-oxy-hydroxides deeper in the profile (Velde and Meunier, 2008; Golightly, 2010; Dublet et al., 2017). In contrast, in the uppermost zones, two distinct processes could have developed: either olivine weathered directly to skeletal goethite, or smectite decomposed to Fe-oxy-hydroxides following the typical paragenetic sequence observed in many laterite profiles worldwide (e.g. Freyssinet et al., 2005 and references therein; Tauler et al. 2017; Teitler et al. 2019; Putzolu et al., 2019). The occurrence of newly formed Ti-phases (i.e. Ti/Al-Fe-oxides) and gibbsite cements in the uppermost section of the deposit indicates that during the ferrugination stage, Ti and Al were liberated from earlier mineral phases (i.e. Ti from Ti/Al-oxide I and Al from chlorite, lithiophorite-asbolane and chromite) and concentrated in late stage oxyhydroxides. The occurrence of oolitic Fe-oxy-hydroxides, and of detrital goethite I and chlorite, from the ferruginous saprolite likely records a partial reworking and collapse of the ferruginous zones, which together with further coeval lateritization, obliterated the original textures.

8.4.2 Element distribution and Ni-Co deportment

In accordance with the model of direct formation of Ni-laterites (e.g. Golightly, 2010), in which groundwater flushing enhances leaching of Mg and Si following the decomposition of ferromagnesian minerals, we also see almost complete leaching of Mg and Si at Santa Fe'. This process normally produces an oxide-dominated regolith, where Ni and other transition metals are enriched into Fe-oxy-hydroxides (e.g. Butt and Cluzel, 2013; Freyssinet et al., 2005; Elias, 2006). However, at Santa Fe', most of the variance of Ni is not correlated with Fe (Fig. 8.5a-b). To explain the Ni distribution in the Santa Fe' deposit, PC1 explains the behavior of elements whose pathways are totally controlled by the lateritization-related leaching (i.e. Mg and Si), or precipitation in neo-formed phases (i.e. Fe). In this context, the geochemical decoupling of the Ti-Al-P-Ca and Mn-Co-Cr-Ni groups from the anticorrelated Mg-Si versus Fe group (Fig. 8.5b) can be explained by some key elements being hosted weathering-resistant phases. In detail, the Ti-Al-P-Ca group is indicative of the occurrence of pre-weathering primary Ti-oxides (Ti/Al-oxide I, ilmenite and perovskite), as well as apatite throughout the weathering profile. The Mn-Co-Cr-Ni group, also includes Cr, suggesting that part of the variance might be controlled by the element distribution in the magmatic to hydrothermal Cr-Fe oxides, widely identified in oxide-dominated zones of the deposit. Therefore, the occurrence of the Ni eigenvector in that group indicates that Ni distribution is not explained only by the distribution of newly formed Ni-bearing Feoxy-hydroxides. At Santa Fe' the highest Ni grades occur in chlorite minerals (up to 11 wt% NiO), which are the main constituents not only of the phyllosilicate-rich zones of the orebody, but are also enriched as detrital minerals in the uppermost section of the regolith profile. Although the formation of chlorite at Santa Fe' cannot be directly ascribed to the lateritization stage s.s. many studies (e.g. Wiewiòra and Szpila, 1975; Noack and Colin, 1986; Suarez et al., 2001) have highlighted that chlorite can act as scavenger for Ni. The importance of chlorite distribution in the Fe-oxyhydroxides-rich units of the orebody can be also deciphered by the MgO-SiO₂-(Al₂O₃+Fe₂O₃) ternary plot (Fig. 8.3), where a significant increase of the UMIA can be followed from the R6 unit up core. In spite of this, many analyses from the transition zone and the lateritic crust fall outside the compositional field of typical oxide-dominated lithologies observed in the in situ deposits (e.g. Aiglsperger et al., 2016; Tauler et al., 2017; Putzolu et al., 2019) and are shifted toward the MgO-rich field of the plot. Therefore, the complex Ni distribution in the Santa Fe' deposit and the noncorrelation between Ni and Fe observed in the full dataset PCA (Fig. 8.5a), are related to the in situ coeval ferrugination, which accounted for both a partial Niscavenging by Fe-oxy-hydroxides, and partial reworking, producing an exotic input of Ni-enriched chlorite. The Co speciation in laterite profiles is commonly controlled by the distribution of Mn-oxy-hydroxides, due to their high capability incorporate trace elements (Burns, 1976; Kay et al., 2001; Manceau et al., 1992; McKenzie, 1989; Lambiv Dzemua et al., 2012; Aiglsperger et al., 2016; Putzolu et al., 2018 and 2019). The enrichment process during lateritization is controlled by the availability of Co and Mn in the magmatic bedrock and by the reaction pathways during the regolith evolution. In most ultramafic-derived laterites, Co and Mn (as well as Ni) are sourced from olivine (e.g. Dublet et al., 2017). Under neutral pH to slightly alkaline conditions, commonly detected in the deeper parts of the laterite profile, the oxidation of Co to the trivalent state (Co^{3+}) and of Mn to the tetravalent state (Mn⁴⁺), would cause the formation of Co-bearing Mnoxy-hydroxides (Burns, 1976; Dublet et al., 2017) and eventually the economic concentration of Co. At Santa Fe', the presence of Co-bearing

Mn-oxy-hydroxides is limited, and their Co-grade is generally lower compared with other oxide-dominated laterite deposits (Fig. 8.11). Moreover, the variation of Co in the whole dataset (Fig. 8.5a-b) suggests that the Co deportment is not entirely controlled by Mn-oxy-hydroxides. Moreover, initial Mn and Co contents of the Santa Fe' ultramafic rocks (mean = 0.01 wt% Co and 0.17 wt% MnO) are comparable with protoliths of other Ni- and Co-fertile laterites, like Wingellina (Western Australia, Putzolu et al., 2019). However, the Santa Fe' weathered profiles are relatively Co- and Mn-depleted (mean = 0.08 wt% CoO and 0.75 wt% MnO), compared to other Ni- and Co-fertile laterites. The most important reasons for the lack of Co enrichment in the Santa Fe' laterites, as well as for its peculiar association not only with Mn but also with Cr is linked to the petrological characteristics of the parent rock and to its hydrothermal alteration history. Here, fresh bedrock represents the mafic to ultramafic plutonic component of a large magmatic province with alkaline affinity (e.g. Barbour et al., 1979; Brod et al., 2005). The behaviour of Co in subalkaline basaltic melts, such as in the parent rocks of the Ni-Co Wingellina deposit in Western Australia (Ballhaus and Glikson, 1995), favours its incorporation in olivine (Kd up to 6.5; Mysen, 2007) and less in clinopyroxene (Kd = 1.32; Bougault and Hekinian, 1974). In basaltic melts with alkaline affinity, Co has instead a higher affinity with spinels (Kd = 4.7-8.3; Horn et al. 1994) than with ferromagnesian minerals (i.e. olivine Kd = 5.1, clinopyroxene Kd = 1.02; Villemant et al., 1981). In the Santa Fe' case, this process would explain the relative high Co content detected in primary Cr-spinels (up to 0.53 wt% CoO in chromite), and the corresponding low Co concentration in olivine (up to 0.08 wt% CoO). Moreover, another factor that has enhanced the trace element gain in Cr-Fe spinels is the hydrothermal alteration of chromite, leading to formation of ferritchromite I and II. At Santa Fe', the significant redistribution of transition metals during the hydrothermal alteration of magmatic spinels is shown by elevated Mn, Ni Co and Zn in late-stage spinels, and by the presence of Ni- and Co-bearing Fe-sulfide inclusions within the spinels themselves (Fig. 8.8e). Moreover, the postmagmatic alteration of spinels at Santa Fe' is also corroborated by their Mg and Cr numbers, highlighting a hydrothermally-related depletion of Al and Mg compared to nominal magmatic chromite (Barnes and Roeder, 2001). Post-magmatic alteration of Cr-spinel plays a primary role also in defining the trace element (mostly Mn, Zn, Co, Ni) budget in late stage spinels (e.g. Economou-Eliopoulos, 2003; Ożóg and Pieczonka, 2019). At the scale of the whole deposit, the Co (and Mn) affinity to spinels has been observed through PCA (Fig. 8.5b-e), where most of the Co variance is correlated to Cr and Mn (Fig. 8.5b-c), while a clear geochemical and thus mineralogical Co differentiation to spinels is visible only in minor components (i.e. PC4 and PC5), highlighting that part of Co has been scavenged to Fe- and Mnoxy-hydroxides (Fig. 8.5d-e). The Co pathway during the pre-lateritic and the early supergene stages in the Santa Fe' deposit is summarized in a threestage model (Fig. 8.14). This model shows that primary Cr-spinels (i.e. chromite) contain Co and Mn, due to their relatively high partitioning during the orthomagmatic stage (Fig. 8.14a). During the early alteration stage, the hydrothermal process was only effective in triggering the olivineto-serpentine transformation (i.e. serpentinization), which led to the leaching of Mg, Si, Ni and Co²⁺ hosted in olivine. In this context, primary Cr-spinels (i.e. chromite) remained unaltered, likely due to the highly reducing conditions occurring during serpentinization (Bach et al., 2006). However, while the SiO₂ and O₂ activity of the hydrothermal fluids increased, chromite lost Al³⁺ and Mg whilst Fe²⁺ in the Cr-spinels oxidized to Fe³⁺ (Gonzáles-Jimenez et al., 2009). These processes, occurring during the retrograde metamorphic amphibolite stage, led to the formation of the Fe³⁺bearing ferritchromite rims, the chlorite alteration patches on spinels and the ferro-pargasite inclusions (Fig. 8.14b). A big part of Ni released by dissolution of olivine was uptaken by chlorite, with less concentrated in late-stage spinels (i.e. ferritchromite I and II). On the contrary, the bulk of available Co was concentrated in spinels, the only phases able to do so at this time. When early supergene processes were superimposed on prelateritic processes (Fig. 8.14c), goethite I pseudomorphs formed from relict olivine and Mn-oxy-hydroxides replaced Ni-chlorite and Fe-oxy-hydroxides rims formed upon spinels. In this scenario, the close paragenetic association between chlorite and Mn-oxy-hydroxides is clear evidence of the Ni-uptake in lithiophorite-asbolane and in other Mn species. However, as most of the Co was concentrated in late-stage spinels, little Co was available for redistribution and enrichment in supergene Mn-oxy-hydroxides, leading to the low Co concentrations displayed by these phases at Santa Fe' (Fig. 8.11, 8.12). The characteristics of the Santa Fe' bedrock is also a likely strong control to the paucity of Mn-oxy-hydroxides in the laterite profile. Many studies (e.g. Taylor et al., 1964; McKenzie, 1989; Dowding and Fey, 2007; Roqué-Rosell et al., 2010; Lambiv Dzemua et al., 2013; Putzolu et al., 2018) have highlighted the primary role of late stage lithiophorite and/or

lithiophorite-asbolane intermediates in improving the stability of Mn-oxyhydroxides.



