



Article Evaluation of Sc Concentrations in Ni-Co Laterites Using Al as a Geochemical Proxy

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Abstract: Scandium (Sc) is used in several modern industrial applications. Recently, significant Sc concentrations (~100 ppm) were reported in some nickel-cobalt lateritic ores, where Sc may be valuably co-produced. However, Sc is typically not included in routine analyses of Ni-Co ores. This contribution examines the relevance of using routinely analysed elements as geochemical proxies for estimating Sc concentration and distribution. Three Ni-Co lateritic deposits from New Caledonia were investigated. In each deposit, Sc is well correlated with Al₂O₃. The slopes of deposit-scale Sc-Al₂O₃ regression lines are remarkably controlled by the composition of enstatite from the parent peridotite. In all deposits, maximum Sc enrichment occurs in the yellow limonite, above the highest Ni and Co enrichment zones. Sc- and Al-bearing crystalline goethite is predominant in the oxide-rich zones, though Sc shows a higher affinity for amorphous iron oxides than Al. We propose that, in already assayed Ni-Co lateritic ores, the concentration and distribution of Sc can be estimated from that of Al. Deposit-scale Sc-Al₂O₃ correlations may be determined after analysing a limited number of spatially and chemically representative samples. Therefore, mining operators may get a first-order evaluation of the Sc potential resource in Ni-Co lateritic deposits at low additional costs.

Keywords: scandium; laterite; Ni-laterite; sequential extraction; New Caledonia

1. Introduction

Scandium (Sc) is mainly used as a hardening additive to aluminium to form Al-Sc alloys for aerospace industries and high-quality sports equipment [1,2]. In addition, Sc is notably used in high-temperature lights, lasers, and ceramics manufacturing and finds promising applications in the development of Solid Oxide Fuel Cells (SOFCs). The global Sc supply and consumption remain marginal (~15 to 25 t/yr Sc₂O₃, [3]). Sc is solely recovered as a by-product through titanium, zirconium, uranium, cobalt, and nickel process streams. Nevertheless, the development of energy-saving technologies and Sc extraction techniques have raised interest in this metal. In the last decade, Sc-rich occurrences with economically attractive grades and tonnages have been identified in some oxide-rich laterites developed after mafic and ultramafic rocks [4–14]. There, Sc enrichment is largely residual and results from the intense leaching of mobile cations during the lateritisation of the parent rock. Scandium is, thus, trapped and concentrated in neo-formed goethite, and moderate remobilisation can occur during repeated stages of goethite dissolution-recrystallisation and transformation into hematite. The chemical speciation of Sc in laterites from Australia and the Philippines has been investigated using a combination of X-ray absorption nearedge structure (XANES) spectroscopy and sequential extractions [7,8,11]. These studies



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Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). further support the preferential affinity of Sc for goethite compared to hematite or smectite. However, the relative importance of adsorption and incorporation processes and the impact of goethite crystallinity in the formation of Sc-rich goethite zones remain debated. They may vary from one deposit to another. In New Caledonia, significant Sc concentrations were reported in several Ni-Co lateritic oxide ores [13,14]. There, maximum Sc grades reach ~100 ppm in the yellow limonite horizon. Although such concentrations are too low to be economically attractive as primary resources, Sc could be a valuable by-product of Ni and Co processing, provided that Sc-rich zones sufficiently overlap Ni- and Co-rich zones [13].

Scandium is, however, not routinely analysed during exploration and resource estimation of Ni-Co laterites. Consequently, mining operators do not evaluate the potential Sc resources hosted in Ni-Co lateritic ores. In contrast, Fe, Al, and Cr are routinely analysed. As suggested by previous investigations, they could serve as geochemical proxies for inferring the distribution of Sc concentrations in lateritic Ni-Co ores [13]. Although Fe is the predominant constituent of lateritic oxide ores with up to 80 wt% Fe₂O₃, Teitler et al. [13] suggested that Fe may be correlated to Sc only in the lower to intermediate sections of the lateritic profiles and that the Sc-Fe₂O₃ correlation is usually not valid in the Sc-rich, yellow limonite horizon. In contrast, Sc is better correlated with Al in all the facies of the lateritic profiles, except for the uppermost ferruginous duricrust. The similar distribution patterns of Sc and Al in nickel laterites may result from a similar behaviour during weathering. Indeed, as for Sc, Al is mostly immobile during lateritic weathering though it can be, to some extent, expelled from iron oxides-oxyhydroxides during repeated stages of dissolution-recrystallisation [6,13].

Nevertheless, the Sc-Al₂O₃ correlation proposed by Teitler et al. [13], based on the combined analysis of individual vertical profiles from several deposits, shows significant dispersion and does not assess how reliable the Sc-Al₂O₃ proxy is at the deposit scale. In this contribution, we discuss the relevance of the Sc-Al₂O₃, Sc-Fe₂O₃ and Sc-Cr₂O₃ correlations at the deposit scale in three Ni-Co deposits from the Koniambo, Cap Bocage, and Tiébaghi massifs, New Caledonia, based on the geochemical analysis of spatially and lithologically representative samples from each deposit. Using laser ablation inductively coupled mass spectroscopy (LA-ICP-MS), we then examine the dependency of bedrock mineral compositions on the Sc-Al₂O₃ regression coefficients and the variability of Al and Sc contents in secondary-formed minerals. Third, we conduct selective chemical leaching on some Sc-bearing samples to provide further insights into the speciation of Sc in the investigated deposits. These results are used to discuss the potential of the Al proxy for the evaluation of Sc concentrations and distribution in peridotite-hosted laterites in the perspective of Ni-Co-Sc co-valorisation.

2. Regional Geology

The "Grande Terre" island of New Caledonia (Figure 1a) consists of a 300 km long allochthonous peridotite ophiolite referred to as the "Peridotite Nappe". The Peridotite Nappe, formed at ca. 35 Ma [15–17], is primarily composed of harzburgite locally interlayered with dunite, except in the northernmost klippes where lherzolite dominates [18]. The extensive lateritisation of the peridotite ophiolite led to the formation of world-class Ni-Co(-Sc) lateritic resources representing about 10% of the world's nickel reserves [19]. The development of Ni-Co(-Sc) laterites in New Caledonia resulted in the formation of two main ore types, (i) the saprolite ore dominated by Ni-bearing phyllosilicates and (ii) the oxide ore dominated by Ni-bearing ochreous goethite [20–27]. The Ni-rich (>2.0 wt% Ni) saprolite ore reserves are rapidly being depleted as they have been actively mined since the late 19th century. Lower-grade (1.0-2.0% Ni) oxide ore ("limonite") reserves will therefore represent the bulk of Ni reserves of New Caledonia in the future. Moreover, Ni oxide ores often yield elevated Co (>2000 ppm) and Sc (60-100 ppm) concentrations adding significant value to the ore (Figure 1b, [6,13]). Maximum Co concentrations (>2000 ppm) typically occur at the interface between saprolite and limonite (referred to as transition zone), where Co is mainly associated with Mn-oxides. Upwards in the limonitic horizons, Co concentrations decrease, partially scavenged and trapped in ochreous goethite [28]. Maximum Sc grades are reached in the yellow limonite horizon (Figure 1b). Therefore, Ni-, Co-, and Sc-rich zones in limonite may partly overlap, and the degree of such overlap is critical for co-valorising Ni, Co, and Sc from lateritic Ni ores [6,13].



