Ni cycling in mangrove sediments from New Caledonia

Vincent Noël^{a,b}, Guillaume Morin^{a*}, Farid Juillot^{a,c}, Cyril Marchand^{a,c}, Jessica Brest^a, John R. Bargar^d, Manuel Muñoz^{e,f}, Grégory Marakovic^b, Sandy Ardo^a, and Gordon E. Brown Jr.^{d,g}

^a*Institut de Minéralogie, de Physique des Matériaux et de Cosmochimie (IMPMC), UMR 7590, CNRS, Sorbonne Universités - UPMC, UR IRD 206, MNHN
4 place Jussieu, 75252 Paris Cedex 05, France*

^b*Koniambo Nickel SAS (KNS), B.P.679, 98860 Koné, Nouvelle Calédonie*

^c*Institut de Recherche pour le développement (IRD), UR 206/UMR 7590 IMPMC,
98848 Nouméa, New Caledonia*

^d*Stanford Synchrotron Radiation Lightsource, SLAC National Accelerator Laboratory,
2575 Sand Hill Road, MS 69, Menlo Park, California 94025, USA*

^e*Univ. Grenoble Alpes, ISTERre, CNRS, F-38000 Grenoble, France*

^f*European Synchrotron Radiation Facility, F-38043 Grenoble, France*

^g*Surface & Aqueous Geochemistry Group, Department of Geological & Environmental Sciences,
Stanford University, Stanford, California 94305-2115, USA*

to be submitted to

Geochimica et Cosmochimica Acta

* Corresponding author: Guillaume Morin; e-mail: guillaume.morin@impmc.upmc.fr

Abstract

Covering more than 70% of tropical and subtropical coastlines, mangrove intertidal forests are well known to accumulate potentially toxic trace metals in their sediments, being thus generally considered as playing a protective role in marine and lagoon ecosystems. However, the chemical forms of these trace metals in mangrove sediments are still uncompletely elucidated, even though their molecular-level speciation controls their long-term behavior. Here we report the vertical and lateral changes in the chemical forms of nickel, which accumulates massively in mangrove sediments downstream from lateritized ultramafic deposits from New Caledonia, where one of nature's largest accumulations of nickel occurs. To accomplish this, we used Ni K-edge Extended X-ray Absorption Fine structure (EXAFS) spectroscopy data in combination with microscale chemical analyses using Scanning Electron Microscopy coupled with Energy-Dispersive X-ray Spectroscopy (SEM-EDXS). After Principal Component and Target Transform analyses (PCA-TT), the EXAFS data of the mangrove sediments were reliably Least-Squares fitted by linear combination of 3-components chosen from a large model compounds spectra database including synthetic and natural Ni-bearing sulfides, clay mineral, oxyhydroxides and organic complexes. Our results show that in the inland salt flat Ni is hosted in minerals inherited from the eroded lateritic materials, i.e. Ni-poor serpentine (44-58%), Ni-rich talc (20-31%) and Ni-goethite (18-24%). In contrast, in the hydromorphic sediments beneath the vegetated *Avicennia* and *Rhizophora* stands, a large fraction of Ni is partly redistributed into a neoformed smectite pool (20-69% of Ni-montmorillonite) and Ni speciation significantly changes with depth in the sediment. Indeed, Ni-rich talc (25-56%) and Ni-goethite (15-23%) disappear below ~15 cm depth in the sediment and are replaced by Ni-sorbed pyrite (23-52%) in redox active intermediate depth layers and by pyrite (34-55 %) in the deepest sediment layers. Ni-incorporation in pyrite is especially observed beneath a inland *Avicennia* stand where anoxic conditions are dominant. In contrast, beneath

47 a *Rhizophora* stand closer to the ocean, where the redox cycle is intensified due to the tide cycle, partial
48 re-oxidation of Ni-bearing pyrites favors nickel mobility, as confirmed by Ni-mass balance estimates
49 and by higher Ni concentration in the pore waters. These findings have important environmental
50 implications for better evaluating the protective role of mangroves against trace metal dispersion into
51 marine ecosystems. They may also help in predicting the response of mangroves ecosystems to
52 increasing anthropogenic pressure on coastal areas.

53

54

1. Introduction

Mangrove intertidal forests cover more than 70% of tropical and subtropical coastlines and play a major role in the ecological balance of these areas (Valelia et al. 2001; Duke et al. 2007; Nagelkerken 2008). They receive inputs from natural or anthropogenically impacted watersheds and may act as filters between land and sea for various metallic contaminants (Harbison 1986; Lacerda et al. 1993; Tam and Wong 1995; 2000). As a result, and due to their potential toxicity to living organisms (Di Toro et al., 1992), the distribution of trace metals in mangrove ecosystems has received significant attention during the last decade (Otero et al. 2009; Lewis et al. 2011; Bayen 2012; Nath et al. 2013). This is especially true in New Caledonia where mangroves act as a buffer zone between massive lateritic deposits enriched in transition metals such as Fe, Cr, Ni, Co, and Mn (Becquer et al. 2001; Quantin et al. 2001; Dublet et al. 2012), and a lagoon of over 20,000 km², recently registered as an UNESCO World Heritage site.

Mangrove sediments are known to have a large capacity to accumulate metallic elements (Tam and Wong 2000; Qiu et al. 2011; Marchand et al. 2012), which is partly attributed to their large content of organic matter that can act as a complexing agent (Nissenbaum and Swaine 1976). In addition, mangroves sediments are subjected to sulfate-reduction processes (Howarth and Merkel 1984; King 1988), which lead to precipitation of sulfide minerals that are able to trap chalcophile elements as well as Co and Ni in sulfidic coastal or marine sediments (Huerta-Diaz and Morse 1992; Morse and Luther 1999; Burton et al. 2006, 2008). In mangrove sediments, trace metal trapping processes are however expected to depend on biogeochemical gradients in salinity, redox and organic matter content that are driven by the distance to the seafront, the magnitude of the tide, and the types of mangrove tree species (Otero et al. 2009; Marchand et al. 2011; 2012). In addition, oxic and anoxic diagenetic reactions can operate in coastal sediments as a function of time, due to tide cycles (Otero et al. 2009), seawater

79 flooding (Johnston 2010; Wong et al. 2010, 2013), as well as freshwater inputs (Burton et al. 2008).
80 Complex redox cycling in mangrove sediments may thus significantly impact the speciation of metallic
81 elements across the intertidal zone (Tam and Wong 2000; Marchand et al. 2012; Clark et al. 1998;
82 Marchand et al. 2006a; Otero et al. 2009). Such biogeochemical cycles were studied in the mangrove
83 sediments of the Island of Pai Matos (Cananeia — SP, Brazil), where Fe speciation, determined from
84 sequential chemical extractions, changes significantly as a function of the redox boundaries delineating
85 intertidal and depth zonations (Otero et al. 2009). Similarly, Noël et al. (2014) determined iron
86 speciation in mangrove sediments from New Caledonia using X-ray Absorption Fine Structure (XAFS)
87 spectroscopy and confirmed that the major variations in the distribution of Fe-oxyhydroxides, pyrite
88 and iron-bearing clays, rely on the redox gradients generated by both the topographic position across
89 the intertidal zone and the depth within the sediments. Compared to that of iron, the speciation of
90 nickel in mangrove sediments has been less studied. Chemical extraction studies have however
91 reported the potential role of sulfides, oxyhydroxides and carbonate minerals as well as of organic
92 matter in nickel trapping (Clark et al. 1998; Marchand et al. 2012).

93 The objective of the present study was to improve our understanding of the biogeochemistry of nickel
94 in mangrove sediments as a function of chemical gradients and of vegetal cover changes across the
95 intertidal zone. For this purpose, we chose mangrove sediments that exhibit exceptional nickel content,
96 downstream from lateritized ultramafic ore deposits from New Caledonia. Complemented by X-ray
97 Diffraction (XRD) and Scanning Electron Microscopy – Energy Dispersive X-ray Spectroscopy (SEM-
98 EDXS) analyses, X-ray Absorption Spectroscopy (XAS) was used for this purpose because it has been
99 shown to be suitable for quantifying the variety of Ni-species in lateritic materials that are the source of
100 nickel for mangrove sediments in New Caledonia (Dublet et al. 2012, 2014). The spatial distribution of
101 the nickel species was quantified in three cores drilled beneath typical mangrove tree covers
102 (*Rhizophora* spp., *Avicennia marina*, and salt flat) in order for evaluating the long-term influence of the
103 redox gradients on the speciation and mobility of Ni in the sediments of these fragile ecosystems.

2. Materials and Methods

2.1. Sampling site and sampling procedures.

The studied site is typical of the topographic, vegetal and redox gradients of the New Caledonian mangroves. It is located in the Vavouto Bay (20°59'S; 164°49'E), at the mouth of the Talea-Coco River that drains the ultramafic Koniambo regolith (Noël et al. 2014). It stands on the west coast of the main New Caledonia island (20°S – 23°S), which is characterized by a semi-arid climate (~750 mm/year; Maitrepierre, 2004). As in many mangrove ecosystems, the intertidal zone in New Caledonia can be divided into three areas defined in terms of changes in vegetation type from the sea front to the inland salt flat (Marchand et al. 2011, 2012). The first zone nearest the shore is swept daily by tides and is dominated by *Rhizophora* spp. Previous study of iron cycling in these mangrove sediments has shown that this zone, being the closest to the shore, is subjected to intense reduction-oxidation events during tidal fluctuations (Noël et al. 2014). The second zone is located between the first zone and the salt flat and is dominated by *Avicennia marina*, beneath which the reducing conditions are more persistent. The third zone is the salt flat which is not colonized by vascular plants and is characterized by oxidizing conditions. One sediment core was collected in each of these three zones, at low tide. Sediment cores were sampled with an Eijkelpkamp gouge auger in May 2011, at the end of the rainy season. After being collected in PVC tube, sediment cores were sampled every 5 cm from 0 to 60 cm depth, samples being immediately placed in glass vials under N₂ gas flux and sealed with butyl stoppers. Sealed sediment samples were then kept frozen until being placed in a glove box under N₂ atmosphere at the laboratory, where they were vacuum dried, hand-ground in an agate mortar, homogenized, and sealed again. Upon the solid sampling campaign, pore-waters were extracted from sediment cores using soil moisture samplers Rhizon®, within a glove-bag under N₂ atmosphere, as

reported by Noël et al. (2014). Pore water samples were then acidified to pH 2 with Suprapur® HNO₃, and stored in a cold room (T = 4 °C) until analysis of aqueous Ni concentration.