Fig. 14: Schematic sketch illustrating the mineralogical and compositional changes in prelateritic and syn-lateritic phases at Santa Fe'. Emphasis is given to the relationship between the element pathways and the paragenetic evolution of the mineralogical assemblage.

Minerals abbreviations: ol = olivine; chr = chromite; srp = serpentine; Fe-chr = ferritchromite; am = amphibole; chl = chlorite; sulf = sulfide; FeO/OH = Fe-oxy-hydroxide; MnO/OH = Mn-oxy-hydroxide. Notes: a and b = correspond to the incipient and late phases, respectively, of the (ii) stage in the paragenetic sketch; c = corresponds to the (iv) phase in the paragenetic sketch.

The formation of significant amounts of lithiophorite occurs if sufficient Al is available in the system (Cui et al., 2009). In the specific case of laterites, lithiophorite formation is restricted to those deposits derived from a magmatic intrusion containing Al-rich phases (e.g. plagioclase; Putzolu et al, 2018). Low levels of such minerals at Santa Fe' in the protolith would have limited the formation of stable Mn-oxy-hydroxides. In fact, the majority of the lithiophorite-asbolane is associated with chlorite, the only phase containing significant Al. The residual enrichment of Mn and Ni in late-stage goethite reflects the dissolution of preexisting Mn-Ni phases, such as more unstable Mn-oxy-hydroxides (e.g. asbolane and romanèchite). A similar partitioning of Mn has been observed by Dublet et al. (2015, 2017) in the New Caledonia laterites, with the notable exception that here, the dissolution of Mn-oxy-hydroxides do not lead to a significant Co enrichment in the latest goethite formed.

8.4.3 Implications for ore processing and metal recovery

The Santa Fe' lateritic ore, characterized by a dominant oxide-rich zone (goethite and hematite), is different to other major laterite deposits of the Goiás State, as Niquelândia and Barro Alto (de Oliveira et al., 1992). In both these latter deposits, the exploitation is focused on Ni, recovered from the saprolitic layers enriched in Mg(Ni)-phyllosilicates (e.g. Colin et al., 1990; Ratié et al. 2015). In the Niquelândia deposit the main ore mineral is Ni-smectite, while at Barro Alto the main orebody is composed of Ni-serpentine and garnierite (Ratié et al., 2015). The chemistry of the saprolite ore in these deposits, also characterized by negligible Fe contents and by low SiO₂/MgO ratios, is ideal for pyrometallurgical ore processing (i.e. smelting), to produce ferronickel alloys with a favourable Fe/Ni ratio (Crundwell et al., 2011; Ratié et al., 2016 and references therein). In the specific case of Santa Fe', the most significant characteristics to take into account while planning the processing method are: (i) oxide-bearing units dominate compared to phyllosilicate-rich layers; (ii) the highest Ni grades

occur within the ferruginous saprolite, associated with goethite and chlorite; (iii) the cobalt deportment in the laterite profile is controlled by both newly formed oxy-hydroxides and spinels. A key observation is the strong affinity of Co to spinel phases. Metallurgical processes most widely adopted for Nilaterites are not effective at dissolving spinels, leaving behind a residuum consisting either of silicates slag produced by pyrometallurgical methods, or of quartz, spinels and other minerals and/or alloys if leaching methods as HPAL (Valix and Cheung, 2002; Dalvi et al., 2004 and references therein). The proportions of Co locked in spinels vs. Co concentrated in late-stage minerals can be assessed by looking at the results of preliminary metallurgical tests undertaken on the Santa Fe' oxide ore (Dreisinger et al., 2008). Metal recoveries were tested using HPAL, by using H₂SO₄ (at 250°C for 60 minutes) as leaching agent and saprolite lithologies (R7 unit) as acid neutralization agent. The feeds consisted of several blends of the R3, R5 and R6 units (Table 8.8). Prior to the leaching test, and in order to upgrade the Ni content of the feed, test material was subjected to a mineral beneficiation step using magnetic and heavy mineral separation, likely resulting in the removal of the bulk of the Co-bearing spinels. By comparing the chemistry of the feeds after the mineral beneficiation step with the chemistry of the average Santa Fe' ore (Fig. 8.15), it can be observed that the pre-treatment of the ore was effective only in upgrading Ni and not Co. Increase in Mg can be explained by its occurrence in chlorite together with Ni. Cobalt and Cr were actually downgraded during beneficiation with respect to the chemistry of the R3, R5 and R6 ore zones (Fig. 8.15), thus confirming that Co-bearing spinels are removed during the beneficiation. The observed downgrade indicates that the portion of Co locked in spinels varies between 20% to 50% in the various ore zones (Table 8.8).

8.5 Conclusions and implications

The Santa Fe' laterite has a complex multistage history, starting with a post magmatic hydrothermal alteration of the parent rock, followed by two main supergene alteration stages, involving an early stage silicification followed by a lateritization *sensu stricto*. The Santa Fe' deposit can be classified as an oxide-type deposit, where goethite and hematite represent the most abundant Ni-containing minerals. The silicate-dominated sections of the orebody host also a Ni-enriched chlorite and serpentine. Despite the above classification, the Ni pathway in the Santa Fe' deposit is different from other

oxide-dominated ores and thus cannot be only explained by its uptake by Fe-oxy-hydroxides. As shown by multivariate analyses, in situ ferrugination does not account for the statistical distribution of Ni throughout the laterite facies of the Santa Fe' ore. The process accounting for the geochemical decoupling between the Fe₂O₃- and Ni-rich facies of the deposit is the extensive erosion of the regolith during the lateritization stage, which resulted in the reworking of Ni-bearing chlorite in the ferruginous units of the ore that has obscured the in situ geochemical footprint of Ni.



Fig. 15: Elemental ratios between the average composition of the screened feeds used for metallurgical testwork and the various Santa Fe' laterite ore facies. It can be seen that Ni and Mg are enriched in the feed in respect to the ore, whereas Co and Cr are depleted, this suggesting that the Co-bearing phases have been removed during the screening. For tabulated data see Table 8.8.

The Santa Fe' deposit is an atypical oxide-type laterite also in terms of the observed Co distribution and speciation. According to the multivariate

analyses, most of the statistical distribution of Co is correlated with that of Cr, rather than following the typical association with Mn and thus with Mnoxy-hydroxides. The Co-Cr association is mainly related to the relatively high Co-content detected in magmatic and hydrothermal (i.e. chromite and ferritchromite, respectively), which are residual phases inherited from the parent rock and are ubiquitous throughout the laterite profile. The prelateritic processes accounting for the Co enrichment in spinels can be related to the formation of the parent rock during the orthomagmatic stage and to its later hydrothermal history. During the orthomagmatic stage, part of Co was concentrated in chromite due to its high partitioning in Cr-spinels in alkaline melts. The occurrence of the ferritchromite + amphibole + Fe-Ni(Co)sulfide + chlorite + silica assemblage overprinting the magmatic mineralogical assemblage (i.e. olivine + pyroxene + Cr-spinels) suggests that during the hydrothermal stage the Santa Fe' ultramafic suite experienced amphibolite facies retrograde metamorphic conditions, which were able to trigger a mineralogical and chemical reset of primary spinels that enhanced the Co concentration in late-stage spinels. Both magmatic and hydrothermal processes ended with the Co concentration in phases that Cobearing spinels hardly experience significant dissolution during lateritization, thus limiting the Co availability during the supergene ore formation stage and its secondary precipitation in the newly formed Mnand Fe-oxy-hydroxides. Considering that during orthomagmatic processes, the Co enrichment in primary Cr-spinels might be significant in ultramafic alkaline systems, it is reasonable to suppose that Co is unlikely to be become enriched in the laterites formed over alkaline intrusions in general. However, as the Santa Fe' case represents to date the first mentioned Nilaterite ore developed from an alkaline ultramafic body, this conclusion has to be verified conducting further studies on deposits originating from similar magmatic suites. Since that the Co enrichment in late-stage Fe-spinels is closely related to the formation of ferritchromite and Al-chlorite, these phases can be used as indicators warn of potentially refractory Co in laterite systems. In the Santa Fe' case, the interpretation of preliminary metallurgical testworks suggests that spinels control a significant fraction of Co ranging between 20% and 50%.

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Table 8.1: Average chemical composition (wt%) of the Santa Fe' la	terite regolith units (R8 to R1*), of the magmatic bedrock (U1, U2,
U_{3} and of the silcrete horizon (R4)	

(5) and of the shere horizon (K4).												
	SiO_2	Al_2O_3	MgO	MnO	Fe_2O_3	TiO_2	P_2O_5	CaO	Cr_2O_3	Co	Ni	UMIA
Avg. Regolith units (R8 to R1)*	27.16	3.5	9.74	0.75	43.93	2.01	0.11	0.83	2.96	0.08	0.84	-
Avg. Dunite (U1)	40.6	0.34	34.77	0.17	10.99	0.23	0.04	0.62	0.51	0.01	0.21	4.57
Avg. Peridotite (U2)	41.38	0.13	36.07	0.16	9.68	0.13	0.04	0.34	0.66	0.01	0.19	3.81
Avg. Pyroxenite (U3)	41.95	1.88	28.08	0.18	11.67	1.15	0.27	4.28	0.39	0.01	0.14	6.88
Avg. Bedrock (U1, U2, U3)	41.31	0.78	32.97	0.17	10.78	0.5	0.12	1.75	0.52	0.01	0.18	-
Avg. Silcrete (R4)	64.67	0.71	16.51	0.19	11.47	0.36	0.09	0.24	0.78	0.04	0.34	5.59

* = The silcrete horizon is not included in the calculation.

Table 8.2: Chemical composition (wt%) of selected ferromagnesian minerals.