Figure 1. (a) Geological map of New Caledonia and location of the investigated mining massifs. Modified from Maurizot and Vendé-Leclerc [29]. (b) Geochemical evolution along a typical Ni-lateritic profile in New Caledonia (modified from Bailly et al. [6]).

3. Methodology

3.1. Sampling Strategy

Sampling was conducted in multiple locations within the investigated deposits, along several drillcores and pit walls, encompassing the diversity of representative lithofacies. The objective was to check whether Sc-Al₂O₃ correlations may be generalised at the deposit scale. At the Ma-Oui deposit (Koniambo massif), 39 samples were collected along six drillcores and one pit wall profile (Figure 2a). At the Coquette Red tenement (Cap Bocage massif), 27 samples were collected along two drillcores and one outcrop profile (Figure 2b). At the East Alpha deposit (Tiébaghi massif), 48 samples were collected along nine pit wall profiles, including three samples of saprolitised gabbro (Figure 2c).



Number of samples collected

Figure 2. Outline of the investigated deposits and location of collected samples. (**a**) Ma-Oui deposit (Koniambo massif). (**b**) Coquette Red tenement (Cap Bocage massif). (**c**) East Alpha deposit (Tiébaghi massif).

(East Alpha)

3.2. Analytical Strategy

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Among the 114 samples collected for whole-rock geochemical analysis, 49 samples (batch 1) were analysed at the SARM analytical service of the CRPG (France), and 65 samples (batch 2) were analysed at the NILAB laboratory (New Caledonia). Batch 1 sample pulps were analysed for whole-rock major- and trace-element geochemistry using the procedure of Carignan et al. [30]. Major element oxides and Sc were analysed using an iCap6500 ICP-OES with Li borate fusion. Trace elements were analysed using an iCap6500 ICP-OES with Li borate fusion. Trace elements were analysed using an iCap6500 icp-OES with Li borate fusion followed by nitric acid digestion. Analytical accuracy (2 s standard deviation) lies within the typical uncertainty of the analytical data for both major element oxides and trace elements, which is less than 1% for major oxides and less than 5% for most trace elements. Batch 2 samples were analysed for major elements, Ni, Co, and Sc, using an Axios FAST Wavelength Dispersive XRF spectrometer with LiF200 crystal. The detection limit for Sc is 12 ppm, and analytical accuracy is less than 7% in the 50–120 ppm concentration range. The relative analytical precision between the two datasets, tested by duplicating the analysis of three samples in both laboratories, is better than 2% for Sc.

Principal Component Analysis (PCA) was conducted on whole-rock geochemical data using the atomic weight percentages of Mg, Al, Si, Sc, Cr, Mn, Fe, Co, Ni, and LOI following centred log-ratio (CLR) transformation to avoid spurious proportionality and boundary effects [31,32]. PCA consists in transforming a multivariate dataset—here, each elemental concentration represents a variable—into a lower-dimensional dataset while preserving as much of the data's variation as possible. The dataset is projected into a new coordinate system based on the principal components, which are orthogonal linear combinations of original variables corresponding to the eigenvectors of the covariance matrix. The advantage of such analysis is that mineral stoichiometry likely controls principal components, providing a more realistic representation of geological variability. Centred log-ratio transformation of Mg, Al, Si, Sc, Cr, Mn, Fe, Co, and Ni concentrations and LOI performed before PCA has the benefit of removing the proportionality effect (i.e., the predominance of major elements on the geochemical variability) and the boundary effects (negative bias and spurious correlation effect [33]). Saprolitised gabbro samples from East Alpha were excluded from PCA calculations to better explore the impact of weathering

on peridotite bedrocks alone. In a covariance biplot of log-ratio transformed data, a short distance between the ray tips of two variables (i.e., coincident rays) indicates that these variables are highly proportional [32].

Sixteen polished, thin sections were prepared and examined using reflected/transmitted light and scanning electron microscopy with a JEOL JSM7600F at Georessources Laboratory and SCMEM. In situ mineral chemistry analysis for major/minor elements (Mg, Al, Si, Ca, Cr, Mn, Fe, Co, and Ni) was conducted using a CAMECA SX100 electron probe micro analyser (EPMA) at the SCMEM with typical beam conditions of 15 kV and 10 nA. In situ analysis for Sc and minor/trace elements was conducted using LA-ICP-MS (193 nm MicroLas ArF Excimer coupled with Agilent 7500c quadrupole ICP-MS). LA-ICP-MS analysis of Sc and Al in silicates and phyllosilicates was performed with the NIST610 reference standard using Si concentration obtained from EPMA as the internal standard. For oxides, analysis was performed with the StdGoe 1.1 pelletised goethite standard developed and validated by Ulrich et al. [14] and using Fe concentration as an internal standard. Reference standards were analysed before and after every 15 ablations conducted on samples. Before each analysis, the background signal, or gas blank, was measured for 25 s. Ablation time, spot sizes, and laser pulse frequency were 45 s, 60 μ m, and 5 Hz, respectively. Data processing was conducted using the SILLS program [34]. The detection limit was below 1 ppm for most trace elements.

Sequential extractions were performed at the CEREGE laboratory on seven Sc-bearing samples from Coquette Red and East Alpha, encompassing earthy saprolite, smectitic saprolite, and yellow and red limonite facies. Sequential extractions were not conducted on Ma-Oui samples as their mineralogy and chemistry are similar to that of Coquette Red samples. Four reagents were successively used to extract major and trace elements selectively: (i) ultrapure water for easily soluble elements; (ii) 0.1 mol·L⁻¹ hydroxylamine hydrochloride NH₂OH-HCl at pH = 3.5, which is particularly efficient and selective for manganiferous phases; (iii) 0.2 mol·L⁻¹ ammonium oxalate (NH₄)₂C₂O₄ at pH = 3 for amorphous and poorly crystallised iron oxides; and (iv) citrate-bicarbonate-dithionite Na₂S₂O₄ (22% Na-citrate and 1 g Na-dithionite) for well-crystallised iron oxides [6]. For each extraction, approximately 1 g of sample powder (<50 µm) was weighed into 50 mL of reagent solution and agitated for 76 h. Each tube was then centrifugated at 10,000 rpm, and the supernatant liquid was filtered at 0.2 µm before ICP-AES analysis. The residue was then rinsed with Milli-Q[®] water and used for subsequent extraction after re-suspension.