2.2. Chemical and Mineralogical analyses.

The Ni, Fe and Ti chemical compositions of the mangrove sediments and of the natural and synthetic model compounds were determined by X-Ray Fluorescence (XRF) spectrometry at IMPMC with a XEPOS (Spectro X Lab) X-ray fluorescence spectrometer equipped with a Pd cathode and operating at 50 kV and 40 mA. The morphology, organization, and chemical composition of the mangrove sediments were studied by SEM-EDXS at IMPMC with a Field Emission Gun Scanning Electron Microscope (GEMINI ZEISS Ultra55) operating at 15 kV with a 60 µm diaphragm. Ni/Fe ratios were estimated as ~1/10 of the Ni K α to Fe K β lines intensity ratio measured by EDXS, according to corresponding fluorescence yields (Kortright and Thompson 2009). Sediment samples to be analyzed were deposited as ground powder on carbon tape and coated with a thin carbon film. The mineralogical composition of these samples was previously determined using powder X-ray Diffraction (XRD) analysis (Noël et al. 2014). In addition, the mineralogical purity of the Ni-model compounds synthesized for the present study was assessed by powder XRD. Data were collected at the Co K α radiation wavelength using a Panalytical® X'Pert Pro diffractometer equipped with an X'celerator® detector. Continuous scans were collected between 3 and 120° 2 θ with a 0.033° 2 θ step, counting 4h per sample. Samples were mounted within the glove box and transferred in an anoxic sample chamber for XRD data collection to avoid any changes in the mineralogy related to possible redox reactions with air.

Aqueous Ni concentrations in the pore-waters were measured at University Paris Diderot with an Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) Icap ThermoFisher Scientific

153 spectrometer and a High-Resolution Inductively Coupled Plasma Mass Spectrometry (HR-ICP-MS)
154 Element 2 Thermofisher scientific spectrometer equipped with an integrated FAST (ESI) injection
155 system. For these analyses, a dilution of 100 was used and the SLRS4 certified reference material was
156 intercalated during the analytical series.

157

158 **2.3. Model compounds for XAS analyses.**

159

160 A large set of experimental Ni K-edge XAS spectra for natural and synthetic model compounds was
161 used for interpreting the extended X-ray Absorption Fine Structure (EXAFS) spectra of the mangrove
162 sediments. Our set of Ni K-edge EXAFS spectra includes those of Ni-goethites, Ni-bearing Mn-oxides,
163 as well as Ni-silicates, Ni-phylosilicates and Ni-bearing siderite that have already been recorded and
164 analyzed in [Dublet et al. \(2012; 2014\)](#). Ni-montmorillonite and Ni-rich talc EXAFS spectra recorded by
165 [Dublet et al. \(2012\)](#) are analyzed in the present study. In addition, Ni K-edge EXAFS spectra were
166 recorded for Ni-bearing sulfide mineral and Ni-sorbed sulfides samples synthesized for the present
167 study

168 Ni-pyrite reference samples consisted of a natural Ni-rich pyrite ($\text{Fe}_{0.9}\text{Ni}_{0.1}\text{S}_2$), referred to as Ni-
169 pyrite10% as well as of synthetic a synthetic Ni-pyrite containing 1 mol% Ni, and referred to as Ni-
170 pyrite1%. This latter sample was synthesized according to a protocol derived from that reported by [Wei](#)
171 [and Osseo-Asare \(1997\)](#). For this purpose, 0.67 g $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 6 mg $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ were dissolved
172 separately in 10 mL of double-distilled and oxygen-free water, in an anaerobic chamber. Meanwhile,
173 0.6 g $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ was dissolved in 30 mL of double-distilled and oxygen-free water, and subsequently
174 added to the metal solution while stirring. The suspension obtained was sealed under anoxic conditions
175 and was gently stirred in the anaerobic chamber during 14 days. The solid fraction was collected after
176 centrifugation at 8,500 G for 10 min, and it was then rinsed three times with double-distilled and

oxygen-free water, and finally dried in a dessicator. XRD analyses confirmed the purity of the synthetic pyrite (Fig. S1) and XRF analyses indicated that it contains 1mol% Ni.

Ni-Mackinawite ($\text{Fe}_{0.99}\text{Ni}_{0.01}\text{S}$) was synthesized following the procedure of Donald and Southam (1999). 0.93 g $\text{Fe}(\text{SO}_4) \cdot 7\text{H}_2\text{O}$ and 6 mg $\text{Cl}_2\text{Ni} \cdot 6\text{H}_2\text{O}$ were dissolved separately in 10 mL of double-distilled and oxygen-free water, in an anaerobic chamber. Meanwhile, 0.6 g $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ was dissolved in 10 mL of double-distilled and oxygen-free water, and subsequently added to the metal solution while stirring. The suspension obtained was sealed under anoxic conditions and was gently stirred in the anaerobic chamber for 24h. The solid fraction was collected after centrifugation at 8,500 G for 20 min, and it was then rinsed three times with double-distilled and oxygen-free water, and finally dried in dessicator. XRD analyses confirmed the purity of the synthetic mackinawite (Fig. S1) and XRF analyses indicated that it contains 1mol% Ni.

Amorphous NiS (am-NiS) was prepared by neutralizing a Ni(II) salt solution with a basic Na_2S solution, following a procedure modified from Huang et al. (2009).

For Ni-adsorbed pyrite, the pyrite substrates were synthesized according to the protocols described above without adding Ni. For sorption experiments, 100 mg of synthetic pyrite was suspended in 100 mL of double-distilled water and dispersed with 15 min ultrasonic waves. In order to yield a constant ionic strength during the Ni sorption experiments, pH was adjusted to 5 with a 0.1 M HNO_3 solution. Then 500 mL double-distilled and oxygen-free water was added to the pyrite suspension. The pH of these suspensions was again adjusted to 5 with a 0.1 M HNO_3 solution. Finally, 800 mg KNO_3 was dissolved in 300 mL double-distilled and oxygen-free, and the pH was adjusted to 5 with a 0.1 M HNO_3 solution. This solution was added to the pyrite suspension, and the pH was adjusted to 5 with a 0.1 M HNO_3 solution. Meanwhile, 2.4 mg of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was dissolved in 100 mL double-distilled water. This solution was then adjusted to pH 5 with a 0.1 M HNO_3 solution and was added to the pyrite suspension while stirring. After 24 h reaction, the final pH was controlled and the solid fraction was separated by centrifugation at 8,500 G for 10 min, washed three times and dried in dessicator. The

same protocol was repeated for mackinawite. XRD analysis indicated that the products obtained after this treatment were still pure pyrite and mackinawite. XRF analyses indicated that these pyrite and mackinawite sorption samples both contained ~1mol% Ni.

Finally, Ni K-edge EXAFS spectra of Ni-bearing organometallic complexes were also recorded. Ni-citrate was synthesized by first dissolving 2.3 mg of $\text{Cl}_2\text{Ni} \cdot 6\text{H}_2\text{O}$ in 0.5 mL of a solution of 1 M citric acid and 1 mL of a solution of 1 M NaOH. The solution was then stirred and heated while at 50 ° C until total evaporation and precipitation of the complex. XRF analyses indicated that it contains 1mol% Ni. Ni- (Ni-GSH) and Ni-cysteine were obtained by dissolving 10 mg of $\text{Cl}_2\text{Ni} \cdot 6\text{H}_2\text{O}$ in 10 mL of double-distilled and oxygen-free water containing 200 mg of glutathione or cysteine. The pH was then raised to and stabilized at 8 with NaOH. The suspensions obtained were gently stirred during 2 h. The solid fraction was collected after evaporation in a dessicator. XRF analyses indicated that it also contains 1 mol% Ni.

2.4. X-ray Absorption Spectroscopy (XAS) data collection.

Ni K-edge XAS data for 12 selected samples from the three sediment cores were collected in X-ray fluorescence detection mode at 10K on the wiggler beamline BL 11-2 at the Stanford Synchrotron Radiation Lightsource (SSRL, CA, USA). The XAS data for model compounds were recorded at 20 K in fluorescence detection mode on the bending magnet SAMBA beamline (SOLEIL, Saint-Aubin, France) and at 40K in transmission detection mode on the bending magnet BM23 beamline at the European Synchrotron Radiation Facility (ESRF, Grenoble, France). Fluorescence-yield spectra were collected with a Canberra® high-throughput Ge 30-element solid-state array detector on the BL 11-2 and SAMBA beamlines. The energy of the incoming X-ray beam was monitored with a Si(220) double-crystal monochromator on BL 11-2 and SAMBA, and with a Si(111) double-crystal monochromator on BL BM23. Focusing of the second mirror on BL11-2 yielded energy resolution of

~0.9 eV at the Ni K-edge with a beam height of 0.5 mm. Dynamic sagittal focusing of the second crystal was used at the SAMBA beamline (Briois et al. 2010), yielding energy resolution of ~0.7 eV at the Ni K-edge. Energy resolution was ~0.9 eV at the BM23 beamline with mono-slits set at 0.5 mm height. For all experiments, the energy of the XAS spectra was calibrated by setting the first inflection point of the absorption edge of a Ni metal foil at 8333 eV recorded in double-transmission setup. In order to preserve the oxidation state of the samples during XAS data collection, sample pellets were mounted on the cryostat sample rod within a glove box and carried to the beamline in a liquid nitrogen bath before being rapidly transferred into the He cryostat. Depending on the Ni concentration in the sample, between 2 and 18 XAS scans were averaged and normalized using the ATHENA code (Ravel and Newville 2005) to insure a reliable signal-to-noise ratio up to k of 11-12 Å⁻¹. EXAFS spectra were then extracted from these normalized data using the XAFS code (Winterer 1997) with E_0 value fixed to 8345 eV. Fourier transforms (FT) of the EXAFS spectra were obtained by Fast-Fourier-transformation of the k^3 -weighted experimental $\chi(k)$ function using a Kaiser-Bessel function window with the Bessel weight fixed at 2.5.