Oxides	Olivine	Olivine	Cpx	Срх	Amphibole	Amphibole
Na	0.04	0.00	0.27	0.38	5.61	5.31
Mg	46.19	45.61	16.68	16.53	21.62	21.82
Al	0.00	0.08	1.10	1.23	0.15	0.09
Si	37.97	37.80	53.40	53.27	54.89	53.91
Κ	0.02	-	-	-	2.63	2.58
Ca	0.14	0.08	24.79	25.28	6.69	6.65
Ti	-	0.03	0.98	1.05	1.10	1.08
Cr	-	0.00	0.63	0.92	0.04	-
Mn	0.27	0.21	0.04	0.01	-	0.06
Fe	11.42	11.08	3.92	3.67	1.96	2.02
Co	0.01	0.08	0.08	-	0.05	0.03
Ni	0.33	0.41	0.25	0.17	0.06	0.17
Fo#	87.82	88.01	-	-	-	-
Total	96.41	95.38	102.14	102.51	94.81	93.72

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Table 8.5: Chemical composition (Wt%) of selected Fe-Cr oxides.										
Oxides	Chro	omite	Ferritchromite I		I Ferritchromite		Magnetite			
Na ₂ O	0.16	0.17	0.05	-	-	0.35	-	0.01		
MgO	0.4	0.53	3.57	3.67	0.44	0.21	0.06	-		
Al_2O_3	8.88	7.34	0.01	1.18	5.16	5.08	2.56	3.15		
SiO ₂	1.19	0.94	0.05	0.03	4.14	4.91	1.13	0.89		
K_2O	0.01	0.01	-	-	-	0.05	0.09	-		
CaO	-	-	0.11	0.09	0.41	0.23	0.03	-		
TiO ₂	2.85	2.6	5.64	3.76	2.03	2.29	2.6	0.42		
Cr_2O_3	62.93	58.33	13.94	17.87	39.25	40.49	0.62	0.35		
MnO	1.72	1.88	0.59	0.27	0.06	-	-	0.28		
Fe ₂ O ₃	-	-	45.27	43.57	7.58	6.1	57.87	61.66		
FeO	20.99	26.25	25.83	24.8	23.16	24.14	34.45	32.14		
CoO	0.52	0.52	1.63	1.25	1.23	0.7	0.4	0.26		
NiO	0.11	0.12	0.48	0.45	1.35	1.9	0.2	0.28		
ZnO	-	-	2.26	2.68	13.75	12.51	-	-		
Tot	99.77	98.7	97.17	96.93	84.81	86.44	100.02	99.45		
Cr/[Cr+Al]	0.83	0.84	1	0.91	0.84	0.84	0.14	0.07		
$Fe^{2+}/[Fe^{2+}+Fe^{3+}]$	1.6	1.23	0.39	0.39	0.77	0.81	0.4	0.37		
$Fe^{3+}/(Fe^{3+}+Fe^{2+})$	0	0	0.61	0.61	0.23	0.19	0.6	0.63		
Mg/[Mg+Fe ²⁺]	0.03	0.03	0.2	0.21	0.03	0.02	0	0		

Table 8.3: Chemical composition	(wt%) of selected Fe-Cr oxides
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 Fe^{2+} and Fe^{3+} by stoichiometry. Notes: - = not detected.

Table 8.4: Chemical composition (wt%) of selected Ti-oxides.										
Oxide	Ilmenite		Ti/Fe-A	l-oxide	Perov	Perovskite				
Na ₂ O	-	0.11	0.24	0.05	0.73	0.57				
MgO	8.3	2.59	0.18	-	-	0.09				
Al_2O_3	0.01	0.24	8.29	6.21	0.06	0.13				
SiO ₂	0.01	0.13	0.91	0.86	0.02	-				
K ₂ O	-	-	0.03	-	0.07	0.1				
CaO	-	-	-	0.02	38.68	38.93				
TiO_2	54.62	46.9	86.24	88.53	56.46	56.23				
Cr_2O_3	0.06	0.22	0.1	0.29	-	-				
MnO	0.71	1.87	0.17	0.02	-	-				
FeOt	35.68	47.35	2.78	2.89	0.66	1.24				
CoO	0.03	0.15	-	0.08	0.24	-				
NiO	0.03	0.11	0.09	0.08	0.21	0.12				
Total	99.46	99.67	99.03	99.02	98.9	99.76				

Oxides	Oxides Serpentine		Serper	ntine II	Sme	ectite		Chlorite		
Na ₂ O	-	0.01	-	-	-	-	-	0.03	0.08	
MgO	37.04	37.46	31.82	31.12	20.78	22.72	20.43	20.01	23.2	
Al_2O_3	0.64	0.47	0.83	0.85	2.87	2.65	15.15	16.02	12.7	
SiO ₂	40.99	39.53	37.52	37.89	50.74	55.22	30.87	30.57	37.82	
K ₂ O	-	-	-	0.04	0.08	0.05	0.02	-	-	
CaO	0.11	0.06	0.06	0.14	0.28	0.14	-	-	0.01	
TiO ₂	0.12	0.03	0.05	0.32	0.15	0.23	1.63	1.58	5.22	
Cr_2O_3	0.07	0.1	0.16	0.12	0.7	0.77	0.15	0.13	1.14	
MnO	0.04	0.05	0.21	0.22	0.01	0.05	0.04	-	0.09	
FeOt	8.88	8.66	12.8	14.4	6.69	7.26	4.79	4.48	5.3	
CoO	-	0.1	0.25	0.14	0.08	0.14	0.04	-	-	
NiO	1.07	1.03	2.18	2.07	2.2	2.27	11.5	11.49	1.08	
Total	88.96	87.52	85.87	87.3	84.59	91.49	84.63	84.32	86.65	
APFU		on the basis	s of O ₅ (OH) ₄		on the basis on O ₁₀ (OH) ₂		on the basis of O_{10}		10(OH)8	
Si	1.95	1.92	1.92	1.92	3.81	3.83	3.2	3.17	3.59	
Al ^{IV}	0.04	0.03	0.05	0.05	0.19	0.17	0.8	0.83	0.41	
Fe ^{IV}	0.01	0.05	0.03	0.03	-	-	-	-	-	
Sum_{Tet}	2	2	2	2	4	4	4	4	4	
A 1VI					0.07	0.05	1.06	1 12	1.02	
	-	-	-	-	0.07	0.05	1.00	1.15	1.02	
Fe	0.34	0.3	0.51	0.57	0.42	0.42	0.42	0.39	0.42	
Mg	2.63	2.71	2.42	2.35	2.33	2.35	3.16	3.1	3.29	
Ti G	-	-	-	0.01	0.01	0.01	0.13	0.12	0.37	
Cr M:	-	-	0.01	-	0.04	0.04	0.01	0.01	0.09	
Mn Co	-	-	0.01	0.01	-	-	-	-	0.01	
Ni	-	-	0.01	0.01	- 0.13	0.01	-	-	-	
Sum	3.02	3.04	2.05	3.02	2	3.01	5 72	5 71	5 27	
Sumoct	5.02	5.00	5.05	3.05	3	5.01	3.73	3.71	3.27	
Na	-	-	-	-	-	-	-	0.01	0.01	
K	-	-	-	-	0.01	-	-	-	-	
Ca	0.01	-	-	0.01	0.02	0.01	-	-	-	
Sum _{Int}	0.01	-	-	0.01	0.03	0.01	-	0.01	0.02	

Mineralogy and geochemistry of Ni and Co in lateritic profiles

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Table 8.6: 0	Chemical comp	osition (wt%) o	of selected Mn-	oxy-hydroxide	s.		
Oxides	Roma	nèchite	Asbo	olane	Lithio	phorite	
Na ₂ O	-	0.03	-	-	-	-	
MgO	3.61	1.53	0.98	1.53	0.17	0.23	
Al_2O_3	0.36	0.49	0.62	0.45	19.79	17.3	
SiO_2	4.6	2.55	0.89	1.06	0.43	1.11	
K ₂ O	0.01	0.05	-	-	-	-	
CaO	0.07	0.18	-	-	-	-	
TiO ₂	0.23	0.13	0.18	0.23	0.12	0.1	
Cr_2O_3	0.04	-	-	-	0.03	-	
MnO	37.74	41.86	42.56	46.7	39.17	40.43	
FeOt	4.76	3.16	8.64	6.17	9.64	6.21	
CoO	3.71	3.55	2	2.52	2.8	3.56	
NiO	12.52	13.79	20.13	19.39	6.87	9.46	
BaO	5.29	4.97	-	-	-	0.32	
Total	72.88	72.27	76.01	78.06	79.02	78.72	
APFU	on the ba	sis of O ₁₀	on the O ₂ (basis of OH)2	on the basis of O ₂ (OH) ₂		
Na	-	0.01	-	-	-	-	
Mg	0.6	0.26	0.05	0.07	0.01	0.01	
Al	0.05	0.07	0.02	0.02	0.64	0.57	
Si	0.51	0.29	0.03	0.03	0.01	0.03	
Κ	0	0.01	-	-	-	-	
Ca	0.01	0.02	-	-	-	-	
Ti	0.02	0.01	-	0.01	-	-	
Cr	-	-	-	-	-	-	
Mn	2.92	3.32	0.96	1.02	0.74	0.78	
Fe	0.4	0.27	0.21	0.15	0.2	0.13	
Co	0.3	0.3	0.05	0.06	0.06	0.07	
Ni	1.13	1.28	0.53	0.49	0.15	0.21	
Ва	0.23	0.22	-	-	-	-	

Table 8.6 [.]	Chemical (composition (wt%	of selected Mn	-ovv-hydrovides
I ADIC 0.0.	Chemical	composition (wt/0	of selected with	-OAY-IIYUIOAIUCS.

Notes: - = not detected.

 Table 8.7: Chemical composition (wt%) of selected Fe-oxy-hydroxides.