4. Lithofacies and Mineral Assemblages

The investigated Ni-Co deposits exhibit a continuum of alteration facies with specific mineral assemblages and textures. At Ma-Oui, moderately serpentinised harzburgite is the predominant parent rock of Ni-Co laterites (Figures 3a and 4). At Coquette Red, the laterite is developed both on harzburgite and dunite. At East Alpha, lherzolite dominates over harzburgite, although the intensive serpentinisation of the peridotite complicates its univocal recognition in the field. In the saprock, weathering initiates through the progression of the mantle silicate alteration front, marked by the onset of forsterite and enstatite hydrolysis and the development of Ni-rich (up to 15-20 wt% Ni), greenish talc-like (kerolite) veins that root into the unweathered peridotite (Figure 4). Serpentine (mostly lizardite) is preserved from dissolution in the saprock. The evolution from the saprock to the saprolite, wherein weathering is more pronounced but remains isovolumetric, is characterised by the complete disappearance of mantle silicate and the partial replacement of serpentines by goethite. In contrast, at East Alpha, smectite extensively develops from primary silicates and serpentine (Figures 3b and 4). It remains preserved throughout most of the saprolite until it is eventually replaced by ochreous goethite. The interface between the saprolite and the overlying limonite, referred to as the transition zone, is marked by the progressive accumulation of Mn-Co-Ni oxides (lithiophorite, asbolane). Upwards, the transition zone evolves into the yellow limonite, wherein ochreous goethite predominates. The yellow limonite then grades into the red limonite, wherein hematite forms at the

expense of ochreous goethite resulting in a mineral assemblage dominated by goethite but containing significant amounts (>5 vol%) of hematite (Figure 4). Lateritic profiles are capped by a ferruginous duricrust that is either directly developed after the underlying limonite or derived from the ferrugination of transported material (Figures 3b–d and 4). Following Anand et al. [35], the term duricrust describes regolith materials cemented by Fe, irrespective of the substrate origin. When it is residual, the iron-cemented material is called a lateritic residuum, and when it is formed and indurated in a transported cover, ferricrete. Lateritic residuum exhibits, at the microscopic scale, some locally preserved textural relics (Figure 3e). There, both goethite and hematite are largely recrystallised into coarser crystallites. In contrast, ferricrete shows angular goethite and hematite nodules with goethite pisolitic envelopes. They are cemented by vitreous goethite (Figure 3f). Subvertical dykes of amphibolitic gabbros locally exposed at East Alpha alter to form a mineral assemblage composed of kaolinite-gibbsite-hematite (Figure 3g,h and Figure 4).



Figure 3. (a) Typical sharp transition from silicate-dominated bedrock and saprock to oxidedominated saprolite and limonite (Ma-Oui). (b) Well-developed Ni smectite-rich zone (up to >15 m in vertical thickness) above lherzolitic serpentinite at East Alpha. (c) Vesicular hematite-goethite-bearing lateritic residuum (East Alpha). (d) Nodular/pisolitic ferricrete (East Alpha). (e) Recrystallisation of goethite and hematite with local preservation of inherited textures at the microscopic scale in the lateritic residuum, East Alpha (BSE imaging). (f) Goethitic pisolitic cortexes overgrowing onto nodular hematite in a goethite-bearing cement, ferricrete horizon, East Alpha (BSE imaging). (g,h) Kaolinite-gibbsite-hematite mineral assemblage in saprolitised gabbro at East Alpha (BSE imaging). Mineral abbreviations: Gth = goethite, Hem = hematite, Kln = kaolinite, Gbs = gibbsite. Onset (b) is modified after [13].



Figure 4. Stratigraphic logs of representative Ni-Co laterites from the Ma-Oui deposit, Coquette Red tenement, and East Alpha deposit. Modified after [13].

5. Whole-Rock Geochemical Correlations at the Deposit Scale

Whole-rock geochemical analysis of the investigated lateritic profiles shows that the lateritisation of unweathered peridotites is associated with the progressive enrichment of poorly mobile elements. In particular, Fe, Al, Cr, and Sc concentrations co-increase during weathering, exhibiting positive correlation trends (Figure 5, Table S1). In the Ma-Oui deposit, Al_2O_3 , Fe_2O_3 , Cr_2O_3 , and Sc concentrations progressively increase from the bedrock to the oxide-rich horizons up to about 6 wt%, 80 wt%, 4.5 wt%, and 80 ppm, respectively. The Sc-Al_2O_3, Sc-Fe_2O_3, and Sc-Cr_2O_3 linear regression models encompassing variable lithofacies (unweathered harzburgite, saprock, saprolite, Mn-Co-rich transition zone, and yellow and red limonite) provide a particularly relevant fit of the data (Figure 5a). Scandium concentrations may be approximatively estimated from the Al_2O_3 , Fe_2O_3 , and Cr_2O_3 concentrations from the bedrock to the red limonite as follows:

Sc (ppm) =
$$12.03 \times Al_2O_3$$
 (wt%) + 2.42; R² = 0.93 (1)

Sc (ppm) =
$$0.92 \times \text{Fe}_2\text{O}_3 \text{ (wt\%)} + 0.07; \text{ } \text{R}^2 = 0.86$$
 (2)

Sc (ppm) =
$$16.27 \times Cr_2O_3$$
 (wt%) + 0.31; R² = 0.91 (3)



Figure 5. $Sc-Al_2O_3$, $Sc-Fe_2O_3$, and $Sc-Cr_2O_3$ scatter plots and regression lines obtained for samples collected at (**a**) the Ma-Oui deposit (Koniambo massif), (**b**) the Coquette Red tenement (Cap Bocage massif), and (**c**) the East Alpha deposit (Tiébaghi massif). Peridotite-derived duricrust and gabbro-derived saprolite samples lie out of the correlation trends and are therefore excluded from the regression line modelling.

The Sc-Fe₂O₃ correlation trend shows low dispersion in the low-Sc concentration range (0–50 ppm) but significant dispersion in the higher-Sc concentration range (50–80 ppm). In

addition, two samples collected in the transition and yellow limonite zone, respectively, fall well out of the Sc-Fe₂O₃ regression line. The Sc-Cr₂O₃ correlation trend is better defined, yet it presents moderate data dispersion. Comparatively, the best fit is obtained for the Sc-Al₂O₃ regression line, which exhibits the lowest dispersion of the data. Notably, the decrease in Al and Sc concentrations from the yellow to red limonite, as commonly identified by Teitler et al. (2019) in New Caledonian lateritic profiles, is not observed in the Ma-Oui geochemical dataset. In the Coquette Red tenement (Cap Bocage massif), Al₂O₃, Fe₂O₃, Cr₂O₃, and Sc concentrations increase to about 5 wt%, 80 wt%, 5.5 wt%, and 65 ppm in the limonite, respectively. Like the Ma-Oui deposit, the Sc-Al₂O₃ regression line efficiently fits the data from the bedrock to the red limonite, although the laterite is developed on dunite and harzburgite (Figure 5b). Analysed duricrust samples exhibit a large offset from the trend, with a substantial depletion in Sc relative to Al₂O₃. It is worth noting that the Sc-Al₂O₃ regression lines obtained at Ma-Oui and Coquette Red have similar regression coefficients (respectively 12.03 and 12.84; Equations (1) and (4)).