241

2.5. X-ray Absorption Spectroscopy (XAS) data analysis.

243

The Ni K-edge EXAFS spectra of 12 samples from the three sediment cores were analyzed by Principal Component Analysis (PCA) using the SIXPACK code (Webb 2005), in order to estimate the minimum number of components necessary to fit the whole set of these EXAFS spectra (Wasserman et al. 1999; Ressler et al. 2000). Appropriate model compound spectra were then selected by Target Transform (TT) analysis of our large set of natural and synthetic model compound spectra. The Ni K-edge EXAFS spectra of the 12 samples from the three sediment cores were then fit in k -space by a linear combination-least squares (LC-LS) fitting procedure using custom-built software based on the Levenberg-Marquardt minimization algorithm (Dublet et al. 2012; Noël et al. 2014). The quality of the

252 LC-LS fits was estimated using an R -factor ($Rf = NSSR$) of the following form: $Rf = \sum [k^3\chi(k)_{\text{exp}} -$
 253 $k^3\chi(k)_{\text{calc}}]^2 / \sum [k^3\chi(k)_{\text{exp}}]^2$. The accuracy of this fitting procedure ranges between $\pm 5\%$ and $\pm 25\%$ of
 254 the stated values for each individual contribution, and the detection limit for minor species is estimated
 255 to be $\geq 10\%$. Contributions below this limit are considered not to be statistically significant (Ostergren
 256 et al. 1999; Cancès et al. 2005).

257 The local structure around Ni in the model compounds used for the abovementioned LC-LS procedure
 258 was determined by analyzing their Ni K-edge EXAFS spectra, either via an *ab initio* calculation on an
 259 atomic cluster, or via a classical shell-by-shell fitting procedure, and using phase-shift and amplitude
 260 functions calculated with the Feff8.1 code in both cases.

261 For *ab initio* calculations, atomic clusters around the Ni atom were generated using the Atoms code
 262 (Ravel 2001) on the basis of relevant available crystal structure after appropriate changes of site
 263 occupancies and of cell parameters. The employed crystal structures were those of talc (Perdikatsis and
 264 Burzlaff, 1981), lizardite (Mellini, 1982), pyrite and vaesite (Wyckoff, 1963), and mackinawite
 265 (Lennie, 1995). For each cluster, a few hundred theoretical phase-shift and amplitude functions were
 266 calculated using the FEff8.1 code (Ankudinov et al. 1998), over a radius of 8 Å, including multiple
 267 scattering paths up to nleg=6 with criteria=1.5, and without using the self-consistent potential option in
 268 order to faster the calculations. The theoretical EXAFS spectrum was reconstructed using all theses
 269 path functions and was then Least-Squares fit to the experimental EXAFS spectrum of the chosen
 270 model compound using a custom-built software based on a Levenberg-Marquardt minimization
 271 algorithm, refining only an overall Debye-Waller parameter σ and a threshold energy shift ΔE_0
 272 parameter, with S_0^2 fixed to 1. The fit quality was estimated using a Rf value. Uncertainty on each
 273 refined parameter was estimated as $3 \times \sqrt{VAR(p) \chi_R^2}$, where $VAR(p)$ is the variance of parameter p returned
 274 by the Levenberg–Marquardt routine for the the lowest Rf .

For the shell-by-shell fitting procedure, the unfiltered k^3 -weighted spectra were Least-squares fit in k -space with the plane-wave EXAFS formalism (Teo, 1986), using a custom-built software based on Levenberg–Marquardt minimization algorithm, with S_0^2 fixed to 1. The phase theoretical phase-shift and amplitude functions used in this procedure were calculated with the FEF8.1 code using the crystal structures of goethite, talc and vaesite reported by Forsyth et al. (1968), Perdikatsis and Burzlaff (1981) and Wyckoff (1963), respectively. Goodness of fit was estimated by a reduced chi-squares $\chi_R^2 = \frac{N_{ind}}{(N_{ind}-N_p)N_{points}} \frac{1}{\varepsilon^2} \sum (k^3\chi_{exp}(k) - k^3\chi_{calc}(k))^2$, where $N_{ind} = (2\Delta k\Delta R)/\pi$ is the number of independent parameters, N_p is the number of free fit parameters, N_{points} the number of data points and ε is the measurement uncertainty (Ravel and Newville 2005). The ε value was estimated as the root mean square of the Fourier back-transform of the data in the 15-25 Å R -range. Uncertainty on each refined parameter was estimated as $3 \times \sqrt{VAR(p)} \chi_R^2$, where $VAR(p)$ is the variance of parameter p returned by the Levenberg–Marquardt routine for the the lowest χ_R^2 .

3. Results

3.1. Mineralogy of the mangrove sediments.

Located upstream of the mangrove forest studied, the Koniambo regolith consists of deeply weathered ultramafic rocks and thus hosts high concentrations of Fe, and to a lesser extent, Ni, Co, Cr, and Mn (Becquer et al. 2001; Quantin et al. 2001; Fandeur et al. 2009; Dublet et al. 2012; 2015). It is composed of an upper laterite unit consisting of goethite with minor amounts of hematite and Mn-oxides, and of a deeper saprolite unit consisting of serpentine and talc, with minor amounts of olivine and pyroxene (Fandeur et al. 2009; Dublet et al. 2012; 2015). Erosion of these materials down to the mangrove areas has influenced the mineralogy of the mangrove sediments (Noël et al. 2014). In the top

sediment horizons, serpentine ($\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$), quartz (SiO_2), and halite (NaCl) are then associated with talc ($\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$) and goethite ($\alpha\text{-FeOOH}$). However, due to the strong redox gradient observed with depth in the mangrove sediments from inland salt flat to the sea front (Noël et al. 2014), some mineralogical changes are observed and goethite disappears in favor of pyrite (FeS_2) in the deeper horizons beneath both the *Avicennia* and *Rhizophora* stands.

3.2. Distribution of Ni in the mangrove sediments.

Ni concentrations in the sediment samples from the salt flat to the *Rhizophora* stand range from 0.05 wt% to 0.52 wt%, with an average concentration of 0.27 wt% (Table 1). This average concentration is higher than the background level reported for mangrove sediments in other parts of the world (Lewis et al. 2011), but the highest Ni concentration measured in our samples is similar to that measured in other mangrove sediments from New Caledonia (Marchand et al. 2012). Such large Ni concentrations likely result from erosion of the Koniambo lateritic regolith (Noël et al. 2014) that has developed over ultramafic rocks and contains $\sim 0.5 - 1.5$ wt% Ni (Dublet et al. 2012). In order to evaluate the mass balance for Ni in the studied mangrove sediments, we used a simplified approach on the basis of the approach developed by Brimhall and Dietrich (1987). The Ni concentration in each selected horizon was compared to that of Ti, which is classically considered as a geochemical invariant. For each mangrove stand, the Ni/Ti ratio was then normalized to that of the upper sediment level (0 - 2.5 cm), which was considered as representative of the detrital sedimentation. In the sediments beneath the salt flat, this normalized Ni/Ti ratio remains constant with increasing depth (0-50 cm; Fig. 1). In contrast, the normalized Ni/Ti increases below 20 cm depth in the sediments beneath the *Avicennia* stand, and a maximum is observed at ~ 25 cm depth (Fig. 1). In the sediments beneath the *Rhizophora* stand, the normalized Ni/Ti ratio increases significantly down to 7.5 cm depth and then decreases to values slightly lower or equal to that of the detrital source at greater depths (12-50 cm; Fig. 1). This latter

observation suggest that the relative mobility of Ni with respect to Ti varies across the intertidal redox gradient, with a relative accumulation beneath the *Avicennia* stand and a relative depletion at depth in beneath the *Rhizophora* sediments. These results are in agreement with dissolved Ni concentration measured in pore-waters that also suggest greater mobility of nickel beneath *Rhizophora* stand (between 10 and 49 $\mu\text{mol/L}$) than beneath *Avicennia* stand (between 0.7 and 2.5 $\mu\text{mol/L}$; Table1). Better understanding of these variations motivated further investigation on Ni speciation in the mangrove sediments, as reported below.

3.3. Qualitative Ni speciation in mangrove sediments.

SEM-EDXS analyses reveal that Ni is associated with two distinct types of pyrites in the samples collected in the deeper anoxic levels of the sediments beneath the *Avicennia* and *Rhizophora* stands (Fig. 2). Small-sized spherulitic pyrites showed the highest Ni/Fe atomic ratio (0.01 – 0.04),, whereas cuboctahedral pyrites with a diameter above 300 nm do not contained detectable amounts of Ni (Fig. S2). In addition, SEM-EDXS analyses indicated that Ni was systematically detected in minor amounts in goethite from the upper layers and in phyllosilicate minerals.

Ni K-edge EXAFS spectra of bulk sediment samples collected in the salt flat and beneath the *Avicennia* and the *Rhizophora* stands are shown in Fig. 3, together with their corresponding Fourier-Transforms. The EXAFS spectra of the samples from the top of the three cores compare well with those of Ni-bearing phyllosilicates and Ni-bearing goethite (Fig. 4 and 5). In addition, the white line at ~ 8352 eV in the XANES spectra of these top layer sediment samples show characteristic features of a Ni-bearing phyllosilicate (Fig. S3). In contrast, the Ni K-edge EXAFS spectra of the bottom core samples beneath the *Avicennia* and *Rhizophora* stands (Fig. 3) more resemble those of Ni-pyrite model compounds (Fig. 4). In addition, their XANES spectra exhibit a shoulder at the low energy side of the edge, consistent with the presence of Ni-sulfide as Ni-pyrite (Fig. S3), likely in mixture with other Ni

species. Owing to the similarity in XANES spectra for the various Ni model compounds used in this study (e.g., between Ni-goethite and Ni-citrate [Fig. S3](#)), determining the speciation of Ni in the complex natural samples studied thus required quantitative analysis of the EXAFS spectra.