Oxide		Hem	atite			Goe	thite	
Na ₂ O	0.15	-	0.31	0.19	0.07	-	-	-
MgO	1.53	0.38	0.02	0.13	0.02	0.27	-	-
Al_2O_3	0.09	2.78	2.57	2.95	5.57	5.42	4.69	3.4
SiO ₂	1.3	2.46	2.8	2.59	2.74	1.58	2.91	2.05
K_2O	-	-	-	-	0.04	-	0.01	0.02
CaO	0.06	0.07	0.07	0.06	-	-	-	-
TiO_2	0.12	0.38	0.3	0.58	0.32	0.68	1.52	0.83
Cr_2O_3	0.13	0.45	0.77	0.67	1.89	0.66	0.66	1.8
MnO	1.59	0.43	0.14	0.34	0.14	0.26	0.59	0.14
FeO _t	94.82	91.1	90.52	89.69	78.08	79.02	78.68	80.71
CoO	0.36	0.43	0.37	0.34	0.36	0.37	0.39	0.19
NiO	0.22	0.55	0.61	0.85	0.74	1.63	0.41	0.59
Total	100.36	99.03	98.48	98.39	89.95	89.89	89.86	89.84

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Tuble 0.0. Comparison between the chemistry	of the feeds for filet	anuigie	ui testw	orks and	i ule ussu	y data.			
				Meta	llurgical	tests data	(wt%)		
Description	Reference	Al	Co	Cr	Fe	Mg	Mn	Ni	Si
Pressure acid leach blend 1		1.50	0.06	2.05	34.30	6.30	0.63	1.59	10.30
Pressure acid leach blend 2		1.15	0.05	1.70	30.50	6.50	0.53	1.47	12.70
Pressure acid leach blend 3	Dreisinger et al. 2008	1.73	0.04	1.06	30.20	6.20	0.52	1.49	12.70
Saprolite neutralization blend 1	2000	1.71	0.02	0.83	14.50	15.00	0.28	1.66	16.60
Saprolite neutralization blend 2		0.40	0.02	0.71	17.70	13.80	0.31	1.76	16.10
				Whole	rock che	mical da	ta (wt%))	
Description		Al	Co	Cr	Fe	Mg	Mn	Ni	Si
R3 unit avg. chemistry (assay)		2.12	0.10	2.89	38.40	1.88	0.66	0.91	10.59
R5 unit avg. chemistry (assay)		1.46	0.09	2.11	39.29	2.42	0.72	1.43	9.82
R6 unit avg. chemistry (assay)	This study	2.27	0.06	1.44	30.22	4.67	0.53	1.37	13.11
Average chemistry R3+R5+R6 (assay)		1.95	0.09	2.15	35.97	2.99	0.64	1.24	11.17
Santa Fe' bulk chemistry (assay)		1.85	0.08	2.03	30.73	5.87	0.58	0.84	12.70
				Co	ncentratio	on ratios	(a.u.)		
Description		Al	Co	Cr	Fe	Mg	Mn	Ni	Si
Avg. chemistry of blends/R3 avg. assay		0.69	0.50	0.55	0.82	3.37	0.85	1.67	1.12
Avg. chemistry of blends/R5 avg. assay		1.00	0.55	0.76	0.81	2.61	0.78	1.06	1.21
Avg. chemistry of blends/R3+R5+R6 avg. assay	This study	0.64	0.80	1.11	1.05	1.36	1.05	1.11	0.91
Avg. chemistry of blends/R6 avg assay		0.75	0.59	0.75	0.88	2.12	0.88	1.23	1.07
Avg. chemistry of blends/Santa Fe' bulk chemistry		0.79	0.64	0.79	1.03	1.08	0.96	1.81	0.94

Table 8.8: Comparison between the chemistry of the feeds for metallurgical testworks and the assay data.



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Appendix 8.1: Stratigraphic columns of the analysed drillcores showing the position of the collected samples for the petrographic and mineralogical studies.

Mineralogy and geochemistry of Ni and Co in lateritic profiles

Appendix	x 8.2: Che	emical co	omposition of the	he laterite	profile c	of drillco	re FDSF-	01									
							Drillcon	e: FDSF-	-01								
Sample ID	From (m)	To (m)	Lithology Code	Fe_2O_3	SiO ₂	MgO	Cr ₂ O ₃	Al_2O_3	TiO_2	CaO	Co	Ni	MnO	Cu	P_2O_5	LOI	UMIA
B-1451	0	1	R1	67.1	13.1	1.2	6.4	4.2	1.9	0.03	0.15	0.57	0.95	0.01	0.09	3.75	65.77
B-1452	1	2	R2	71.1	7.2	0.7	4.4	6.1	1.6	0.01	0.14	0.7	1.1	0.01	0.07	8.14	79.33
B-1453	2	3	R3	72.9	7.8	0.96	5.1	4.1	1.8	0.01	0.15	0.77	1.3	0.01	0.06	6.04	76.89
B-1454	3	4	R5	73.6	7.7	1.1	5.5	2.9	1.7	0.01	0.13	0.94	1.2	0.01	0.05	6.53	76.27
B-1455	4	5	R5	78.3	3.6	0.98	2.9	1.4	1.2	0.02	0.1	1.42	1.3	0.01	0.05	9.18	85.8
B-1456	5	6	R5	75.4	4.6	1.5	2.4	1.6	1.2	0.01	0.09	1.92	1.2	0.01	0.06	9.5	81.26
B-1457	6	7	R5	66.8	8.8	4.6	2.9	2.7	1.4	0.03	0.08	2.62	1.1	0.01	0.05	9.67	63.55
B-1458	7	8	R6	45.1	20.3	11.8	1.7	3.9	2.3	0.12	0.05	3.49	0.73	0.01	0.05	9.79	34.65
B-1459	8	9	R6	57.2	16.5	8.3	2.9	1.1	0.96	0.04	0.08	2.5	0.92	0.01	0.07	9.58	43.69
B-1460	9	10	R7	35.2	29	19.2	1.5	0.58	0.5	0.04	0.06	2.4	0.57	0.01	0.04	11.01	19.22
B-1461	10	11	R7	33.8	29.5	20.1	1.1	1	0.57	0.03	0.05	2.31	0.55	0.01	0.04	11.39	18.52
B-1462	11	12	R7	22.2	35.2	28.3	0.61	0.37	0.2	0.09	0.04	0.89	0.38	0.01	0.03	11.99	10.05
B-1463	12	13	R7	22.3	34.3	28.6	0.79	0.6	0.25	0.12	0.04	0.96	0.35	0.01	0.03	12.14	10.34
B-1464	13	14	R8	13.2	39	34.2	0.58	0.35	0.15	0.36	0.03	0.27	0.22	0.01	0.02	12.9	5.51

Unit abbreviations: R1: pisolitic topsoil, R2: lateritic duricrust; R3: transition zone; R5: ochre saprolite; R6: ferruginous saprolite; R7: green saprolite; R8: saprock: U1: ultramafic bedrock.

Appendix	8.3: Chemi	cal compos	sition of the later	ite profile	of drillco	re SFDD	-041.										
						Dri	llcore: SF	DD-041									
Sample ID	From (m)	To (m)	Lithology Code	Fe ₂ O ₃	SiO_2	MgO	Cr_2O_3	Al_2O_3	TiO ₂	CaO	Co	Ni	MnO	Cu	P_2O_5	LOI	UMIA
SF-912	0	1	R1	66.1	11.6	0.76	4.34	6.49	2.49	0.11	0.12	0.33	0.82	0.01	0.18	4.64	70.25
SF-914	1	2	R1	66.05	11.19	0.76	4.28	7.29	2.45	0.08	0.13	0.32	0.85	0.01	0.14	4.07	71.35
SF-915	2	2.75	R1	65.98	10.89	0.74	4.64	6.57	2.52	0.14	0.15	0.36	0.96	0.01	0.14	4.46	71.5
SF-916	2.75	3.5	R1	69.1	9.24	0.63	3.83	5.6	2.25	0.1	0.15	0.44	1.09	0.01	0.16	5.65	74.97
SF-6541	3.5	4.5	R3	68.71	8.75	0.85	4.12	4.1	2.41	0.2	0.13	0.61	0.88	0.01	0.12	6.57	74.42
SF-8011	4.5	5.15	R5	73.9	6.06	1	3.24	2.3	1.32	0.07	0.11	1.4	1.04	0.01	0.2	8.13	79.7
SF-8088	5.15	5.8	R5	45.63	19.32	12.37	1.91	5.96	1.48	0.05	0.04	3.11	0.7	0.01	0.15	9.7	36.75
SF-4974	5.8	6.3	R6	67.91	9.74	3.48	2.55	1.72	0.91	0.04	0.08	2.09	1.11	0.01	0.27	8.57	64.34
SF-5053	6.3	7.3	R6	44.58	26.45	11.8	2.18	1.71	0.77	0.19	0.08	1.44	0.8	0.01	0.17	9.29	29.18
SF-5861	7.3	8.3	R7	17.93	41.35	29.87	0.8	0.01	0.11	0.47	0.03	0.55	0.3	0.01	0.03	10.7	7.29
SF-2134	8.3	9.3	R8	12.6	45.66	30.96	0.67	0.01	0.11	0.77	0.03	0.25	0.21	0.01	0.01	10.27	4.91
SF-2145	9.3	10.3	R8	12.74	42.51	33.1	0.56	0.17	0.15	0.58	0.02	0.21	0.25	0.01	0.03	11.16	5.09
SF-3219	10.3	11.05	R8	11.23	43.3	32.54	0.58	0.17	0.2	1.74	0.02	0.16	0.21	0.01	0.04	10.7	4.54

Unit abbreviations: R1: pisolitic topsoil, R2: lateritic duricrust; R3: transition zone; R5: ochre saprolite; R6: ferruginous saprolite; R7: green saprolite; R8: saprock: U1: ultramafic bedrock.