In contrast, Fe_2O_3 , Cr_2O_3 and Sc concentrations do not correlate when considering the limonitic horizons. Therefore, Al_2O_3 here constitutes the only relevant explanatory variable for Sc concentrations among major elements. More specifically, Sc and Al_2O_3 are significantly enriched compared to Fe_2O_3 in the yellow limonite and, on the opposite, depleted in the red limonite. Regression lines obtained from Coquette Red samples, accounting for all lithologies apart from the duricrust, may be expressed as follows:

Sc (ppm) =
$$12.84 \times Al_2O_3$$
 (wt%) + 1.52; R² = 0.93 (4)

Sc (ppm) =
$$0.68 \times \text{Fe}_2\text{O}_3 \text{ (wt\%)} + 3.91; \text{R}^2 = 0.82$$
 (5)

Sc (ppm) =
$$9.20 \times Cr_2O_3$$
 (wt%) + 12.05; R² = 0.62 (6)

The East Alpha deposit (Figure 5c), developed after strongly serpentinised lherzolite, exhibits Sc concentrations up to 115 ppm in the limonite, i.e., significantly higher than those observed at Ma-Oui and Coquette Red. Moreover, Al_2O_3 concentrations reach about 15 wt% in the lherzolite-derived limonite, i.e., about three times more elevated than in the harzburgite \pm dunite-derived limonite at Ma-Oui and Coquette Red. In comparison, gabbro-derived saprolite yields Al_2O_3 concentrations up to about 30 wt%. Maximum Fe₂O₃ and Cr₂O₃ concentrations at East Alpha are similar to those observed in the other investigated sites, at 80 and 4 wt%, respectively. The Sc-Al₂O₃ regression line modelled for East Alpha samples fits the data relatively well, except for duricrust and gabbro samples that fall well out of the correlation trend. The regression coefficient of the Sc-Al₂O₃ line is about two times lower at East Alpha than at Ma-Oui and Coquette Red (Equation (7)). It is worth noting that smectitic saprolite samples from East Alpha exhibit Al, Sc, Fe, and Cr co-variations and a quite extensive concentration range (Figure 5c).

Nevertheless, significant dispersion from the regression line is also observed in the yellow and red limonite horizons compared to the Ma-Oui deposit and the Coquette Red tenement (Figure 5c). Similar to Coquette Red, Sc and Al₂O₃ are significantly enriched in the yellow limonite and depleted in the red limonite compared to Fe₂O₃. The Sc-Fe₂O₃ and Sc-Cr₂O₃ correlations in the East Alpha deposit are poorly defined, especially in the yellow and red limonite, wherein Fe₂O₃, Cr₂O₃, and Sc concentrations do not correlate. Regression lines obtained for East Alpha, modelled after exclusion of duricrust and gabbro-derived samples, may be expressed as follows:

Sc (ppm) =
$$6.56 \times \text{Al}_2\text{O}_3 \text{ (wt\%)} + 7.55; \text{R}^2 = 0.83$$
 (7)

Sc (ppm) =
$$1.18 \times \text{Fe}_2\text{O}_3 \text{ (wt\%)} + 8.47; \text{ } \text{R}^2 = 0.66$$
 (8)

Sc (ppm) =
$$24.08 \times Cr_2O_3$$
 (wt%) + 9.48; R² = 0.62 (9)

Principal Component Analysis (PCA) allows us to explore further the overall compositional variability of the samples and the strength of the colinearity between Sc and poorly mobile elements. The PCA, performed after centred log-ratio transformation of the data, shows that the cumulated explained variance in the PC1-PC2 plane reaches 78.4% of the overall variability of the initial dataset (respectively, 53.0 and 25.4% for PC1 and PC2, Figure 6). All of the elements constitutive of the samples, except Mn and Co, predominantly contribute to PC1, with Mg, Si, and Ni having a positive contribution to PC1. At the same time, Fe, Al, Cr, and Sc negatively contribute to PC1 (Figure 6b). PC1 underlines a contrast between Mg-Si-Ni and Al-Sc-Fe-Cr, and PC2 describes the Mn and Co positive correlation. LOI exhibits a strong negative contribution to PC2. It is worth noting that the angles between Mg, Si, and Ni rays are low, yet these rays are not coincident. Similarly, Sc and Al, on the one hand, and Fe and Cr, on the other hand, form two pairs of strongly coincident rays. These two pairs of coincident rays are at a relatively low angle, yet they are not colinear with one another. Sc is, therefore, better correlated with Al than with Fe or Cr. Regarding sample scores, bedrock samples fall close to the Mg ray. Saprock samples, in contrast, appear globally shifted towards the Si and Ni rays. Most smectitic saprolite samples still display a positive PC1 score, but lower than that of bedrock and saprock samples, with a low PC2 score. Earthy saprolite samples exhibit small positive and negative PC1 scores and a significant shift towards positive PC2 scores. Earthy saprolite samples represent, therefore, intermediate compositions between the Mg-Si-Ni and the Al-Sc-Fe-Cr groups along PC1, together with the onset of an Mn-Co compositional signature along PC2. Comparatively, transition zone samples are slightly shifted towards negative PC1 scores, indicative of an increasing contribution of the Al-Sc-Fe-Cr group. Moreover, transition zone samples exhibit the highest PC2 scores, consistent with their enrichment in Mn and Co. Yellow limonite samples are further shifted towards negative PC1 scores while still displaying positive PC2 scores indicating the subsistence of an Mn-Co signature. Red limonite samples also show negative PC1 scores but appear to be forming two subgroups, one with positive PC2 scores similar to the yellow limonite and one with negative PC2 scores, identical to duricrust samples.



Figure 6. Results of PCA performed after centred log-ratio transformation of Mg, Al, Si, Sc, Cr, Mn, Fe, Co, and Ni concentrations and LOI from the global whole-rock geochemical dataset of peridotite-derived laterites (Ma-Oui, Coquette Red and East Alpha). Saprolitised gabbro samples from East Alpha were excluded from PCA calculations. (a) Scree plot. (b) PC1-PC2 biplot showing variable loadings (arrays) and sample scores (circles). See Figure 5 for lithology colour coding.