3.4. Quantitative speciation of Ni in the mangrove sediments.

The Ni species in the 12 mangrove sediment core samples were determined by linear combination least squares fitting of their Ni K-edge EXAFS spectra, using experimental EXAFS spectra of selected model compounds as fitting components. The choice of these model compounds was based on a Principal Component Analysis and Target Transform (PCA-TT) procedure. In a first step, the Factor Indicator Function (IND parameter; [Malinowski 1977; 1991](#)) obtained from the PCA analysis reached a minimum value (i.e. 0.103) when considering the four first principal components ([Table S1](#)), suggesting that at least four spectral components were needed to fit the 12 EXAFS spectra of the mangrove sediments. Accordingly, systematic reconstruction of these spectra using the two, three and four first components extracted by the PCA indicated that the four first components that explains 83% of the total variance of the system perfectly reconstructed the 12 EXAFS spectra ([Fig. S4](#)). The first three principal components that explains 77% of the total variance, and which corresponded to an IND parameter value of only 0.104, were however sufficient to reliably reconstruct the 12 EXAFS spectra, as shown in [Fig. S4](#).

In the second step target transformation (TT) was then used to select the EXAFS spectra of model compounds that most likely represent the set of experimental spectra. For that purpose, all EXAFS spectra of model compound with a SPOIL value below 6 were considered as possible components ([Malinovsky 1978; Ndiba 2008](#)) and are displayed in [Fig. S5](#). Among these EXAFS spectra, those of Ni-rich phyllosilicates (Ni-kerolite, Ni-saponite, and Ni-rich talc) yielded the lowest SPOIL values ($\text{SPOIL} \leq 1.5$) and could then be classified as excellent model compounds ([Table S2](#)), which suggested

374 that such Ni species are likely to occur in the studied mangrove samples. In addition, the SPOIL values
 375 ($\text{SPOIL} \leq 2.24$ and ≤ 4.75 , respectively) obtained for the EXAFS spectra of Ni-poor serpentine, am-
 376 NiS, Ni-citrate, Ni-glutathione, Ni-rich pyrite, Ni-montmorillonite, Ni-mackinawite, Ni-bearing and Ni-
 377 sorbed goethite, $\text{Ni}(\text{OH})_2$, Ni-sorbed pyrite, Ni-cysteine, and Ni-pyrite indicated that these model
 378 compounds were good to fair according to Malinowski (1978) (Table S2).
 379 All the spectra of these model compounds that had a SPOIL value below 6 were then systematically
 380 evaluated as possible fitting components in three- and four-components fits of the 12 mangrove
 381 sediments EXAFS spectra. During this trial procedure, contributions below 10% were progressively
 382 removed in order to retain only the three or four components with contributions higher than 10%.
 383 The best LC-LS fits of the mangrove sediments EXAFS spectra were then obtained using 3 fitting
 384 components among the 6 following model compounds spectra: Ni-goethite, Ni-rich talc, Ni-
 385 montmorillonite, Ni-poor serpentine, Ni-sorbed pyrite, Ni-pyrite (1 mol% Ni), and Ni-rich pyrite (10
 386 mol% Ni). These three-components LC-LS fits are displayed in Fig. 3 for all mangrove samples
 387 studies, with proportion of the fitting components reported in Fig. 1 and in Table 2. Four-components
 388 fits that are reported in Electronic Annex (Figs. S6 and S7 and Table S3) slightly improved the fit
 389 quality for the Salt flat and *Avicennia* samples. However this improvement only improved the R_f of
 390 $\sim 10\%$ (Table S3 and Table 2) and since it relied on the addition of minor clay components in the 10-17
 391 % range, it was not further considered in our analysis. Moreover, addition of organic Ni-species such as
 392 Ni-citrate or Ni-glutathione, or of other Ni-sulfide compounds as Ni-mackinawite or am-NiS did not
 393 improve the three or four-component fits.
 394 The EXAFS LC-LS fitting results (Fig. 1, Table 2) indicate that, in the sediments collected beneath the
 395 salt flat, Ni is mainly present in the structure of clay minerals with a dominant contribution from Ni-
 396 poor serpentine (44-58%), and at a lesser extent, in the structure of goethite, without significant
 397 variation with depth (Fig. 1). In contrast, in the sediments collected beneath the *Avicennia* and
 398 *Rhizophora* stands, the dominant Ni-clay component consists of Ni-montmorillonite (20-70%) and Ni

speciation changes significantly with depth (Fig. 1, Table 2) with Ni-rich talc and Ni-goethite species being replaced by Ni-sorbed pyrite and Ni-pyrite at depth. Indeed, Ni-goethite and Ni-rich talc that host 15-20% and 25-50% of total Ni in the upper horizon decrease to undetectable amounts below ~20 cm depth. A large fraction of Ni is sorbed to pyrite in the intermediate depth horizons (52% at 17.5 cm depth beneath the *Avicennia* stand, and 24 and 37% at 12.5 and 27.5 cm depth, respectively beneath the *Rhizophora* stand). Finally, beneath the *Avicennia* stands, Ni-pyrite appear as a major Ni pool (34-55%) at 22.5 cm depth and below. Beneath the *Rhizophora* stands Ni-pyrite only appear in the deepest horizon (41% of Ni at 47.5cm depth) (Fig. 1, Table 2). In addition, the presence of a Ni-pyrite10% component is indicated by EXAFS LC-LS fit in the 22.5 and 32.5 cm depth sediments samples under the *Avicennia* stand. Indeed, including the Ni-pyrite10% spectrum as an additional fitting component to the the Ni-pyrite1% spectrum improved the R_f value of 40% for these samples, as illustrated for the 22.5 cm sample in Fig. S8. Mixing such a Ni-rich pyrite component (10 mol% Ni) with the Ni-pyrite1% component (1 mol% Ni), can be considered as building a proxy to match the spectrum of the natural Ni-pyrite of the mangrove sediments that could have intermediate Ni content. Such approach is supported by SEM-EDXS analyses showing that Ni is associated with distinct types of pyrites having Ni content in the 1–4 mol% range. Moreover, the Ni K-edge EXAFS spectrum of Ni substituting for Fe in pyrite is expected to change with Ni substitution rate, because of a progressive structural relaxation of the local environment around Ni in the pyrite structure, as discussed in the next section.

3.5. Local structure around Ni in pyrite and in the other model compounds relevant of the mangrove sediments studied.

In order to better interpret the changes in Ni speciation evidenced from LC-LS fitting of the mangrove sediments, we have conducted a detailed analysis of the local structure around Ni in the various model compounds that represent the dominant Ni species in the sediment studied.

424 *Ab initio* calculations of the Ni K-edge EXAFS spectra for Ni-pyrite (1 mol% Ni) and Ni-rich-pyrite
425 (10 mol%) model compounds (Fig. 4, Table 3) revealed significant differences in the local structure
426 around Ni in pyrite as a function of Ni substitution levels. Indeed, to match the spectrum of our Ni-
427 pyrite1% model compound (Fig. 4), the *a* unit cell parameter of a pyrite cluster was increased from
428 5.41 Å to 5.52 Å for the first shell around the central Ni atom and to 5.45 Å for the second shell, and
429 kept equal to 5.41 Å for longer distances (Table 3). By contrast, in order to match the spectrum of our
430 Ni-pyrite10% model compound (Fig. 4), the *a* unit cell parameter of a vaesite (NiS₂) cluster was
431 decreased from 5.677 Å to 5.615 Å (Table 3). The corresponding differences in the Ni-S first neighbor
432 distance and in the Ni-Fe/Ni second neighbor distance for the Ni-pyrite1% and Ni-pyrite10%
433 compounds ($d(\text{Ni-S}) = 2.31\text{Å}$ and 2.37Å and $d(\text{Ni-Fe/Ni}) = 3.85\text{Å}$ and 3.97Å , respectively) indicate
434 that the local relaxation around Ni²⁺ ions in the pyrite structure increases with Ni²⁺ for Fe²⁺ substitution
435 level. These interatomic distances fall between the corresponding distances in the pyrite ($d(\text{Fe-S})=2.26$
436 Å; $d(\text{Fe-Fe})=3.825\text{Å}$) and vaesite ($d(\text{Ni-S}) 2.396\text{ Å}$; and $d(\text{Ni-Ni})=4.01\text{ Å}$ end-members. These results
437 confirm that different local structural environments can be distinguished by EXAFS spectroscopy for
438 variable amounts of Ni incorporated in the pyrite structure.

439 *Ab initio* EXAFS calculation for our synthetic mackinawite model compounds is reported in Fig. 4 and
440 Table 3 and attests that Ni substitutes for Fe in the mackinawite structure in this sample. Similar
441 calculations for the Ni-rich talc and Ni-poor serpentine model compounds confirm that Ni occupies
442 octahedral sites in the structure of the trioctahedral layer, with local chemical compositions consistent
443 with Ni_{2.5}Mg_{0.5} and Ni_{0.5}Mg_{2.5} in the Ni-rich talc and Ni-poor serpentine respectively. Such
444 approach was successfully used for analyzing the local environment of Zn and Ni in natural
445 phyllosilicates (Juillot et al. 2006; Dublet et al. 2012).

446 Shell-by-shell fit of the synthetic Ni-goethite model compound (Fig. 5, Table 4) confirms that Ni
447 substitutes for Fe in this sample, as already discussed in Dublet et al. (2012). For the Ni-
448 montmorillonite sample, the number of Al/Mg neighbor around Ni at a distance of $\sim 3\text{Å}$ ($N=0.6$) is

lower than the value of 2 expected for Ni substitution in the dioctahedral layer (Table 4). This result suggests that a fraction of Ni might be sorbed to the edges of the layer or present inserted within the interlayer space. The Ni-citrate model compound exhibit Ni-O and Ni-C distances in good agreement with the range of distances reported for the structure of crystalline Ni-citrate (Baker et al. 1983). Our synthetic Ni-glutathione complex (1 mol% Ni) exhibits a coordination number close to ~3, higher than that reported for Ni-GSH complexes obtained for a lower Ni/GSH ratio of 1:4 (Krezel and Bal 2004). Finally the observed distances in the Ni-sorbed pyrite (Table 4, Fig. 5) indicate inner sphere complexes with a local structure close to that of Ni-incorporated in pyrite but with a number of second and third neighbors decreased by a factor of ~3.