Mineralogy and geochemistry of Ni and Co in lateritic profiles

Appendix	8.4: Chem	ical comp	position of the la	terite prof	ile of dril	lcore SFI	DD-003.										
						D	rillcore: S	SFDD-003	3								
Sample	From	То	Lithology	Fe ₂ O ₂	SiO	ΜσΟ	Cr ₂ O ₂	Al ₂ O ₂	TiO	CaO	Co	Ni	MnO	Cu	P2OF	LOI	UMIA
ID	(m)	(m)	Code	10203	5102	mgo	01203	111203	1102	Cuo	00	1.1	millo	Cu	1205	DOI	CIMIT
SF-56	0	0.5	R1	51.62	25.11	0.93	5.38	5.94	2.83	0.36	0.05	0.19	0.34	0.01	0.19	6.54	47.72
SF-57	0.5	1.3	R2	60.38	12.15	0.57	3.5	7.08	2.18	0.11	0.17	0.47	3.13	0.01	0.14	8.37	68.59
SF-58	1.3	2	R2	64.56	11	0.73	2.7	5.63	2.27	0.15	0.13	0.65	2.8	0.01	0.17	8.58	70.44
SF-3754	2	3	R3	46.3	33.15	1.66	3.44	4.62	2.13	0.11	0.06	0.68	1.17	0.01	0.17	6.06	37.22
SF-3755	3	4	R3	37.37	43.12	3.62	2.11	3.67	1.57	0.06	0.04	0.76	0.62	0.01	0.15	5.89	25.95
SF-3219	4	5	R6	48.74	36.93	2.43	1.88	1.36	0.68	0.01	0.06	0.74	0.77	0.01	0.19	6.08	32.39
SF-3755	5	6	R7	17.57	63.3	8.82	0.75	2.27	0.94	0.09	0.02	0.45	0.25	0.02	0.06	5.07	9.93
SF-3929	6	7	R7	16.4	49.08	22.76	0.89	0.25	0.25	0.01	0.02	0.26	0.29	0.01	0.05	8.9	7.13
SF-3930	7	8	R7	12.74	50.55	24.21	0.46	1.29	0.64	0.24	0.01	0.26	0.21	0.02	0.06	9.12	6.3
SF-4126	8	9	R7	14.33	66.16	10.7	0.42	2.09	0.79	0.18	0.02	0.29	0.22	0.03	0.04	5.29	7.92
SF-4127	9	10	R7	9.98	59.22	17.7	0.27	2.7	1.13	0.53	0.01	0.13	0.15	0.02	0.18	7.41	6.47
SF-4031	10	10.6	R7	9.51	50.31	22.42	0.14	4.84	1.8	1.17	-	0.08	0.12	0.02	0.39	8.6	8.18
SF-3543	10.6	11.5	R8	14.35	40.74	31.46	0.55	0.16	0.17	0.01	0.02	0.19	0.24	0.01	0.03	11.58	5.93
SF-3434	11.5	12.5	R8	13.49	43.23	30.68	0.41	0.19	0.14	0.06	0.02	0.19	0.23	0.01	0.09	10.16	5.55
SF-5408	12.5	13.5	R8	6.49	61.06	21.56	0.2	0.51	0.07	0.04	-	0.1	0.14	0.02	0.16	7.58	2.97

Unit abbreviations: R1: pisolitic topsoil, R2: lateritic duricrust; R3: transition zone; R5: ochre saprolite; R6: ferruginous saprolite; R7: green saprolite; R8: saprock: U1: ultramafic bedrock. Notes: - =not detected.

Mineralogy and geochemistry of Ni and Co in lateritic profiles

Appendix	8.5: Chem	ical comp	osition of the la	terite profi	ile of dril	lcore SFI	DD-017.										
						Di	rillcore: S	FDD-017	7								
Sample ID	From (m)	To (m)	Lithology Code	Fe ₂ O ₃	SiO ₂	MgO	Cr_2O_3	Al_2O_3	TiO ₂	CaO	Co	Ni	MnO	Cu	P_2O_5	LOI	UMIA
SF-352	0	1.1	R1	62.96	13.09	1.32	6.03	6.07	2.53	0.11	0.07	0.44	0.88	0.01	0.11	4.34	65.47
SF-353	1.1	2.1	R1	64.4	12.26	1.26	7.17	6.47	2.64	0.04	0.07	0.42	0.88	0.01	0.09	3.09	67.54
SF-358	2.1	3.1	R1	64.29	11.73	1.21	6.58	6.24	2.65	0.04	0.08	0.39	0.88	0.01	0.07	3.28	68.32
SF-359	3.1	4.1	R1	64.61	11.4	1.16	6.22	6.22	2.65	0.03	0.08	0.44	0.98	0.01	0.07	3.44	69.05
SF-360	4.1	5.1	R1	64.33	11.66	1.61	5.82	5.26	2.42	0.03	0.08	0.86	0.99	0.01	0.07	5	66.9
SF-4820	5.1	6	R3	52.84	18.07	5.09	4.14	4.57	2.12	0.01	0.07	2.48	0.89	0.01	0.06	8.24	47.85
SF-6254	6	7	R5	59.44	15.65	3.4	4.58	1.95	0.93	0.02	0.07	1.95	1.11	0.01	0.14	9.26	53.59
SF-6277	7	7.7	R5	61.97	11.58	3.7	5	1.41	0.93	0.02	0.08	2.33	1.12	0.01	0.15	9.71	58.85
SF-6234	7.7	8.7	R7	31.76	35.29	12.45	1.89	4.72	1.99	0.47	0.04	1.86	0.52	0.01	0.06	10.52	22.61
SF-5834	8.7	9.5	R7	17.43	44.68	16.36	0.51	5.53	3.3	0.92	0.02	1.68	0.29	0.01	0.21	10.63	13.73
SF-5980	9.5	10.3	R7	16.64	50.52	20.75	1.15	0.96	0.47	0.07	0.02	0.96	0.31	0.01	0.05	10.07	7.94
SF-6458	10.3	11.2	R7	13.72	46.56	27.79	0.83	0.63	0.3	0.04	0.02	0.88	0.23	0.01	0.05	11.08	6.05
SF-6114	11.2	12.2	R8	10.32	44.95	33.91	0.66	0.45	0.19	0.14	0.01	0.22	0.18	0.01	0.06	11.18	4.25
SF-5820	12.2	13.2	R8	10.34	47.82	28.21	0.57	1.44	0.56	0.4	-	0.16	0.16	0.01	0.17	12.45	5.31
SF-6234	13.2	14	R8	9.43	44.43	35.11	0.76	0.01	0.1	0.2	0.01	0.18	0.17	0.01	0.03	12	3.54
SF-5834	14	14.5	R8	9.37	47.24	32.23	0.57	0.46	0.19	0.05	0.01	0.15	0.15	0.01	0.05	11.89	3.93
SF-5630	14.5	15.2	U1	8.95	40.3	38.34	0.68	0.01	0.1	0.86	0.01	0.18	0.16	0.01	0.03	12.73	3.34
SF-5615	15.2	15.9	U1	9.55	37.27	39.62	0.52	0.01	0.06	0.91	-	0.16	0.15	0.01	0.02	12.81	3.6

Unit abbreviations: R1: pisolitic topsoil, R2: lateritic duricrust; R3: transition zone; R5: ochre saprolite; R6: ferruginous saprolite; R7: green saprolite; R8: saprock: U1: ultramafic bedrock. Notes: - = not detected.

Appendix	8.6: Chem	nical comp	osition of the lat	erite profi	le of dri	llcore SF	DD-308.										
						D	rillcore: S	FDD-308	3								
Sample ID	From (m)	To (m)	Lithology Code	Fe ₂ O ₃	SiO ₂	MgO	Cr ₂ O ₃	Al ₂ O ₃	TiO ₂	CaO	Co	Ni	MnO	Cu	P_2O_5	LOI	UMIA
SF-3188	0	1	R1	60.8	18.3	1.2	7.1	5.5	2.3	0.03	0.16	0.36	0.63	0.01	0.08	3.81	57.59
SF-3189	1	2	R1	62	17.8	1.1	6.8	6	2.2	0.02	0.16	0.35	0.66	0.01	0.07	2.89	59.14
SF-3190	2	3	R1	61	16.8	0.96	6.1	6.6	2	0.01	0.22	0.45	1.4	0.01	0.07	3.9	60.77
SF-3191	3	4	R1	64.4	14.2	0.75	4.8	5.6	2.1	0.01	0.21	0.67	1.8	0.01	0.07	5.45	65.21
SF-3192	4	4.5	R1	64.8	12.3	0.59	3.6	5.2	2.4	0.02	0.19	0.95	2.5	0.01	0.06	7.22	68.42
SF-3193	4.5	5	R3	58.2	16.8	0.9	3.1	7.6	5.7	0.01	0.12	0.65	0.92	0.01	0.06	6	60.67
SF-6177	5	5.6	R6	50.9	19.3	2	2.4	8.8	7.5	0.01	0.09	1.08	0.79	0.01	0.05	7.31	54.04
SF-6254	5.6	6.21	R6	52.9	20.4	2.1	2.3	6.8	5.5	0.02	0.1	1.29	0.87	0.01	0.05	7.86	51.86
SF-6277	6.21	7	R6	50.8	24	3.2	1.5	4.7	3.9	0.03	0.07	1.85	0.77	0.01	0.04	9.38	44.3
SF-4098	7	8	R7	32.7	36	7.9	1.4	4.2	3.7	1.9	0.06	1.7	0.6	0.01	0.02	9.68	24.7
SF-4250	8	9	R7	22.3	40.9	14.8	0.66	3	2.8	5.4	0.03	1.44	0.4	0.01	0.01	9.5	14.63
SF-5021	9	10	R8	8	49.1	16.8	0.29	1.9	1.6	16.2	0.02	0.78	0.14	0.01	0.01	3.97	5.76
SF-5022	10	11	R8	8.1	49.3	16.6	0.26	1.8	1.4	16.8	0.01	0.67	0.13	0.01	0.01	3.48	5.72
SF-4973	11	12	R8	11.9	47.4	18.1	0.3	1.2	1	13.1	0.03	0.62	0.2	0.01	0.01	5.06	6.81
SF-4974	12	13	R8	17.4	50.4	17.3	0.5	1.1	0.89	4.7	0.04	0.88	0.34	0.01	0.02	7.58	8.88
SF-5053	13	14	R8	16.7	42	20.8	0.53	1.3	1.2	7.7	0.03	0.78	0.29	0.01	0.01	7.96	9.12
SF-5180	14	15	R8	12	49.3	19.2	0.35	1.3	1.1	9.2	0.03	0.61	0.2	0.01	0.01	6.57	6.66
SF-5200	15	16	R8	7.4	51.8	17.1	0.28	1.5	1.2	18.4	0.02	0.22	0.11	0.01	0.02	2.64	4.9
SF-5351	16	17	R8	9.9	51	20.1	0.35	1.1	0.96	10.8	0.02	0.35	0.17	0.01	0.01	5.89	5.38
SF-5455	17	18	R8	8.9	55.5	16.8	0.24	1	0.87	12	0.02	0.24	0.16	0.01	0.01	4.28	4.9
SF-5529	18	19	R8	9.6	52.1	19.6	0.23	1	0.89	12.6	0.02	0.14	0.16	0.01	0.01	4.94	5.15
SF-5630	19	19.55	R8	13.8	43.4	21.2	0.28	0.88	0.81	11.4	0.03	0.18	0.22	0.01	0.01	6.27	7.29
SF-5615	19.55	20.5	R8	5.8	79.4	8	0.08	0.48	0.32	1.2	0.04	0.16	0.09	0.01	0.07	3.38	2.73

Unit abbreviations: R1: pisolitic topsoil, R2: lateritic duricrust; R3: transition zone; R5: ochre saprolite; R6: ferruginous saprolite; R7: green saprolite; R8: saprock: U1: ultramafic bedrock.