6. Mineral Chemistry

The mineral chemistry data obtained from LA-ICP-MS analyses (Table S2) allow us to assess the contribution of primary silicates and serpentine to the Al and Sc budget in the unweathered peridotites. Forsterite has a low Sc content in all investigated sites, about 3-6 ppm at Ma-Oui and Coquette Red, about 7 ppm at East Alpha (Figure 7), and Al below detection limits. Enstatite yields higher Sc and Al concentrations, which vary from one site to another. Sc concentrations in enstatite from Ma-Oui and Coquette Red are similar (24 and 22.5 ppm, respectively). Al₂O₃ concentrations in enstatite are slightly higher at Ma-Oui (about 1.8 wt%) than at Coquette Red (about 1.4 wt%). In contrast, enstatite from East Alpha is enriched in Sc (about 32 ppm) and Al_2O_3 (about 3.4 to 3.8 wt%). Diopside yields an Al_2O_3 content similar to that of enstatite, with a higher Sc content (about 50 ppm in Ma-Oui and 65 ppm in Coquette Red). The mineral composition of lizardite developed after mantle silicates (forsterite, enstatite, and rarer diopside) commonly reflects the composition of their precursor mineral. Indeed, lizardite developed after forsterite yields low Sc and very low Al₂O₃ contents, whereas lizardite developed after enstatite and diopside yields higher Sc and Al_2O_3 contents (Figure 7). Lizardite forming the mesh network typically has Sc and Al_2O_3 contents intermediate between forsterite and enstatite. Chromiferous spinel yields elevated Al_2O_3 contents (>12 wt%) together with very low Sc contents (<3 ppm, Table S2). Importantly, Sc-Al₂O₃ regression lines obtained from major bedrock minerals (forsterite, enstatite, lizardite after enstatite and forsterite, and lizardite mesh) in each investigated site (Figure 7) closely match those obtained from whole-rock geochemical analysis throughout the weathering sequences (Figure 5). More specifically, regression coefficients estimated from bedrock mineral chemistry vs. global whole-rock geochemistry, respectively, are (i) 10.95 vs. 11.02 at Ma-Oui, (ii) 13.53 vs. 12.84 at Coquette Red, and (iii) 6.60 vs. 6.56 at East Alpha.

Further support for the intimate relationship between Sc-Al₂O₃ contents of peridotite mantle silicates and Sc-Al₂O₃ contents of peridotite-derived laterite samples is provided by the mineral chemistry data of secondary mineral phases along laterite profiles as analysed at East Alpha (Figure 8, Table S2). Together with forsterite and enstatite, Sc and Al₂O₃ concentrations in smectite, ochreous goethite from the limonite zone, and goethite-hematite from the lateritic residuum appear to be strongly proportional, with a regression line closely similar to that obtained from whole-rock geochemistry. Smectite in the smectitic saprolite and ochreous goethite in the limonite exhibit variable yet proportional Sc and Al₂O₃ concentrations. Indeed, Sc and Al₂O₃ concentrations in smectite vary from 20 to 80 ppm and from 2.5 to 10 wt%, respectively, while Sc and Al₂O₃ concentrations in limonitic, ochreous goethite vary from 55 to 122 ppm and from 7 to 16 wt%, respectively. Goethite-hematite from the lateritic residuum is depleted both in Sc and Al₂O₃. In contrast, goethite and hematite nodules and pisolitic cortexes from the ferricrete are depleted mostly in Sc and therefore fall below the regression line.



Figure 7. Sc-Al₂O₃ scatterplots and regression lines obtained for mantle silicates (forsterite, enstatite, diopside) and lizardite (developed after forsterite, enstatite, and diopside, or as mesh) in peridotite bedrocks from (**a**) Ma-Oui, (**b**) Coquette Red, and (**c**) East Alpha from LA-ICP-MS analyses. The regression line modelling excluded accessory phases (diopside, lizardite developed after diopside, and chromiferous spinel).



Figure 8. Sc-Al₂O₃ scatterplot and regression line obtained for silicates, smectite, and iron oxides in the East Alpha deposit (Tiébaghi massif) from LA-ICP-MS analyses. The regression line calculation excluded spot analyses of diopside from the bedrock and of goethite and hematite from the nodular/pisolitic duricrust.

7. Sequential Extractions

The sequential extractions for Fe, Al, Ni, and Sc are given in Figure 9. During the first extraction step, the ultrapure water did not permit solubilising these elements in any investigated samples. With regards to Fe, the hydroxylamine hydrochloride extraction also proved unsuccessful. In iron-rich samples (earthy saprolite, and yellow and red limonite), about 10-15% of the total Fe mass was extracted during the subsequent extraction step involving ammonium oxalate, while about 50–60% was removed during the last extraction step involving citrate-bicarbonate-dithionite (CBD). In iron-rich lithologies, the overall procedure permits the extraction of 60 to 80% of the total Fe content, and CBD appears to be the most effective reagent to solubilise Fe. In contrast, the general approach only resulted in the extraction of about 25% of the total Fe in the smectitic saprolite sample (TIEA-08) from East Alpha, mainly through the action of CBD and, to a lesser extent, ammonium oxalate. With regards to Al, the overall procedure succeeded in solubilising 40–50% and 10% of the total Al (Figure 9) in iron-rich and smectite-rich samples, respectively. The relative amount of extracted Al is higher in iron-rich samples from Coquette Red (PZ1B-06, PZ1B-09, PZ1B-13 and PZ1B-17) than in their equivalents from East Alpha (TIEA-07 and TIEA-12). Among this fraction, a small portion (less than 5% of the total Al extracted) was solubilised using hydroxylamine hydrochloride. The relative amount of Al removed by ammonium oxalate is similar to that of Fe, about 10% or less. CBD remains the most efficient reagent for Al extraction but seems less effective for solubilising Al than Fe. In addition, Al appears more efficiently extracted by ammonium oxalate in iron-rich samples from Coquette Red (about 10% of the total Al or 15–30% of the whole extracted Al) than in their equivalent from East Alpha (about 5% of the total Al or 10% of the extracted Al).



Figure 9. Results of sequential extractions. Cumulative histograms showing the total quantities of Fe (wt%), Ni (wt%), Al (wt%), and Sc (ppm) extracted with the different reagents, as well as the quantities not extracted. H₂O = Ultrapure water (step 1), HONH₂-HCl = hydroxylamine hydrochloride 0.1 mol·L⁻¹ at pH 3.5 (step 2), (NH4)₂C₂O₄ = ammonium oxalate 0.2 mol·L⁻¹ at pH 3 (step 3), CBD = citrate-bicarbonate-dithionite Na₂S₂O₄ (22% Na-citrate and 1 g Na-dithionite) (step 4). See Figure 5 for lithology colour coding.

Bulk Ni extraction is similar to or higher than Fe extraction. It is, in particular, higher in iron-rich samples from Coquette Red than in their equivalents from East Alpha. More specifically, two samples from Coquette Red (PZ1B-09 and PZ1B-17) show almost complete Ni extraction, while Ni extraction in East Alpha does not exceed 60%. In contrast, Ni is weakly extracted from the smectitic saprolite sample from East Alpha. The relative proportion of Ni removed by hydroxylamine hydrochloride remains low (5 to 15% of the total Ni extraction by ammonium oxalate appears similar to that of Fe (about 5 to 15% of the total Ni extracted) and slightly lower than Al. As for Fe and Al, Ni is best extracted through CBD's last

extraction step. Regarding Sc, the overall procedure proves efficient in oxide-rich samples, resulting in the extraction of about 75% of the total Sc amount, except in one sample (60% extraction efficiency in TIEA-07). Like Fe, neither the ultrapure water nor the hydroxy-lamine hydrochloride successfully extracted Sc from any samples. Sc extraction using ammonium oxalate, which accounts for about 20 to 30% of the total Sc contained, appears significantly more efficient than Fe, Al, and Ni in iron-rich samples.