4. Discussion

4.1. Evolution of the Ni-speciation along the major redox gradients.

The present study shows that nickel in the salt flat sediments as well as in the upper horizon beneath the *Avicennia* and *Rhizophora* stands is hosted primarily by phyllosilicate minerals and goethite, which have been shown by Dublet et al. (2012) to be major Ni species in the Koniambo regolith, located upstream of the mangrove forest. This result confirms that a major Ni input to the mangrove sediments is related to erosion of the lateritized ultramafic outcrops. Beyond these erosion/sedimentation processes, the present study also reveals major changes in Ni speciation along the redox gradients that develop across the intertidal zone, from land to the sea and with depth in the hydromorphic mangrove sediments beneath the *Avicennia* and *Rhizophora* stands. In these suboxic to anoxic sediments, Ni-bearing goethite and Ni-rich talc disappears gradually with depth and new Ni-species appear (Ni sorbed

on pyrite, Ni in pyrite) (Fig. 1; Table 2). These phases formed as the result of reductive dissolution of ferric oxyhydroxydes and, at greater depth, sulfate reduction and pyrite formation.

4.2. Differential stability of Ni-pyrites across the intertidal zone.

The present study shows that pyrite acts as an efficient sink for Ni in the deepest anoxic horizons beneath the *Avicennia* (34 – 55% of total Ni below 22.5 cm depth; Fig. 1, Table 2) and *Rhizophora* stands (42% of total Ni at 47.5 cm depth Fig. 1, Table 2), which is consistent with the fact that Fe and Ni are commonly incorporated in sulfide minerals in sulfidic environments (Huerta-Diaz 1992, Aragon and Miguens 2001). Moreover, Fe-sulfide minerals have been reported to dominate the partitioning of Ni in the solid fraction of recent sediments (Nissenbaum and Swaine 1976, Burton et al. 2006, Baltzer 1982; Doig and Liber 2006). In the present study, Ni K-edge EXAFS results show that the Ni sulfide pool in the mangrove sediments consists primarily of Ni²⁺-bearing pyrite with no evidence for pure Ni-sulfide phases from SEM-EDXS analyses. Furthermore, no Ni-mackinawite could be detected in the present Ni K-edge EXAFS analysis, which is in agreement with the results of a precedent study using Fe K-edge EXAFS data, which indicated that no Acid Volatile Sulfide (AVS) in the form of mackinawite or greigite could be detected in the same sediments samples (Noël et al. 2014). The absence of these intermediate phases, which are known to transform with time into pyrite (Morse et al. 1987), suggests that the pyritization process is particularly intense in the studied mangrove sediments (Rickard and Morse 1987). However, the results of the LC-LS fitting of experimental EXAFS spectra suggest that the pyrite forming under *Avicennia* stand is more enriched in Ni than that under *Rhizophora* stand. Such result could be explained by a differential stability of distinct generations of pyrites with respect to re-oxidation processes related to tidal fluctuations (Noël et al. 2014) since two generations of pyrites, differing in their morphologies and Ni contents, were recognized by SEM-EDXS analyses (Fig. 2). Following this hypothesis, the small Ni-rich pyrites would be more sensitive

to oxidative dissolution, since it has been reported that the size and crystallinity of pyrite can directly influence its resistance to oxidation (Silverman 1961). Such reoxidation process would explain the lower abundance of small Ni-rich pyrites in the *Rhizophora* zone that is the closest to the shore and is thus subjected to more frequent reduction-oxidation cycles during tidal fluctuations (Noël et al. 2014) (Fig. 6). Finally, EXAFS results show that a significant fraction of Ni is sorbed to pyrite surfaces in the intermediate depth samples beneath the *Avicennia* and *Rhizophora* stands, without significant incorporation of Ni in pyrite in these samples, which may have significant implications on Ni mobility, as discussed thereafter.

506

4.3. Origin and evolution of the Ni-bearing phyllosilicate minerals in the mangrove sediments and contribution to the Ni cycling

509

Beyond iron oxyhydroxide and sulfide minerals, 52–88% of total Ni is found associated with the phyllosilicate minerals, including montmorillonite, serpentine and talc (Fig. 1; Table 2). Although the serpentine and talc components are of common constituents of the lateritic source materials of the studied sediments, dioctahedral 2:1 phyllosilicates are not. Study of mineralogical composition and Fe speciation of these sediment samples indicated that Fe-rich smectite precipitated in the New Caledonia mangrove sediments studied (Noël et al., 2014). Such mineral has been previously reported as a major Fe-bearing phase in mangrove sediments, and it was proposed to be either newly formed or inherited from past marine transgressions (De Souza-Júnior et al., 2010; Noël et al., 2014). In line with these findings, the high proportion of Ni associated to montmorillonite evidenced by our EXAFS analysis suggests that neoformed smectites may have trapped a major fraction of Ni in the sediments beneath vegetated stand (38–69% of total Ni; Fig. 1 and Table 2; Fig. 6).

For the sediment cores collected beneath vegetated zones (*Avicennia* and *Rhizophora* stands) montmorillonite represents the dominant Ni-clay pool all along the core depth, the other Ni-clay hosts

being talc in the upper horizons and serpentine in deeper horizons (Fig. 1). The disappearing with depth of the Ni-rich talc component inherited from erosion of lateritic material, suggests either that the sedimentary regime of the Vavouto mangrove evolved over time, or that this phyllosilicate pool dissolved in hydromorphic, and sulfidic conditions that prevail at depth in the sediments beneath the vegetated zones. By contrast, in the salt flat where the ferric oxyhydroxides to pyrite transition is not observed (Noël et al., 2014), the serpentines and the Ni-rich talc inherited the lateritic material are both preserved. Among the Ni-bearing phyllosilicates inherited from detrital sedimentation, serpentine is relatively poor in nickel and well crystallized, while talc is enriched in Ni and more poorly ordered (Dublet et al., 2012). The occurrence of a Ni-poor serpentine pool in the deep horizons beneath the vegetated zones, although in a much lower amount than in the salt flat (Fig. 1) might reflect a higher stability of these well-crystallized minerals compared to poorly ordered Ni-rich talc. We thus infer that Ni-rich phyllosilicates are unstable in the hydromorphic and sulfidic conditions developed in mangrove sediments beneath vegetated zones and progressively dissolve, thus releasing Ni to pore-water, which may then be redistributed between neorformed smectites and pyrites via incorporation and sorption reactions (Fig. 6). However, even if reductive dissolution of phyllosilicates has been suggested for Brazilian mangrove (Otero et al., 2009) and for New Caledonia mangrove (Noël et al., 2014), the importance of this process, so far observed only in laboratory experiments (Kostka et al., 1999; Li et al., 2004), remains to be demonstrated under field conditions.

4.4. Environmental Implications.

Our results show major changes in Ni speciation, both vertically and laterally, across the intertidal zone in the mangrove sediments. These changes are accompanied by significant variations in Ni concentration across the intertidal zone and with depth. Beneath the salt flat, in which Ni species inherited from the erosion of lateritic material are preserved, the Ni concentration normalized to that of

548 Ti suggests that Ni is neither stored nor leached. This result is in agreement with those from previous
549 studies which showed that the salt flat is characterized by the quasi absence of redox cycling (Otero et
550 al. 2009). Beneath the *Avicennia* stand, the average Ni concentration normalized to that of Ti suggests a
551 storage of Ni at depth, supported by low dissolved Ni concentration in pore-waters ($\sim 1.55 \mu\text{mol/L}$;
552 Table 1), which could be related to the dominant incorporation of Ni in pyrite observed in these
553 sediments (Fig. 1; Fig.6). In contrast, beneath the *Rhizophora* stand, the change in this ratio with depth
554 indicates that Ni does not accumulate but is rather slightly leached at depth. This suggestion is supported
555 by high dissolved Ni concentration in pore-waters ($\sim 18.74 \mu\text{mol/L}$; Table 1). Such behavior could be
556 interpreted as resulting from reoxidation of Ni-bearing pyrites, which may favor Ni leaching (Fig. 6).
557 This hypothesis is supported by a previous study of Fe speciation in these mangrove sediments, which
558 showed that Fe-sulfides are subject to periodic reoxidation in the *Rhizophora* stand likely because of
559 tidal fluctuations (Noël et al. 2014). By contrast, the apparent relative accumulation of Ni in the deepest
560 horizon of the *Avicennia* stand emphasizes the importance of Fe(II)-sulfides for mitigating the
561 dispersion of Ni in mangrove sediments from New Caledonia.

562 In active redox boundaries beneath vegetated zones (10-30 cm depth), Ni K-edge XAS data indicate
563 the occurrence of Ni sorbed on pyrite, in addition to Ni-bearing goethite, sulfide and phyllosilicates
564 (Fig. 1, Table 2). Ni sorption on pyrite is not surprising considering the reported affinity of this element
565 and other divalent cations for the surface of Fe(II)-sulfides (Kornicker et al., 1991; Parkman et al.,
566 1999) and intense pyritization process reported in this system (Noël et al., 2014). However, the
567 presence of such Ni-sorbed species suggests that a fraction of the Ni pool that may be mobilized either
568 via reductive dissolution/sulfidization of goethite and Ni-rich talc or by reoxidation of pyrite readsorbs
569 first sorbs onto the pyrite surface, and may thus be potentially more labile, at this redox boundary, than
570 when incorporated in pyrite in the deeper sediment layers. Consequently, we hypothesize that Ni is
571 potentially more mobile in active redox boundaries beneath vegetated zones (10-30 cm depth),

especially under the *Rhizophora* stand, while the deepest horizon where Ni is co-precipitated with pyrite are an efficient sink for Ni especially under the *Avicennia* stand (Fig. 6).