Appendix 8.7: Summary of the PCA	A perform	ed on the	e full da	taset.											
	Summary PCA														
	PC1	PC2	PC3	PC4	PC5	PC6	PC7	PC8	PC9	PC10	PC11				
Standard deviation	2.40	1.46	0.88	0.76	0.67	0.64	0.60	0.46	0.43	0.31	0.27				
Proportion of Variance	0.52	0.19	0.07	0.05	0.04	0.04	0.03	0.02	0.02	0.01	0.01				
Cumulative Proportion	0.52	0.72	0.79	0.84	0.88	0.92	0.95	0.95	0.98	0.99	1.00				

Appendix 8.9: Summary of the PCA performed on the isolated variables.

	Summar	y PCA				
	PC1	PC2	PC3	PC4	PC5	PC6
Standard deviation	2.00	0.92	0.65	0.62	0.49	0.34
Proportion of Variance	0.67	0.14	0.07	0.06	0.04	0.02
Cumulative Proportion	0.67	0.81	0.88	0.94	0.98	1.00

	Bedro	ck (U1, U2,	U3)				Saprock ((R8)						Green saprol	ite (R7)	
N = 200	Factor1	Factor2	Factor3	Uniqueness	N = 3382	Factor1	Factor2	Factor3	Factor4	Uniqueness	N = 2121	Factor1	Factor2	Factor3	Factor4	Uniqueness
MnO	0.9		0.38	0.02	MnO	0.92		-0.22		0.11	MnO	0.88				0.17
Fe ₂ O ₃	0.9		0.38	0.01	Fe ₂ O ₃	0.9	0.29	-0.22		0.05	Fe ₂ O ₃	0.91	0.34			0.03
Cr ₂ O ₃	0.87			0.14	Ni	0.54				0.67	Cr ₂ O ₃	0.56	-0.28			0.58
Co	0.76			0.34	Al ₂ O ₃		0.78			0.34	Co	0.69				0.49
Al ₂ O ₃		0.93		0.04	TiO ₂		0.9			0.13	Ni	0.54				0.64
MgO	-0.68	-0.68		0	SiO ₂			0.89		0.2	Al ₂ O ₃		0.92			0.16
TiO ₂		0.96		0	MgO	-0.21	-0.53	-0.66	-0.48	0	MgO	-0.49	-0.64	0.53	-0.25	0
P_2O_5		0.89		0.19	CaO	-0.2	0.45		0.87	0	TiO ₂		0.86			0.24
CaO		0.62		0.57	P ₂ O ₅		0.36			0.87	SiO ₂	-0.31		-0.93		0
SiO ₂	-0.41		-0.83	0.14	Cr ₂ O ₃	0.2				0.91	CaO	-0.3			0.93	0
Ni	0.39			0.84	Co	0.49				0.72	P ₂ O ₅		0.35			0.85
SS loadings	3.87	3.52	1.3		SS loadings	2.33	2.16	1.36	1.14		SS loadings	3.11	2.4	1.28	1.03	
Proportion Var	0.35	0.32	0.12		Proportion Var	0.21	0.2	0.12	0.1		Proportion Var	0.28	0.22	0.12	0.09	
Cumulative Var	0.35	0.67	0.79		Cumulative Var	0.21	0.41	0.53	0.64		Cumulative Var	0.28	0.5	0.62	0.71	
p-value	2.63E-33				p-value	0					p-value	3.30E-261				

Appendix 8.10: Results of the factor analysis after Varimax rotation for the bedrock, saprock and green saprolite units.

	Fern	iginous sapr	olite (R6)				0	chre saprolit	te (R5)						Silcrete	(R4)	
N = 745	Factor1	Factor2	Factor3	Factor4	Uniqueness	N = 171	Factor1	Factor2	Factor3	Factor4	Uniqueness	N = 433	Factor1	Factor2	Factor3	Factor4	Uniqueness
Al ₂ O ₃	0.69		0.27	0.65	0	SiO ₂	-0.73	-0.34	-0.23	-0.54	0	MnO	0.85		0.22		0.22
TiO ₂	0.97		0.24		0	MgO	-0.72			0.53	0.15	Fe ₂ O ₃	0.92		0.35		0.03
MgO	-0.56	-0.64	0.35	-0.37	0.01	MnO	0.7				0.47	Cr ₂ O ₃	0.72				0.43
MnO		0.54	0.2		0.64	Fe ₂ O ₃	0.93				0	Ni	0.56				0.67
Fe ₂ O ₃	0.3	0.78	0.51		0.03	Co	0.61		0.43		0.42	SiO ₂	-0.32	0.94			0
Co		0.63			0.59	Al ₂ O ₃		0.92			0.13	MgO		-0.94			0.05
SiO ₂	-0.26		-0.96		0	TiO ₂		0.83			0.31	Al ₂ O ₃	0.32		0.85		0.16
P_2O_5	0.25				0.92	Cr ₂ O ₃	0.43		0.9		0	TiO ₂	0.27		0.87		0.16
CaO					0.98	Ni				0.53	0.7	P_2O_5				0.87	0.24
Cr ₂ O ₃	-0.5	0.48			0.5	P ₂ O ₅		0.28			0.91	CaO				0.98	0.04
Ni			0.47		0.73	CaO	-0.25				0.92	Co	0.46	0.36			0.66
SS loadings	2.25	1.99	1.72	0.62		SS loadings	3.06	1.79	1.15	0.98		SS loadings	2.92	1.96	1.74	1.72	
Proportion Var	0.2	0.18	0.16	0.06		Proportion Var	0.28	0.16	0.1	0.09		Proportion Var	0.27	0.18	0.16	0.16	
Cumulative Var	0.2	0.39	0.54	0.6		Cumulative Var	0.28	0.44	0.54	0.63		Cumulative Var	0.27	0.44	0.6	0.76	
p-value	1.04E-50					p-value	8.07E-07					p-value	3.13E-06				

Appendix 8.11: Results of the factor analysis after Varimax rotation for the ferriginous and ochre saprolite units and for the silcrete.

	Ti		Lateritic crust (R2)							Pisolitic topsoil (R1)								
N = 531	Factor1	Factor2	Factor3	Factor4	Uniqueness	N = 80	Factor1	Factor2	Factor3	Factor4	Uniqueness	N = 1846	Factor1	Factor2	Factor3	Factor4	Factor5	Uniqueness
SiO ₂	-0.96		-0.2		0	SiO_2	-0.84	-0.29		-0.44	0	SiO_2	-0.96					0
MnO	0.64		0.39	-0.21	0.4	MgO	-0.64		0.62		0.18	Fe ₂ O ₃	0.96		-0.22			0
Fe ₂ O ₃	0.92		0.25	-0.29	0	Fe ₂ O ₃	0.98				0	MgO		0.75			0.23	0.36
Al ₂ O ₃		0.88			0.2	MnO		0.98			0.01	CaO		0.52				0.68
TiO ₂		0.68			0.49	Co		0.7			0.47	Ni		0.64	-0.24	0.38		0.38
Co	0.23		0.95		0	Cr ₂ O ₃			0.57		0.65	Al ₂ O ₃		-0.58	0.73			0.11
MgO				0.91	0.05	Ni		0.4	0.52	-0.28	0.48	TiO ₂			0.63	-0.26		0.49
P ₂ O ₅		0.33			0.89	Al ₂ O ₃		0.21	-0.62	0.72	0	MnO				0.88		
CaO					0.92	TiO ₂				0.36	0.8	Cr ₂ O ₃		0.28	-0.37		0.88	0
Cr ₂ O ₃	0.3		0.48		0.64	P ₂ O ₅					0.96	P2O5						0.95
Ni	0.34	-0.3		0.33	0.68	CaO			0.41		0.79	Co			-0.28	0.45	0.27	0.65
SS loadings	2.52	1.59	1.44	1.17		SS loadings	2.24	1.87	1.57	0.96		SS loadings	1.97	1.68	1.34	1.24	0.95	
Proportion Var	0.23	0.14	0.13	0.11		Proportion Var	0.2	0.17	0.14	0.09		Proportion Var	0.18	0.15	0.12	0.11	0.09	
Cumulative Var	0.23	0.37	0.5	0.61		Cumulative Var	0.2	0.37	0.52	0.6		Cumulative Var	0.18	0.33	0.45	0.57	0.65	
p-value	4.45E-87					p-value	5.82E-05					p-value	3.02E-122					

Appendix 8.12: Results of the factor analysis after Varimax rotation for the transition zone, the lateritic crust and pisolitic topsoil.



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Appendix 8.13: Boxplots showing the mineral chemistry of pre-lateritic phases in the Santa Fe' laterite deposit (data are reported as wt%, except for Fo# expressed as absolute unit).



Appendix 8.14: Boxplots showing the mineral chemistry of supergene phases in the Santa Fe' laterite deposit (data are reported as wt%)

Chapter 9:

Summary and conclusions

In this thesis, the mineralogical and geochemical properties of two Ni-Co laterite deposits located in word-class, yet geologically contrasting, mining districts have been investigated. The results of each step of the present study have been discussed at the end of the previous chapters. Here is reported a summary and major outcomes of the research conducted on the studied deposits, their parent rocks, the laterite facies, the ore mineralogy, the genetic processes, as well as the metallurgical implications.

9.1 Metallogenetic and minerogenetic processes

Despite the Wingellina and Santa Fe' deposits are both classified as *oxide-type* laterites, they show several peculiarities different from each other and even do not fully match with the supposed characteristics of oxide-dominated ores.