Nevertheless, in these samples, CBD remains the most efficient reagent for Sc extraction. In contrast, in the smectitic saprolite sample from East Alpha, Sc is almost exclusively extracted using ammonium oxalate. However, the total amount of extracted Sc from this sample remains moderate (about 50% of the bulk Sc content). To summarise, it should be noted that, in oxide-rich facies, (i) the extraction procedure is globally efficient for solubilising Fe, Al, Ni, and Sc, though significant differences in global extraction efficiencies are observed depending on the considered element and the sample provenance; (ii) only Al and Ni can be slightly extracted using hydroxylamine hydrochloride; (iii) Fe, Al, Ni, and Sc are best solubilised using CBD and, to a lesser extent, ammonium oxalate; and (iv) the efficiency of Sc extraction using ammonium oxalate is significantly greater than that of Fe, Al, and Ni. In contrast, the overall procedure is less well suited for the sequential extraction in smectitic saprolite, so the greater extraction efficiency of ammonium oxalate relative to other reagents must be considered cautiously.

8. Discussion and Implications for the Evaluation of Sc in Ni-Co Laterites

This study aims to assess in which conditions Al may be reliably used as a geochemical proxy for a first-order evaluation of Sc grades and distribution in Ni-Co lateritic ores. In the following, we discuss the causes of the Al-Sc co-variation regarding the mineralogical evolution in lateritic profiles and the relevance of using deposit-scale Sc-Al₂O₃ correlations to assess the distribution of Sc in Ni-Co laterites.

8.1. Co-Evolution of Al and Sc Concentration and Speciation through Weathering

Analytical data documented in the present contribution reveal significant correlations, at the deposit scale, between Sc and Al_2O_3 concentrations in some lateritic Ni deposits of New Caledonia. The high proportionality between Sc and Al_2O_3 , observed in the investigated lateritic deposits from the bedrock to the red limonite, is identified from whole-rock geochemistry (scatterplots of untransformed data and PCA of centred log-ratio-transformed data) and mineral chemistry data (Figures 5, 6 and 8). This correlation has already been documented [13], but not at the deposit scale. Furthermore, the study conducted by Santoro et al. [36] on trace element concentrations in goethite from various Ni-laterite deposit (Australia). The authors interpreted such association as being primarily controlled by the composition of the parent rock, highlighting the influence of Al-and Sc-bearing pyroxenite lenses on the composition of their goethite-bearing, weathered derivatives. The Sc-Al₂O₃ proportionality, documented in the present contribution throughout the weathering sequences of various Ni-laterites from New Caledonia (i.e., from the bedrock to the red limonite), argues for a similar behaviour of Al and Sc during weathering.

In the unweathered mantle silicates, Ni is exclusively bound to forsterite. In contrast, virtually all of the Al is hosted in pyroxenes (enstatite and diopside), and, to a lesser extent, in chromiferous spinel, as it is highly incompatible with forsterite. Sc is also preferentially hosted in pyroxenes, as forsterite only incorporates Sc up to a few ppm. Diopside contains Sc concentrations up to about 65 ppm (Table S2, [13,14]) but is not abundant (Table S1) and has a minor influence on the bulk Sc content of unweathered lherzolite. It has been proposed that serpentinisation of the peridotite most likely has a marginal effect on Sc concentrations in the bedrock [13]. The mineral chemistry data documented on lizardite in the present contribution supports such an assumption, as lizardite composition primarily reflects the composition of its mineral precursor. Although Cr-spinel yields elevated Al_2O_3 contents, it is an accessory phase in the bedrock. Considering (i) the mineral composition of

Cr-spinel, (ii) the bulk Cr content of bedrock samples, and (iii) conservatively assuming that all Cr is hosted in Cr-spinel in the bedrock, the contribution of Cr-spinel on the bulk Al_2O_3 content does not exceed 10% in the bedrock. Therefore, the global Sc and Al_2O_3 contents in unweathered peridotite largely depend on the relative proportion of enstatite and its chemical composition. Nevertheless, forsterite being the predominant mantle silicate in peridotite, it also significantly contributes to the global Sc budget of the bedrock.

In the lower part of the weathering sequence (saprock and smectitic saprolite), Sc and Al concentrations co-increase with Fe and Cr concentrations, suggesting that Sc and Al enrichments are residual. Co-variations, along an extensive concentration range, of Al, Sc, Fe, and Cr in smectitic saprolite samples from East Alpha (Figure 5), result from inherent co-variation of smectite composition, as evidenced by mineral chemistry data (Figure 8). The sequential extraction procedure proved relatively ineffective in solubilising Fe, Ni, and Al and from the smectitic saprolite. These elements are typically present in octahedral and tetrahedral positions in nickeliferous smectite and are not leached easily from smectite [37,38]. However, the significant amounts of Sc extracted from the smectiterich saprolite using ammonium oxalate raise questions regarding the speciation of Sc in this horizon. Together with the elevated Sc concentrations measured in smectite from LA-ICP-MS analysis, the lack of Fe extraction by ammonium oxalate rules out any significant contribution of amorphous iron oxides/oxyhydroxides to the Sc budget in the smectite-rich zone. Based on the scandium K-edge XANES analysis, Chassé et al. [8] proposed that Sc in the plasmic horizon of the Syerston-Flemington Sc laterite (Australia) is efficiently trapped in smectite through incorporation into octahedral sites. Such interpretation seems unable to account for the high quantities of Sc extracted using ammonium oxalate. Further investigations remain to evaluate the Sc speciation in the smectitic saprolite from the East Alpha deposit.

Contrasting with the Fe-Al-Sc-Cr collinearity identified in the lower portion of the weathering sequences, Sc and Al exhibit a relative enrichment compared to Fe in the earthy saprolite/yellow limonite and a relative depletion in the red limonite. This distribution pattern, observed at Coquette Red and East Alpha (Figure 5b,c), as well as in several New Caledonian Ni-Co laterites [13], but not at Ma-Oui (Figure 5a), supports specific mobility of Sc and Al. It is suggested that these elements are, to some extent, remobilised from the red limonite and accumulated downwards in the yellow limonite. The remobilisation of Sc and Al possibly results from the release of Sc and Al after the dissolution/recrystallisation of increasingly crystallised goethite during the maturation of the lateritic profile [13,39]. Such a model is commonly accepted for explaining the distribution pattern of Ni concentrations, which generally decrease gradually from the earthy saprolite upwards in conjunction with an increase of the mean coherent domain (MCD) size of the goethite crystallites [39,40]. This typical Ni distribution pattern is, for instance, well-evidenced at Coquette Red, where a gradual decrease of Ni concentrations occurs from the earthy saprolite (1.5 wt% Ni) to the red limonite (0.5 wt% Ni). There, Sc and Al distribute differently from Ni, as Sc and Al concentrations are higher in the yellow limonite than in the earthy saprolite. Although the release of Sc during dissolution/recrystallisation of goethite has been proposed as a relevant model for explaining some elevated Sc concentrations in the yellow limonite [8,13], the mobility of Sc released during this process must therefore be lower than that of Ni. In addition, the formation of hematite at the expense of goethite in the red limonite likely results in the downward redistribution of Sc and Al, as both Sc and Al substitute more easily for Fe in goethite than in hematite [41-43], thus contributing to Sc enrichment in the yellow limonite.