Our EXAFS results suggest that Ni is not significantly bound to organic ligands. This result contrasts with some previous studies of mangrove sediments which suggested Ni was partly associated to organic, on the basis of chemical extractions (Marchand et al. 2012) or chemical correlations (Ray et al. 2006). However the nature, distribution, and persistence of organic molecules in mangrove sediments may be highly variable (Alongi et al. 2000, Kristensen et al. 2008). Further studies may thus be required to better explore the affinity of nickel for organic ligands, in mangrove sediments and especially for dissolved organic matter in the pore waters of mangrove sediments, where concentrations can as high as 9 mmol.L⁻¹ (Marchand et al. 2006b).

5. Acknowledgments

This study was performed in the framework of a UPMC Paris 6/CNRS (IMPMC)/IRD - Koniambo Nickel SAS (KNS) joint project. Field sampling campaigns were greatly facilitated by Sylvain Capo (KNS-GLENCORE), Andy Wright (KNS), Gregory Marakovic (KNS), and Jacques Loquet (Koniambo Environmental Committee). The authors thank Imene Esteve (IMPMC) for her help during Scanning Electron Microscope observations and analyses and Ludovic Delbes (IMPMC) for carrying out the X-ray diffraction experiments under anoxic conditions. SEM and XRD equipments of IMPMC were granted by Region Ile de France, CNRS and UPMC. Partial support for this project was provided by the U.S. National Science Foundation through the Center for Environmental Implications of Nanotechnology (GB). The technical staffs at SSRL (Stanford, USA), ESRF (Grenoble, France), and SOLEIL (Saint-Aubin, Paris) are also acknowledged for their technical support during XAS

596 measurements. SSRL and SLAC are supported by the U.S. Department of Energy, Office of Science,
597 Office of Basic Energy Sciences under Contract No. DE-AC02-76SF00515, the DOE Office of
598 Biological and Environmental Research, and by the National Institutes of Health, National Institute of
599 General Medical Sciences (including P41GM103393). Partial support was provided by the U.S.
600 Department of Energy, Office of Biological and Environmental Research (BER), Subsurface
601 Biogeochemical Research (SBR) program under subcontract DE-AC02-76SF00515.

602

603 **6. References**

604

605 Alongi D.M., Tirendi F., Clough B.F. (2000) Below-ground decomposition of organic matter in forests
606 of the mangroves *Rhizophora stylosa* and *Avicennia marina* along the arid coast of Western
607 Australia. *Aquatic Botany* **68**, 97-122.

608 Ankudinov A.L., Ravel B., Rehr J.J., Conradson S.D. (1998) Real-space multiple-scattering calculation
609 and interpretation of X-ray-absorption near-edge structure. *Phys. Rev. B* **58**, 7565–7576.

610 Aragon G., Miguens F. (2001) Microscopic analysis of pyrite in the sediments of two Brazilian
611 mangrove ecosystems. *GeoMar. Lett.* **21**, 157–161.

612 Baker E.N., Baker H.M., Anderson B.F., Reeves R.D. (1983) Chelation of nickel(II) by citrate. The
613 crystal structure of a nickel–citrate complex, $K_2[Ni(C_6H_5O_7)(H_2O)_2]_2 \cdot 4H_2O$. *Inorganica Chimica*
614 *Acta.* **78**, 281–285.

615 Baltzer F. (1982) Geodynamique de la sedimentation et diagenese precoce en domaine ultrabasique –
616 Nouvelle Caledonie. *Travaux et Documents de l'ORSTOM* **152**, 283p.
617 http://horizon.documentation.ird.fr/exl-doc/pleins_textes/pleins_textes_5/pt5/travaux_d/02460.pdf

618 Bayen S. (2012) Occurrence, bioavailability and toxic effects of trace metals and organic contaminants
619 in mangrove ecosystems : A review. *Environ. Internat.* **48**, 84-101.

620 Bayliss P. (1977) Crystal structure refinement of a weakly anisotropic pyrite. *Am. Mineral.* **62**, 1168-
621 1172.

622 Becquer T., Petard J., Duwing C., Bourdon E., Moreau R., Herbillon A.J. (2001) Mineralogical,
623 chemical and charge properties of Geric Ferralsols from New Caledonia. *Geoderma* **103**, 291-306.

624 Brimhall G.H., and Dietrich W.E. (1987) Constitutive mass balance relations between chemical
625 composition, volume, density, porosity, and strain in metasomatic hydrochemical systems: Results
626 on weathering and pedogenesis. *Geochimica et Cosmochimica Acta* **51**, 567-587.

627 Briois V., Fonda E., Belin S., Barthe L., Fontaine C.L., Ribbens M. (2010) SAMBA : The 4 – 40 keV
628 X-ray absorption spectroscopy beamline at SOLEIL. *EDP Science* **2010**, 41-47.

629 Burton E.D., Bush R.T., Sullivan L.A. (2006) Fractionation and extractability of sulfur, iron and trace
630 elements in sulfidic sediments. *Chemosphere* **64**, 1421-1428.

631 Burton E.D., Bush R.T., Sullivan L.A., Johnston S.G., Hocking R.K. (2008) Mobility of arsenic and
632 selected metals during re-flooding of iron- and organic-rich acid-sulfate soil. *Chem. Geol.* **253**,
633 64–73.

634 Cancès B., Juillot F., Morin G., Laperche V., Alvarez L. Proux O., Hazemann J-L, Brown Jr. G.E.,
635 Calas G. (2005) XAS Evidence of As(V) Association with Iron Oxyhydroxides in a Contaminated
636 Soil at a Former Arsenical Pesticide Processing Plant. *Environ. Sci. Technol.* **39**, 9398-9405.

637 Clark M.W., McConchie D., Lewis D.W., Saenger P. (1998) Redox stratification and heavy metal
638 partitioning in *Avicennia*-dominated mangrove sediments: a geochemical model. *Chem. Geol.*
639 **149**, 147–171.

640 Cosmidis J., Benzerara K., Morin G., Busigny V., Lebeau O., Jézéquel D., Noël V., Dublet G.,
641 Othmane G. (2014) Biomineralization of mixed valence iron-phosphates in the anoxic water
642 column of lake pavin (Massif Central, France). *Geochim. Cosmochim. Acta* **126**, 78–96.

643 De Souza-Júnior V.S., Vidal-torrado P., Garcia-González M.T., Macías F., Otero X.L. (2010) Smectite
644 in mangrove soils of the State of São Paulo, Brazil. *Science Agricola*, **67**(1), 47-52.

645 Di Toro D.M., Mahony J.D., Hansen D.J., Scott K.J., Carlson A.R., Ankley G.T. (1992) Acid volatile
646 sulfide predicts the acute toxicity of cadmium and nickel in sediments. *Environ. Sci. Technol.* **26**,
647 96-101.

648 Doig L.E., Liber K. (2006) Nickel partitioning in formulated and natural freshwater sediments.
649 *Chemosphere* **62**, 968–979.

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

653 Dublet G., Juillot F., Morin G., Fritsch E., Noel V., Brest J., Brown Jr. G.E. (2014) XAS Evidence for
654 Ni Sequestration by Siderite in a Lateritic Ni-Deposit from New Caledonia. *American*
655 *Mineralogist* **99**, 225-234.

656 Dublet G., Juillot F., Morin G., Fritsch E., Fandeur D., Brown Jr G.E. (2015) Goethite aging explains
657 Ni depletion in upper units of ultramafic lateritic ores from New Caledonia. *Geochimica et*
658 *Cosmochimica Acta* **160**, 1-15.

659 Duke N.C., Meynecke J.O., Dittmann S., Ellison A.M., Anger K., Berger U., Cannicci S., Diele K.,
660 Ewel K.C., Field C.D., Koedam N., Lee S.Y., Marchand C., Nordhaus I., Dahdouh-Guebas F.
661 (2007) A world without mangroves? *Science* **317**, 41-42.

662 Forsyth J.B., Hedley I.J., Johnson C.E. (1968) The magnetic structure and hyperfine field of goethite
663 (α -FeOOH). *Journal of Physics*, C1, 179-188.

664 Harbison P.A.T. (1986) Mangrove Muds-A Sink and a Source for Trace Metals. *Mar. Pollut. Bull.* **17**,
665 246-250.

666 Howarth R.W., Merkel S. (1984) Pyrite formation and the measurement of sulfate reduction in salt
667 marsh sediments. *Limnol. Oceanogr.* **29**, 598-608.

668 Huerta-Diaz M.A., Morse J.W. (1992) Pyritization of trace metals in anoxic marine sediments.
669 *Geochim. Cosmochim. Acta* **56**, 2681-2702.

670 Johnston S.G., Keene A.F., Burton E.D., Bush R.T., Sullivan L.A., McElnea A.E., Ahern C.R., Smith
671 C.D., Powell B. (2010) Arsenic mobilisation in a seawater inundated acid sulfate soil. *Environ.*
672 *Sci. Technol.* **44**, 2016–2021.

673 Juillot F., Morin G., Ildefonse P., Calas G., and Brown, Jr. G.E. (2006) EXAFS signature of structural
674 Zn at trace levels in natural and synthetic trioctahedral 2:1 phyllosilicates. *American Mineralogist*
675 **91**, 1432-1441.

676 King G.M. (1988) Patterns of sulphate reduction and the sulphur cycle in a South Carolina salt marsh.
677 *Limnol. Oceanogr* **33**, 376-90.

678 Kornicker W.A. and Morse J.W. (1991) The interactions of divalent cations with the surface of pyrite.
679 *Geochim. Cosmochim. Acta* **55**, 2159-2172.

680 Kortright J.B., Thompson A.C. (2009) X-ray emission energies, in *X-ray data booklet*, Albert C.
681 Thomson Ed., Lawrence Berkeley National Laboratory, California, USA.

682 Kostka J. E., Haefele E., Viehweger R., and Stucki J. W. (1999) Respiration and Dissolution of Iron
683 (III) -Containing Clay Minerals by Bacteria. *Environmental Science & Technology* **33**(18), 3127-
684 3133.