Wingellina

The Wingellina laterite derives from the alteration of a subalkaline layered intrusion consisting of both mafic and ultramafic lithologies, where forsteritic olivine represents the main Ni and Co supplier (NiO and CoO = 0.38 wt%). Most of the orebody (approximately 70%) consists of Co- and Ni-bearing Fe- and Mn-oxy-hydroxides occurring in the oxide ore (chapter 3). However, the study carried out on the saprolite units (*chapters 5 and 6*) show that, contrary to most of oxide-dominated laterites worldwide, a conspicuous amount of the Ni resources is located also in association with phyllosilicates. The mineralogical and petrographic data presented in chapter 5 showed that the early stage of lateritization followed several distinct dynamics, that depended mostly on the variable nature of the parent rocks. In the gabbro-derived alteration profile the fo + opx/cpx + an + splassemblage was directly overprinted by minerals formed by supergene processes, during which correspond to replacive and pseudomorphic Nibearing nontronite and Fe-oxy-hydroxides formed from olivine, while as the alteration proceeded the dissolution of pyroxene led to the formation of Nibearing montmorillonite. Previous studies on laterites (e.g. Kadir et al., 2015), mentioned that during the formation of montmorillonite from the alteration of ultramafic-dominated lithologies an external Al supply from high T° fluids circulating in the country rocks is mandatory. However, at Wingellina the genesis of montmorillonite, which is the major Ni-bearing clay, can be rather explained by the occurrence in the bedrock of primary Al-rich phases (i.e. Ca-plagioclase) that are highly reactive to oxidative meteoric fluids. Moreover, the genesis of the above-mentioned saprolite from the alteration of the mafic units is also important in determining the distribution within the Wingellina ore-body of a low-grade mottled-clay unit, where kaolinite forming from the alteration of montmorillonite is the dominant phase. In the ultramafic protolith, prior to lateritization, the hydrothermal alteration overprinted the magmatic assemblage leading to the formation of massive serpentinite units consisting of barren polygonal lizardite-17, Ni-bearing chlorite IIb and dolomite. This assemblage indicates that at Wingellina, prior to lateritization and after the granulite facies metamorphism, the protolith experienced a mineralogical reset at a maximum temperature of 300 °C and relatively low pressures (< 1.0 GPa) (Evans, 2013). The hydrothermal process was followed by the formation of Ni-bearing lizardite and a Ni-bearing and Al-depleted smectite series (i.e. saponite \rightarrow ferrosaponite \rightarrow nontronite). The observed Ni distribution in Alpoor smectite clays is similar to that observed in world-class clay-silicates ore deposits (e.g. Murrin Murrin - Western Australia; Gaudin et al., 2004a,b), with Ni being mainly hosted in trioctahedral species due to their higher capability of retaining trioctahedral coordinated Ni clusters.

The data presented in *chapter 3*, *4* and *6* show that Mn-oxy-hydroxides are the main Co receptors in the Wingellina orebody, and have a multistage formation pathway. The early stage of Mn-oxy-hydroxides formation are observed in the gabbro-derived saprolite (*chapter 6*), where they are found as epigenetic phases replacing Al-rich phyllosilicates as kaolinite ans montmorillonite. This is consistent with previous studies (Nahon et al., 1989; Dzemua et al., 2013; Dublet et al., 2017), that discussed about the role of kaolinite in supplying the Al required for the genesis of stable Mn-phases in oxidative environment (i.e. lithiophorite-asbolane). However, in this study it is also shown that this process can also be favoured by montmorillonite, which is not only able to supply Al during ore formation

process, but also act has structural template favouring the nucleation of Mnoxy-hydroxides.

According to the micro to nano petrographic observations presented in *chapter 3*, a later generation of Mn-oxy-hydroxides (lateritic phase), comprehending transition metals(Al-Ni-Co)-poor and alkali and alkali earth metals(Ba and K)-rich phases as birnessite and romanechite, occurs as cryptocrystalline concretions. The latest stage (diagenetic phase) Mn-oxy-hydroxides were developed through the replacement of former Mn-phases: they belong to the lithiophorite-asbolane series. These oxy-hydroxides, representing the main Co carriers, are Al-enriched and show a general depletion of alkali and alkali earth metals. Similarly to other deposits (e.g. Nkamouna – Cameroon; Lambiv Dzeuma et al., 2013), at Wingellina the multistage formation of Mn-oxy-hydroxides is a primary factor in controlling the Co-endowment, as it results in the formation of more stable phases in oxidative environment, thus preventing the Co loss through its leaching by acidic meteoric waters.

The results obtained by geochemical proxies (UMIA index) coupled with core analysis (chapter 4), as well as the micro to nanometric studies of the clay assemblage (*chapter 5*) point out that at Wingellina a post-lateritization stage of alteration enhanced significant modifications of the original mineralogical and geochemical footprint of the weathering profile. In particular, the topmost section of the profile is capped by a thick unit enriched of late carbonates and silica cements, which formed through an increase of the evapotranspiration rates occurred due to the shift in the environmental conditions from mid-Miocene to the recent period as a result of climatic shift toward arid conditions. Furthermore, the aridity-driven post-formation processes caused the formation of Ni-rich interstratified clays (R0 talc - smectite and R0 chlorite - smectite), which before this study were only recognized in laterites that underwent to syn- and/or postlateritization hydrothermal processes (Christidis and Mitsis, 2006; Christidis and Skarpelis, 2010). The paragenesis of these phases, occurring at Wingellina either as replacement of former smectite clays or as fibrous aggregates in open spaces, suggests a different environment of formation characterized by more saline conditions similar to modern continental evaporitic environments, where alkaline brines drive the formation of authigenetic clays precipitated in association with dolocrete and silcrete.

Therefore, the genesis of Ni-rich clays in a post-laterite stage observed in the Wingellina deposit represents a new model for explaining the evolution of Ni-laterites in stable cratonic settings experiencing a post-lateritization aridity. This model can be seen as a counterpart of the "*per-descensum* fluid flow model" that describes the post-formation process of garnierite ores in deposits occurring in active terrains (e.g. Cluzel and Vigier, 2008; Villanova-de-Benavent et al., 2014).

The lithogeochemical study of the Wingellina profile (*chapter 4*) provided also insights on the deportment of critical elements during lateritization (REEs and Sc). As regards to REEs, a strong control of the parent rock nature during their enrichment has been observed. Overall, the highest, yet subeconomic, REEs grades ($\Sigma REEs = 890 \text{ ppm}$), were observed in the oxide zone of the profile developed over the mafic bedrock. In this section of the orebody, similar to Co, the vast majority of REEs anomalies are closely associated with the Mn-rich core interceptions, thus supporting the observation of previous studies where the potential of Mn-oxy-hydroxides as REEs scavengers has been proposed (Mongelli et al., 2015; Aiglsperger et al., 2016). On the other hand, in this study a high Ce speciation in the mottled-clay zones has been observed, which is consistent with the observation made in similar oxide-type ores (e.g. Moa Bay - Cuba; Aiglsperger et al., 2016), where a potential Ce adsorption into kaolinite was inferred. However, at Wingellina the geochemical signature of Ce, characterized by a close covariance with Al and P and with a decoupling with Si, indicates that its deportment might be locally controlled by the neoformation of LREE-Al-bearing phosphates (florencite-like), rather than by its uptaking in clay minerals. In the ultramafic-derived zones of the orebody, the detected lower REEs amount, coupled with other geochemical proxies (i.e. the lower La/Yb_{N(cho)} ratio, the conservative behaviour of Eu during weathering and the absence of Ce and Eu anomalies) suggest that the REEs enrichment is less effective. This may be due to their lower original content in the more primitive components of the magmatic suite, and to a more homogenous initial REEs-hosting mineralogy, which hampered the REEs fractionation during the supergene process. Similar to REEs, the Sc content detected in the Wingellina orebody is subeconomic when compared with Sc-endowed laterites (e.g. Syerston - Flemington, Australia; Chassé et al., 2016). The vast majority of the variance of Sc grades is explained with the metal association with the Fe-rich zones of the ore, therefore suggesting the uptaking of Sc^{3+} into neo-formed Fe-oxy-hydroxides. However, significant Sc anomalies (e.g. up to 140 ppm Sc) where also detected in the saprolite facies of the orebody, where Sc is covariant with Ni and Si, thus indicating that also smectite clays play a primary role in defining its distribution in laterite ores.

Santa Fe'

The Santa Fe deposit derived from an ultramafic-dominated alkaline intrusion where, as in Wingellina, forsteritic olivine is the main source for Ni (0.35 wt% NiO). However, the mineralogical and geochemical study of the Santa Fe' ore (chapter 8) highlighted distinctive features when compared to the Wingellina case as the low Co amount in olivine in the bedrock (0.03 wt% CoO), as well as the low Co grades detected in the orebody, and the unusual Co association with Cr. Similarly to Wingellina, the magmatic phases of the Santa Fe' bedrock are overprinted by a relatively low T° hydrothermal process leading to the formation of lizardite-1T after ferrognesian minerals, as well as to Ti/Al-oxides rich exsolution in perovskite (Chakhmouradian and Mitchell, 2000; Evans et al., 2013). However, the above process is overprinted by a Fe³⁺-rich spinels (ferritchromite) + Ni-rich chlorite + silica assemblage, which indicate that the pre-lateritic hydrothermal system evolved toward high T°, SiO₂saturation and oxidative conditions that are consistent with an alteration process occurred under retrograde amphibolite facies metamorphic conditions (Barnes and Roeder, 2001; Mellini et al., 2005; Arai et al., 2006; Akizawa and Arai, 2014). The onsent of the early supergene processes (Eocene to Oligocene, Braun, 1970) was characterized by conditions of oversaturation of silicic acid and led to the formation of the silcrete layers scattered thoughtout the profile and on dunite hilltops. The lateritic weathering sensu stricto (Miocene-Pliocene) led to the formation of Nienriched serpentine and skeletal goethite, with negligible smectite clays and Mn-oxy-hydroxides. As regards to Mn-oxy-hydroxides, in the Santa Fe' ore, these phases was solely found as epigenetic and scattered reprecement of Ni-bearing chlorite and show a significant depletion in Co when compared to Wingellina and to other Co-endowed laterites (e.g. Nkamouna -Cameroon; Lambiv Dzeuma et al., 2013).