Sequential extraction provides further insights on the speciation of Sc and its association with other elements in the earthy saprolite, yellow and red limonite. It is worth noting that the extraction procedure here applied differs from the method previously used on ultramafic-derived laterites from the Syerston-Flemington (Australia) and the Berong (Philippines) deposits [8,11]. The extraction procedure is adapted from Hall et al. [44] and Sanematsu et al. [45] in these two studies. It includes sodium acetate as the first reagent to assess the adsorbed and exchangeable species. In contrast, we used ultrapure water, which only allows us to extract the easily exchangeable species and, therefore, does not estimate the adsorbed species.

Nevertheless, the extracted Sc amounts obtained from sodium acetate treatment are low (10–15%) in the Syerston–Flemington laterites to very low (<5%) in the Borong laterites [8,11]. These two studies combine sequential extraction with XANES analysis. Chassé et al. [8] observed that the low proportion of exchangeable goethite-hosted Sc obtained from sequential extraction (10–15%) is at odds with the results of the XANES analysis. The latter reflects an elevated contribution of Sc adsorbed on goethite (up to 80%) in the global Sc budget, with only a small proportion of Sc being substituted in iron oxides and oxyhydroxides. The authors favour better reliability of the XANES spectra interpretation than the sequential extraction results and propose reconciling these data by arguing for the high stability of the Sc adsorption complex on goethite, thus preventing the extraction of adsorbed Sc through sodium acetate treatment. Similarly, in the Gorong deposit [11], the amounts of Sc adsorbed on goethite appear more significant when estimated from XANES spectra (24–49%) than from sequential extraction (below 5%).

Both of these studies then use hydroxylamine hydrochloride to extract amorphous iron oxides. In contrast, we used hydroxylamine hydrochloride at lower concentrations to extract manganiferous species. No Fe or Sc, and only a very slight fraction of Ni and Al, are extracted using hydroxylamine hydrochloride, highlighting the marginal presence of Mn oxides in the investigated samples and the absence of detectable Sc in Mn oxides. Following hydroxylamine hydrochloride treatment, we used ammonium oxalate to extract amorphous iron oxides. Ammonium oxalate has been reported as an efficient and selective dissolving agent for amorphous and poorly crystalline ferric oxides/oxyhydroxides without significant crystalline goethite/hematite or silicate dissolution [46,47]. Chassé et al. [8] and Qin et al. [11] did not pursue sequential extraction further than the amorphous iron oxides/oxyhydroxides extraction step, hypothesizing that the residue is mostly representative of crystalline iron oxides. In the present study, the last extraction step with CBD unambiguously demonstrates that crystalline iron oxides/oxyhydroxides predominates over amorphous iron oxides/oxyhydroxides in oxide-rich horizons. Along with Fe, the elevated Ni, Al, and Sc fractions extracted using CBD confirm that these elements are mainly bound to crystalline goethite. At Coquette Red, a slight decrease in the total extracted Fe is observed from the earthy saprolite to the red limonite, from about 80 to 60% (Figure 9). Such a decrease, resulting from a slight lowering of both CBD and ammonium oxalate extraction efficiencies (from about 60 to 50% and 15 to 8%, respectively), may indicate an increase in goethite crystallinity. Compared to Fe, Al extraction appears globally less effective, especially at East Alpha, wherein the Al contents of oxide-rich facies are higher than at Coquette Red. Such a discrepancy between the extraction efficiencies of Al and Fe possibly results from the presence of extraction-resistant, Al-bearing minerals in the oxide-rich facies. Chromiferous spinel, an accessory phase in the bedrock, is residually enriched in the oxide-rich facies and contains about 15 wt% Al [13]. Therefore, even in minor amounts, the presence of extraction-resistant Cr-spinel implies that a non-negligible portion of the wholerock Al content cannot be extracted through the used procedure. However, such quantities of unextractable Al are likely insufficient to account for the apparent lower extractability of Al, or for the differences in Al extraction rates between Coquette Red and East Alpha, as both sites have similar Cr contents. Although not observed in any of the peridotite-derived limonite samples, trace amounts of kaolinite in the lherzolite-derived limonite cannot be ruled out at East Alpha. Similar to Cr-spinel, the used extraction procedure is ineffective in solubilising kaolinite, whose potential presence in the East Alpha limonite may explain the lower extraction rate for Al. Regarding Sc, total extraction rates in the Fe-rich horizons are similar to that of Fe (and therefore higher than that of Al), supporting the strong association of Sc with iron oxides/oxyhydroxides and, in particular, with crystalline goethite. Nevertheless, ammonium oxalate appears relatively more efficient in extracting Sc (about 20 to 35% of total Sc) than Fe (about 10% of the total Fe). The proportion of Sc extracted from

amorphous iron oxides in the present study is, therefore, slightly higher than that obtained by Chassé et al. [8], that is about 15–25%, and significantly higher than that obtained by Qin et al. [11], that is below 3%. This discrepancy possibly results from a better efficiency of ammonium oxalate to extract Sc from amorphous iron oxides/oxyhydroxides than hydroxylamine hydrochloride. Our results suggest that Sc may have a higher affinity for amorphous iron oxides/oxyhydroxides than crystalline goethite. Thus significant amounts of Sc can be concentrated in amorphous iron oxides/oxyhydroxides despite the predominance of crystalline goethite throughout the lateritic sequence. The speciation of Sc in oxide-rich facies differs probably in part from that of Al. The latter is mainly incorporated in the lattice of crystalline goethite and preserved in weathering-resistant Cr-spinel. However, despite second-order differences between the speciation of Sc and Al₂O₃, these elements show strong proportionality from the bedrock to the red limonite. As these elements (i) are both mainly immobile during the weathering of peridotite, (ii) have a preferential affinity for goethite, and (iii) are only moderately remobilised following recrystallisation and goethite replacement by hematite, the composition of the parent rock remains the first-order control on their concentrations throughout the weathering sequences. Thus, the Sc-Al₂O₃ regression lines obtained from forsterite-enstatite-lizardite mineral compositions are close to those obtained from weathering-related mineral compositions and whole-rock geochemistry along weathering profiles. The slightly lower regression coefficients obtained from whole-rock geochemistry than those obtained from bedrock mineral composition may result from the second-order contribution of Cr-spinel to the global Al budget in whole-rock geochemical compositions. These results indicate that (i) the Sc-Al₂O₃ content of enstatite in a given peridotite bedrock drives the slope of the Sc-Al₂O₃ regression line within its weathered derivatives, and (ii) the relative proportion of enstatite together with its Sc content largely control the maximum Sc concentrations reached in the yellow limonite. It is worth noting that the positive intercepts observed on whole-rock Sc-Al₂O₃ regression lines likely reflect the contribution of Al-free forsterite.