685 Krezel A., Bal W. (2004) Studies of Zinc(II) and Nickel(II) Complexes of GSH, GSSG and Their
686 Analogs Shed More Light on Their Biological Relevance. *Bioinorganic Chemistry and*
687 *Applications* **2**, 293-305.

688 Kristensen E., Bouillon S., Dittmar T., Marchand C. (2008) Organic carbon dynamics in mangrove
689 ecosystems: A review. *Aquatic Botany* **89**, 201-219.

690 Lacerda L.D., Carvalho C.E.V., Tanizaki K.F., Ovalle A.R.C., Rezende C.E. (1993) The
691 biogeochemistry and trace metal distribution of mangrove rhizospheres. *Bio-tropica* **25**, 252-257.

692 Lennie A., Redfern S., Schofield P., Vaugahn D.J. (1995) Synthesis and Rietveld crystal structure
693 refinement of mackinawite, tetragonal FeS. *Min. Mag.* **59**, 677-683.

694 Lewis M., Pryor R., Wilking L. (2011) Fate and effects of anthropogenic chemicals in mangrove

695 ecosystems: a review. *Environ. Poll.* 159:2328–2346.

696 Li Y.-I., Vali H., Sears S.K., Yang J., Deng B., Zhang C. L. (2004) Iron reduction and alteration of
 697 nontronite by a sulfate-reducing bacterium. *Geochimica et Cosmochimica Acta* **68**(15), 3251-
 698 3260.

699 Maitrepierre L. (2004) Bilan des mesures météorologiques effectuées pour le projet Koniambo.
 700 Direction interregionale de Nouvelle Calédonie et de Wallis et Futuna. METEO France.
 701 <http://www.meteo.nc/aller-plus-loin/nous-connaître/les-rapports-dactivite>.

702 Malinowski E.R. (1977) Determination of the number of factors and the experimental error in a data
 703 matrix. *Anal. Chem.* **49**, 612-617.

704 Malinowski E.R. (1978) Theory of error for target factor analysis with applications to mass
 705 spectrometry and nuclear magnetic resonance spectrometry. *Anal. Chim. Acta* **103**, 339–354

706 Malinowski E.R. (1991) *Factor Analysis in Chemistry*. John Wiley, New York.

707 Marchand C., Lallier-Verges E., Baltzer F., Alberic P., Cossa D., Baillif P. (2006a) Heavy metals
 708 distribution in mangrove sediments along the mobile coastline of French Guiana. *Marine Chem.*
 709 **98**, 1-17.

710 Marchand C., Albéric P., Lallier-Verges E., Baltzer F. (2006b) Distribution and characteristics of
 711 dissolved organic matter in mangrove sediment pore waters along the coastline of French Guiana.
 712 *Biogeochem.* **81**, 59-75.

713 Marchand C., Allenbach M., Lallier-Verges E. (2011) Relationships between heavy metals distribution
 714 and organic matter cycling in mangrove sediments (Conception Bay, New Caledonia). *Geoderma*
 715 **160**, 444-456.

716 Marchand C., Fernandez J., Moreton B., Landi L., Lallier-Verges E., Baltzer F. (2012) The partitioning
 717 of transitional metals (Fe, Mn, Ni, Cr) in mangrove sediments downstream of a ferralitized
 718 ultramafic watershed (New Caledonia). *Chem. Geol.* **300-301**, 70-80.

719 Mellini (1982) The crystal structure of lizardite 1T: hydrogen bonds and polytypism *Amer. Mineral.* **67**
720 587-598.

721 Morse J.W., Millero F.J., Cornwell J.C., Rickard D. (1987) The chemistry of the hydrogen sulfide and
722 iron sulfide systems in natural waters. *Earth Sci. Rev.* **24**(1), 1–42.

723 Morse J.W., Luther G.W. (1999) Chemical influences on trace metal-sulfide interactions in anoxic
724 sediments. *Geochim. Cosmochim. Acta* **63**, 3373–3378.

725 Nagelkerken I., Blaber S., Bouillon S., Green P., Haywood M., Kirton L.G., Meynecke J.O., Pawlik P.,
726 Penrose H.M., Sasekumar A., Somerfield P.J. (2008) The habitat function of mangroves for
727 terrestrial and marina fauna: a review. *Aquatic Botany* **89**(2), 155-185.

728 Nath B., Birch G., Chaudhuri P. (2013) Trace metal biogeochemistry in mangrove ecosystems: A
729 comparative assessment of acidified (by acid sulfate soils) and non-acidified sites. *Sci. Total*
730 *Environ.* **463–464**, 667–674.

731 Ndiba P., Axe L., Boonfueng T. (2008) Heavy metal immobilization through phosphate and thermal
732 treatment of dredged sediments. *Environ. Sci. Technol.* **42**, 920–926.

733 Nissenbaum A., Swaine D.J. (1976) Organic–metal interactions in recent sediments: the role of humic
734 substances. *Geochim. Cosmochim. Acta* **40**, 809–816.

735 Noël V., Marchand C., Juillot F., Ona-Nguema G., Viollier E., Marakovic G., Olivi L., Delbes L.,
736 Gelebart F., Morin G. (2014) EXAFS analysis of iron cycling in mangrove sediments downstream
737 a lateritized ultramafic watershed (Vavouto Bay, New Caledonia). *Geochim. Cosmochim. Acta*.
738 **136**, 211-228.

739 Nowack E., Schwarzenbach D., Hahn T. (1991) Charge Densities in CoS₂ and NiS₂ (Pyrite Structure).
740 *Acta Crystallogr.* **B47**, 650-659.

741 Ostergren J.D., Brown Jr. G.E., Parks G.A., Tingle T.N. (1999) Quantitative Speciation of Lead in
742 Selected Mine Tailings from Leadville, CO. *Environ. Sci. Technol.* **33**, 1627-1636.

- Otero X.L., Ferreira T.O., Huerta-diaz M.A., Partiti C.S.M., Souza Jr. V., Vidal-Torrado P., Macías F. (2009) Geochemistry of iron and manganese in soils and sediments of a mangrove system, Island of Pai Matos (Cananeia — SP, Brazil). *Geoderma* **148**, 318-335.
- Parkman R.H., Charnock J.M., Bryan N.D., Livens F.R., Vaughan D.J. (1999) Reactions of copper and cadmium ions in aqueous solutions with goethite, lepidocrocite, mackinawite, and pyrite. *Amer. Mineral.* **84**, 407–419.
- Perdikatsis B. and Burzlaff H. (1981) Strukturverfeinerung am talk $\text{Mg}_3[(\text{OH})_2\text{Si}_4\text{O}_{10}]$. *Zeitschrift für Kristallographie* **156**, 177-186.
- Qiu Y.W, Yu K.F., Zhang G., Wang W.X. (2011) Accumulation and partitioning of seven trace metals in mangroves and sediment cores from three estuarine wetlands of Hainan Island, China. *J. Hazard. Mat.* **190**, 631-638.
- Quantin C., Becquer T., Rouiller J.H., Berthelin J. (2001) Oxide weathering and trace metal release by bacterial reduction in a New Caledonia Ferralsol. *Biogeochem.* **53**, 323-340.
- Ravel B. (2001) ATOMS: crystallography for the X-ray absorption spectroscopist. *J. Synchrotron Rad.* **8**, 314-316.
- Ravel B., Newville M. (2005) *ATHENA, ARTEMIS, HEPHAESTUS*: data analysis for X-ray absorption spectroscopy using *IFEFFIT*. *J. Synchrotron Rad.* **12**, 537-541.
- Ray A.K., Tripathy S.C., Patra S., Sarma V.V. (2006) Assessment of Godavari estuarine Mangrove ecosystem through trace metal studies. *Environ. Internat.* **32**, 219–223.
- Ressler T., Wong J., Roos J., Smith I.L. (2000) Quantitative speciation of Mn-bearing particulates emitted from autos burning (methylcyclopentadienyl) manganese tricarbonyl- added gasolines using XANES spectroscopy. *Environ. Sci. Technol.* **34**, 950–958.
- Rickard D. and Morse J.W. (2005) Acid volatile sulfide (AVS). *Mar. Chem.* **97**, 141–197.

766 Silverman M., Rogoff M., Wender I. (1961) Bacterial oxidation materials in coal. *Appl. Microbiol.* **9**,
767 491-496.

768 Song J., Luo Y.M., Zhao Q.G., Christie P. (2003) Novel use of soil moisture samplers for studies on
769 anaerobic ammonium fluxes across lake sediment – water interfaces. *Chemosphere* **50**, 711-715.

770 Tam N.F.Y., Wong Y.S. (1995) Spatial and temporal variations of heavy metal contamination in
771 sediments of a mangrove swamp in Hong Kong. *Mar. Pollut. Bull.* **31**, 254-261.

772 Tam N.F.Y., Wong Y.S. (2000) Spatial variation of heavy metals in surface sediments of Hong Kong
773 mangrove swamps. *Environ Pollut.* **110**, 195–205.

774 Valiela I., Bowen J.L., York J.K. (2001) Mangrove forests: one of the world's threatened major tropical
775 environments. *Biosci.* **51**, 807-815.

776 Wasserman S.R., Allen P.G., Shuh D.K., Bucher J.J., Edelstein N.M. (1999) EXAFS and principal
777 component analysis: a new shell game. *J. Sync. Rad.* **6**, 284 – 286.

778 Webb S.M. (2005) SIXpack: a graphical user interface for XAS analysis using IFEFFIT. *Phys. Scripta*
779 **T115**, 1011.

780 Winterer M. (1997) XAFS – a data analysis program for materials science. *J. Phys. IV* **7(C2)**-243–244.

781 Wong V.N.L., Johnston S.G., Burton E.D., Bush R.T., Sullivan L.A., Slavich P.G. (2010) Seawater
782 causes rapid trace metal mobilisation in coastal lowland acid sulfate soils: Implications of sea level
783 rise for water quality. *Geoderma* **160**, 252-263.