9.2 The influence of the pre-lateritic history of the parent rock on the Co deportment

The significant differences in the Co deportment, as well as in the nature of the magmatic bedrock, between the Wingellina and the Santa Fe' deposits provided a profitable chance to draw a comparison between fertile and barren ore systems, and to assess the influence of the bedrock nature and of its pre-lateritic alteration history on the Co endowment in Ni-laterites. In the Wingellina case the bulk of the Co variance is explained by its association with Mn and thus to the Co enrichment during the lateritization process (chapter 4), while the multivariate analyses presented in chapter 8 have shown that in the Santa Fe' system most of the statistical distribution of Co is correlated with that of Cr. The Co-Cr association is mainly related to the significantly high Co-content (up to 1.70 CoO wt%) detected in magmatic and hydrothermal spinels (i.e. chromite and ferritchromite, respectively), which are residual phases inherited from the parent rock and are ubiquitous throughout the laterite profile. The contrasting Co behaviour observed between the studied deposits can be ascribed to the diverse behaviour of Co during the orthomagmatic stage and to their significant alteration histories. The significant difference in the Co concentration in the olivines occurring in the Wingellina and Santa Fe' deposits is mainly due to the diverse affinity of Co to various phases during the early stages of crystallization of ultramafic melts with distinct chemical affinity. In subalkaline (tholeiitic) melts, as those at the origin of the Wingellina bedrock, Co has a high partition coefficient with olivine (Kd up to 6.5; Mysen, 2007), whose alteration during chemical weathering supplied the whole Co, initially hosted in the parent rock, during the ore formation process. This ended with the formation of a Co-endowed profile, where is fixed in neo-formed phases (i.e. Mn-oxy-hydroxides through) a process that fits with the models of formation of lateritic ores proposed in the past (e.g. Freyssinet et al., 2005; Butt and Cluzel, 2013; Dublet et al., 2017). Conversely, in ultramafic melts with alkaline affinity, such as those originating the parent rock of Santa Fe', Co has a significant tendency to concentrate in olivine (Kd = 5.1; Villemant et al., 1981), but it can be also potentially incorporated in Cr-spinels (Kd = 4.7 - 8.3; Horn et al. 1994). As regards to the post-magmatic and prelateritic processes, the early alteration of the Santa Fe' ultramafic suite is similar to the alteration pathway observed in the ultramafic body at Wingellina, with a pervasive serpentinization involving ferromagnesian

minerals. This process, resulted in the formation of mesh-like serpentine, yet left unaltered the Cr-spinels. However, during a later hydrothermal stage under amphibolite facies conditions (temperature of fluids of approximately 500 °C, coupled with high SiO₂ and O₂ activity) the lizardite-1*T* + Cr-spinel suite was overprinted by the Fe³⁺-rich spinels (i.e. ferritchromite) + Nibearing chlorite + amphibole + Fe-Ni(Co)-sulfide assemblage. This process triggered a significant mineralogical and chemical reset of the primary spinels that enhanced the concentration of Co and other transition metals (i.e. Zn, Ni and Mn) in late-stage spinels. Moreover, a significant portion of the available Ni was concentrated in chlorite, which explains the poor Ni/Fe association observed through multivariate analyses. However, when supergene processes were superimposed on the pre-lateritic assemblage, the Co redistribution in resistate minerals led to a restricted Co availability during these secondary ore-forming processes that led to the development of Co-depleted alteration profiles.

9.3 The role of poorly- to non-crystalline phases in Ni-Co laterites

The XRPD-QPA and Automated SEM analyses presented in chapter 7 focused on the evaluation of the modal mineralogy and the metals deportment of the Wingellina mineralized facies led to conclude that these methods have both benefits and flaws; however, their joint application can be beneficial to the mineralogical evaluation of Ni-Co laterite ores with similar features as Wingellina. In detail, in the Mn-oxy-hydroxides-rich facies of the ore, representing the main target for the Co exploration, Rietveld-based XRPD-QPA methods, (which rely on the crystal structures of phases) encounter limitations mainly during the mineralogical discrimination between lithiophorite and asbolane and their intermediates. This is mainly due to the poor crystallinity of asbolane, which even in the most favourable cases where it gives rises to d_{hkl} peaks, the positions of the latter is very close to the peaks of lithiophorite making their discrimination quite challenging (Burlet and Vanbrabant, 2015). The XRPD-QPA evaluation can results either in overrating the lithiophorite amount at the expenses of asbolane or in the refinement of the asbolane amount as amorph. This might be an issue as, in general, nominal lithiophorite is barren, while asbolane-like phases can reach grades of up to 15 wt% Co. This could provide a misleading picture of the Co distribution in the mineralized samples and give rise to mismatches between the measured Co

by ICP-MS and the modelled Co by XRPD-QPA and EDS data. In this frame, Automated SEM analyses, based on the chemistry of the mineral entries, offered a breakthrough to bypass this problem by classifying Mnoxy-hydroxides based on the Al/(Ni+Co) ratio: a) lithiophorite (Al >10%, Ni <0.5%, Co <0.5%, Fe <0.5% and Mn 30-40%), b) lithiophorite-asbolane (Al 3-10%, Ni >10%, Co >2%, Fe <10% and Mn 25-40%) and c) asbolane (Al <2%, Ni >10%; Co >2%). Another relevant issue related to XRPD-QPA quantification of the Wingellina samples was observed during the analysis of the saprolite ores (i.e. smectite and serpentinite ore subtypes), where orebearing phases with a poor structural order as smectite clays are dominant. Like in the Mn-oxy-hydroxides case, during Automated SEM analyses the clay minerals classification was performed based on a chemical parameter, i.e. the Si/ Σ R ratio (Σ R = sum of the octahedral cations), which allowed the distrimination between smectite and serpentine phases. However, in the saprolite facies the efficiency of Automated SEM analyses was affected by the fine-grained textures of the ore, which caused mixed EDS spectra and thus produced a range of mixed-mineral classes.

9.4 Metallurgical implications

As shown in *chapters 5 and 6*, although in the Wingellina deposit most of the ore reserves are hosted in the oxide zone, a significant aliquot of Ni (approximately 30% of tonnage) is hosted in the clay-enriched saprolite, thus making this ore type a strategic asset for future explansion of the exploitable ore reserves. However, is has been shown that Ni is not equally distributed in the wide range of smectite clays species occurring at Wingellina. Contrasting trends of Ni speciation have been observed between the saprolites developing from the mafic and ultramafic bedrock. In particular, in the gabbro-derived saprolite, the Ni grade is high in the Fe-rich dioctahedral smectite members (i.e. Fe-montmorillonite). Conversely, in the serpentine-derived saprolite, high Ni grades has been observed in the Mgrich, trioctahedral smectites (i.e. saponite), while the Fe-rich dioctahedral counterpart (i.e. nontronite) is barren to very low-grade. Mano et al. (2019) has shown for the word-class Ni-smectite Niquelândia deposit (Brazil), that the rate of Ni recovery though Caron process when applied to clay-silicate ores is closely related with the chemistry of smectites and, in particular with their Fe content. This is due to the fact that Caron process recovers Ni by means of a reduction-roasting step, during which the ore is roasted at 750 °C

to produce a Ni(Co)-Fe metallic alloy (Rhamdhani et al., 2009). This means that low Fe smectites does not allow an effective formation process of Ni-Fe, which lead to significant low recoveries (10%). Therefore, in the case of Wingellina, whether the saprolite will be targeted as exploitable ore, the most amenable ore type will be that developed from the gabbro bedrock where Ni and Fe are jointly enriched in dioctahedral smectite clays. Conversely, the metallurgy of smectite clays derived from the serpentinite, where high Ni contents were observed in the Mg-rich, but Fe-poor species, will likely end up with uneconomic ore recoveries.

As regards to Co, the study conducted on the Santa Fe' deposit (*chapter 8*) has shown that its distribution in a laterite ore can be also controlled by its partitioning in spinel group minerals. Since that the metallurgical process applied to oxide ores (e.g. HPAL) are only effective in the digestion of Feand Mn-oxy-hydroxides and clay minerals, leaving behind a residuum consisting of refractory phases, among which spinels, this might be a problematic issue leading to low Co recoveries. The impact of the Co fixing in spinels at Santa Fe' has been estimated comparing the feed used for the metallurgical testworks, which underwent a spinel screening step via magnetic and heavy mineral separation, with the bulk chemistry of the mineralized facies of the Santa Fe' orebody. The results showed that up to 50% of the bulk Co was concentrated in the screened spinel fraction, which represents the refractory Co fraction of the ore that cannot be recovered when treated with conventional hydro- and pyrometallurgical methods.

Main conclusions

In conclusion, the mineralogical and geochemical study carried out on the Wingellina (Western Australia) and Santa Fe' (Brazil) deposits has increased the knowledge on the metallogenetic processes of oxide-type laterites. At the same time it has also significant implications for their exploration, mineralogical evaluation and processing route. The main findings defining the update on the state of the art are:

(i) The investigation on the nature of the the parent rock and of the climatic control on the genesis of Ni-rich clays suggests that post-formation minerogenetic process in the saprolite ores do not occur solely in garnieriterich concentrations, but also in deposits located in stable cratons where arid climate-derived associations are superimposed on lateritization-related assemblages;

(ii) The nanometric investigation carried out on samples from the saprolite zones of the Wingellina deposit has demonstrated that: i) Ni-rich clays can form after the alteration of chlorite, and ii) Co-bearing Mn-oxy-hydroxides can evolve from the weathering of smectite clays. The former point has been never described so far, even in world-class clay-silicate ores as Murrin Murrin or Niquelândia, where the surficial alteration overprints chlorite-bearing metamorphic assemblages. The detection of nanometric Co-bearing Mn-oxy-hydroxides substituting for montmorillonite demonstrates that Ni-and Al-bearing smectite clays can act similarly to kaolinite during the epigenetic formation of lithiophorite-like phases; it is therefore important to better define the Co targets in unconventional laterite facies;

(iii) The comparative study of the Co deportment between the Wingellina and Santa Fe' cases demonstrates that the Co endowment in laterite systems is strongly controlled by its behaviour during the orthomagmatic stage and by the eventual hydrothermal redistribution in resistate minerals (spinels). The concentration of Co in spinels has strong implications both in terms of exploration and of processing strategies. As regards to the former point, if considering that the Co enrichment in primary Cr-spinels might be significant in ultramafic alkaline systems, it is reasonable to suppose that Co is unlikely to become enriched in the laterites formed over alkaline intrusions in general. However, further studies on laterite ores developed over parent rocks similar to those of the the Santa Fe' massif are needed to refine this hypothesis. Moreover, since the Co enrichment in late-stage Fespinels is closely related to the formation of ferritchromite and Al-chlorite, these phases can be used as indicators of potentially refractory Co in laterite systems. Lastly, as the interpretation of the metallurgical testworks clearly indicates a downgrading of the Co grade due to the removal of the spinel fraction from the Santa Fe' feeds, great care must be paid to this issue during the economic evaluation of similar laterite systems.
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