Contrasting with the proportionality observed between Sc and Al_2O_3 from the bedrock up to the red limonite, samples from the duricrust are out of the Sc-Al₂O₃ whole-rock correlation trends. Such offset, previously documented by Teitler et al. [13], possibly results from the contribution of allochthonous material to the duricrust. Indeed, in situ Sc analysis of goethite-hematite in lateritic residuum matches the Sc-Al₂O₃ regression line obtained on saprolitic and limonitic minerals. On the opposite, nodular and pisolitic goethite and hematite from the ferricrete exhibit a relative depletion in Sc compared to Al, similar to the offsets identified in the whole-rock geochemical dataset. In the East Alpha deposit, the offset of gabbro-derived saprolite from the Sc-Al₂O₃ correlation trend also results from the allochthonous nature of the gabbro compared to the peridotite-derived Ni-Co laterite, together with the specific mineral assemblage of the gabbro-derived saprolite. The formation of kaolinite during the weathering of gabbro is related to its Al content [13,48,49]. As Sc is typically poorly concentrated into kaolinite [7,13,14], gabbro weathering may lead to Sc remobilisation and trapping into nearby yellow limonite. At the same time, Al remains concentrated in saprolitised gabbro as kaolinite. Consequently, Sc and Al₂O₃ may be positively correlated in lateritic deposits if kaolinite, or other Al-bearing phases such as gibbsite, are mostly absent from the lateritic profiles. The formation of kaolinite (or gibbsite) during the lateritisation process requires that the parent rock contains significant amounts of Al, so that Sc-Al₂O₃ correlation trends may only be observed in ultramafic-derived laterites, wherein the Al content is low.

8.2. Implications for the Assessment of Sc in Ni-Laterites

Using Al as a geochemical proxy to conduct a first-order estimation of Sc concentration and distribution in a given Ni-Co deposit depends on the specific reliability of the Sc-Al₂O₃ correlation at the deposit scale and on the method used to characterise Al concentration and distribution. The reliability of the Sc-Al₂O₃ correlation may be influenced by (i) potential heterogeneities in the parent rock lithology, (ii) the occurrence of alteration facies containing Al-rich phases such as kaolinite or gibbsite, and (iii) the inherent data dispersion in Sc-Al₂O₃ scatterplots. Interestingly, the alternate presence of harzburgite and dunite in the bedrock does not seem to significantly affect the Sc-Al₂O₃ regression coefficient nor the dispersion of the data, providing that the composition of enstatite remains similar in both facies. Nevertheless, lithological heterogeneities involving a change in the composition of enstatite, elevated amounts of diopside and plagioclase (e.g., in some lherzolite facies), or the occurrence of mafic intrusive dykes, may cause significant variations of the Sc/Al_2O_3 concentration ratio both in the parent rocks and in their weathered derivatives. These potential variations of the parent rock lithology at the deposit scale may be tested by geological characterisation and geochemical assay data analysis. In addition, alteration facies containing significant amounts of Al-rich phases (e.g., kaolinite, gibbsite) are commonly characterised by a substantial deviation from the Sc-Al₂O₃ correlation trend established from smectite- and Fe-oxide-dominated lithologies. The possible occurrence of Al-rich phases, typically poor in Sc, must be examined to prevent over-estimation of the Sc content. Al-rich phases are commonly associated with weathered intrusive rocks such as gabbros. Still, they may also form during the weathering of some peridotites that yield significant Al concentrations. In particular, some plagioclase-bearing lherzolites (not investigated in the present study) can exhibit Al_2O_3 contents up to ~4 wt% [18,50] and may consequently alter to kaolinite or gibbsite.

Therefore, geochemical homogeneity and low Al-content of the parent rock are necessary conditions for a reliable $Sc-Al_2O_3$ correlation trend at the deposit scale. Determination of a reliable, deposit-scale Sc-Al₂O₃ correlation requires assessing the range of Al₂O₃ concentrations for which Sc is well correlated with Al₂O₃ through an adequate sampling strategy that encompasses the whole range of Al₂O₃ concentrations and the mineralogical diversity throughout the deposit. Finally, the inherent data dispersion in Sc-Al₂O₃ biplots may be variable depending on the investigated deposit. Therefore, the number of samples used for establishing the Sc-Al₂O₃ correlation must be adapted to the inherent data dispersion to develop a reliable correlation with a good correlation coefficient. Once verified, deposit-scale Sc-Al₂O₃ correlations may first prove useful to estimate Sc concentrations on surface outcrops or pit walls using portable devices such as pXRF. Indeed, the relatively low Sc concentrations observed in Ni-laterites (<100 ppm) limit the use of pXRF to directly assess Sc [51], whereas Al concentrations, typically about a few wt%, can be confidently estimated using such a device. The slightly lower accuracy obtained on Al analysis from pXRF than from a classical assay analysis would only marginally affect the estimation of Sc. More importantly, applying this approach to deposits where Al is routinely assayed could provide a first-order Sc concentration and distribution estimate. The reliability of such estimation would depend on the Sc-Al₂O₃ correlation and the reliability of the Al distribution model. Indeed, block models are developed firstly to estimate the resource and distribution of Ni both in saprolitic and limonitic facies. They rely on statistical variograms set explicitly for several metals (e.g., Si, Mg, Fe, and Ni) but not necessarily Al. In such a case, a specific evaluation of the variability of Al in the limonitic facies may be beneficial.

9. Conclusions

This contribution examines the relevance of using Al as a geochemical proxy for firstorder Sc distribution and concentration estimates in some peridotite-hosted, Ni-Co laterites from New Caledonia. Apparent correlations are identified at the deposit scale between Sc and Al₂O₃ concentrations from the bedrock to the red limonite. These correlations put forward the similar behaviour of Al and Sc in weathered peridotite as their concentrations are primarily issued from residual enrichment. Local remobilisation from the uppermost horizons is shown. Al and Sc are predominantly hosted in crystalline goethite, but Sc has a relatively higher affinity for amorphous iron oxides than Al. In all investigated deposits, the Sc-Al₂O₃ regression coefficient remarkably depends on the Sc content in enstatite. Since the parent lithology is homogeneous and relatively depleted in Al, reliable Sc-Al₂O₃ correlations may thus be determined at the deposit scale after analysing a limited number of spatially and chemically representative samples. An adequate sampling strategy is required to cover the range of Sc and Al_2O_3 concentrations throughout the deposit. In addition, it is necessary to consider potential occurrences of specific alteration facies that may affect the relevance of the deposit-scale correlation (ferricrete, weathered intrusive rocks, and kaolinite- or gibbsite-bearing alterite). Although the zones of maximum Sc enrichment are situated above the top Ni and Co enrichment zones, Sc-rich limonite may overlap the Co-rich transition zone. The base of the limonite zone may therefore contain exploitable Co and Sc together with sub-economic Ni grades.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/min12050615/s1, Table S1: Whole-rock geochemical data; Table S2: Mineral chemistry (LA-ICP-MS) data.

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