784 Wong V.N.L., Johnston S.G., Burton E.D., Bush R.T., Sullivan L.A., Slavich P.G. (2013) Seawater-
785 induced mobilization of trace metals from mackinawite-rich estuarine sediments. *Water Research*
786 **47**, 821-832.

787 Wyckoff R.W.G. (1963) *Crystal Structures*, 2nd ed., Volumes 1-6, Interscience, New York.

788

789

Table 1. Selected chemical and mineralogical data for the mangrove sediment core samples studied. Concentrations of Ni, Fe, Ti and Total Organic Carbon (TOC) in the solids are given in weight percentage. Qualitative mineralogical composition is reported for OxFe: goethite, ferrihydrite and lepidocrocite; Smec: smectite; Srp: serpentine; and Py: pyrite; with (-) not observed, and, from (+) to (++++), observed to major phase, respectively. All samples contain quartz. Aqueous Ni concentration in the pore waters are given for the sediments collected under the *Avicennia* and *Rhizophora* stand. TOC, Eh, pH and mineralogical data are from Noël et al. (2014). Uncertainties on last digit are given in parenthesis and were estimated as standard deviation within triplicates.

Sample (cm)	Ni (wt%)	Fe (wt%)	Ti (wt%)	TOC (%)	OxFe	Talc	Smec	Serp	Py	Eh (mV)	pH	Ni (μM)
Salt flat												
2.5	0.50(1)	13.9(1)	0.22(1)	1.5	++	++	+	+++	-	347	7.7	
7.5	0.48(1)	13.2(2)	0.19(1)	0.9						299	7.5	
12.5	0.46(2)	12.9(3)	0.17(1)	0.4						267	7.2	
17.5	0.48(1)	13.7(1)	0.17(1)	0.4						275	7	
22.5	0.47(1)	13.2(1)	0.17(1)	0.3						289	7	
27.5	0.47(1)	13.6(3)	0.17(1)	0.4						304	6.9	
32.5	0.40(1)	12.9(2)	0.18(1)	0.4						268	6.9	
37.5	0.39(1)	13.2(2)	0.20(1)	0.2						274	6.8	
42.5	0.38(1)	13.9(3)	0.20(1)	0.3						87	6.9	
47.5	0.34(1)	13.3(4)	0.26(1)	0.4	++	++	+	++++	-			
<i>Avicennia</i>												
2.5	0.19(1)	8.7(1)	0.69(1)	6.5	+	+	+	++	-	147	5.9	2.53(5)
7.5	0.18(1)	7.6(2)	0.56(1)	7.3						66	6.6	
12.5	0.23(1)	8.1(1)	0.64(1)	9.4						36	6.8	1.96(6)
17.5	0.21(1)	6.9(2)	0.42(1)	7.7	+	+	+	+	+	-179	6.8	
22.5	0.11(1)	6.0(3)	0.18(1)	14.7						-70	6.7	1.17(4)
27.5	0.13(1)	6.8(5)	0.19(1)	15.3						-93	6.6	
32.5	0.17(1)	8.2(2)	0.30(1)	11.6						-83	6.7	1.39(6)
37.5	0.10(1)	6.2(2)	0.26(1)	7.3						-160	6.6	
42.5	0.12(1)	6.2(2)	0.31(2)	10.3	-	+	+	+	+	-142	6.5	0.70(8)
47.5	0.12(1)	7.0(2)	0.24(1)	8.7						-131	6.5	
<i>Rhizophora</i>												
2.5	0.23(1)	9.8(1)	0.28(1)	13.7	+	+	+	++	-	241	5	48.48(9)
7.5	0.52(1)	12.4(4)	0.15(2)	15.5	+	+	+	++	-	-127	6.5	
12.5	0.13(1)	6.1(2)	0.31(2)	9.2	+	-	+	+	+	-72	6.6	12.54(5)
17.5	0.08(1)	6.3(3)	0.16(1)	6						-65	6.6	
22.5	0.15(1)	4.3(1)	0.27(1)	9.2						-116	6.6	9.75(7)
27.5	0.19(1)	8.5(4)	0.23(2)	5.4	-	+	+	+	+	-121	6.5	
32.5	0.05(1)	4.4(2)	0.43(4)	8.9						-118	6.5	9.29(5)
37.5	0.13(1)	6.9(2)	0.20(1)	4						-167	6.5	
42.5	0.22(1)	8.8(2)	0.27(1)	5.5						-117	6.3	13.64(8)
47.5	0.35(1)	12.5(3)	0.34(2)	10.2	-	+	+	++	+	-52	6.3	

Table 2. Results of LC-LS fits performed on the k^3 -weighted Ni K-edge EXAFS data of the mangrove sediment samples, expressed in percentage of the fitting components corresponding to experimental spectra of the model compounds : Ni-goethite (1%mol Ni), Ni-rich talc, Ni-montmorillonite, Ni-poor serpentine, Ni-sorbed pyrite, Ni-pyrite (Ni-pyrite 1%) , Ni-rich pyrite (Ni-pyrite10%). Errors on fitting components are estimated to $\pm 20\%$ of the stated value. ⁽¹⁾Fit quality was estimated by a *R*-factor calculated as $Rf = \sum (k^3\chi_{exp}(k) - k^3\chi_{calc}(k))^2 / \sum (k^3\chi_{exp}(k))^2$.

Sample depth (cm)	Ni-goethite	Ni-rich Talc	Ni-Montmo.	Ni-poor serp.	Ni-sorbed pyrite	Ni-pyrite1%	Ni-pyrite10%	Sum (%)	$Rf^{(1)} \times 10^{-2}$
Salt flat									
2.5	24	31	-	44	-	-	-	99	1.9
47.5	18	20	-	58	-	-	-	96	2.6
<i>Avicennia</i>									
2.5	15	50	38	-	-	-	-	103	3.0
17.5	-	25	25	-	52	-	-	102	5.0
22.5	-	-	69	-	-	23	13	105	3.1
32.5	-	-	56	-	-	41	14	111	3.3
47.5	-	-	67	16	-	34	-	117	6.8
<i>Rhizophora</i>									
2.5	20	41	38	-	-	-	-	99	1.9
7.5	17	56	20	-	-	-	-	93	2.8
12.5	23	-	52	-	23	-	-	98	4.4
27.5	-	-	47	18	37	-	-	103	4.7
47.5	-	-	41	28	-	41	-	110	2.5

Table 3. Crystallographic data used for *ab initio* Feff8.1 calculations of the unfiltered Ni K-edge EXAFS data for selected model compounds samples based on fixed atomic clusters (see text). Corresponding experimental and calculated curves are plotted in Fig. 4. Interatomic distances between the central Ni atom and its closest neighbors in cluster are reported. To adjust the amplitude and the energy position of the spectra, refined parameters were an overall Debye-Waller parameter σ and a threshold energy shift ΔE_0 parameter. The S_0^2 parameter was fixed to 1. Fit quality was estimated using an *R*-factor (*Rf*) and uncertainty on the refined parameters are given in parentheses (see text).

Sample	Crystal Structure	Unit-cell			closest neighbors			Refined parameters		
		<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	atom	<i>R</i> (Å)	<i>N</i>	σ (Å)	ΔE_0 (eV)	<i>Rf</i>
Ni-rich talc	talc ¹ (<i>P</i> -1)	5.291	9.460	5.290	O	2.05 – 2.13	6	0.088(5)	3(1)	0.17
					Ni5 Mg1	3.04 – 3.07	6			
					Si	3.24 – 3.25	4			
					Si	4.45	4			
					Ni5 Mg1	5.3	6			
					Si	5.4	8			
					Ni5 Mg1	6.1	5			
Ni-poor serpentine	lizardite ² (<i>P</i> 31m)	5.332		7.233	Ni – O	2.05 – 2.12	6	0.079(5)	4(1)	0.11
					Mg	3.07 – 3.08	6			
					Si	3.29	2			
					Si	4.5	2			
					Si	4.8	2			
					Mg	5.3	6			
					Si	5.5-5.7	6			
					Mg	6.1	6			
Ni-pyrite1%	pyrite ³ (<i>Pa</i> 3)	5.52 5.45			S	2.31	6	0.088(4)	2(1)	0.07
					S	3.46	6			
					S	3.64	2			
					Fe	3.85	12			
					S	4.48	6			
Ni-pyrite10% (bravoite)	vaesite ³ (<i>Pa</i> 3)	5.615			S	2.37	6	0.065(4)	0(1)	0.10
					S	3.50	6			
					S	3.84	2			
					Fe	3.97	12			
					S	4.62	6			
Ni-Mack.	Mack. ⁴ (<i>P</i> 4/nmm)	3.698		5.067	S	2.27	4	0.083(6)	1(1)	0.20
					Fe	2.62	4			
					Fe	3.70	4			

¹Perdikatsis B. and Burzlaff H. (1981) ; ²Mellini (1982); ³Wyckoff (1963) ; ⁴mackinawite (Lennie et al. 1995).

Table 4. Results of shell-by-shell fitting of unfiltered Ni K-edge EXAFS data for selected model compounds samples. Corresponding experimental and calculated curves are plotted in Fig. 5. Refined parameters included: R the interatomic distance between the absorbing atom and the neighboring shell, N is the number of atom neighbors in the shell, σ the Debye-Waller parameter and ΔE_0 the energy shift between the Feff8 threshold energy and the user-defined threshold energy. During the fitting procedure, all parameter values indicated by (-) were linked to the parameter value placed above in the table and those followed by (*) were fixed. Uncertainty on the refined parameter is given in parenthesis (see text).

sample	path	R (Å)	N	σ (Å)	ΔE_0 (eV)	χ^2_R
Ni-goethite	Ni – O	2.053(5)	5.6(5)	0.073(5)	4(1)	9.9
	Ni – Fe	2.98(1)	1.9(7)	0.07(2)	-	
	Ni – Fe	3.17(2)	1.9(8)	-	-	
	Ni – Fe	3.57(2)	1.0(4)	-	-	
	O – Ni – O	4.2(1)	6*	-	-	
	Ni – Fe – Fe	6.13(2)	3(1)	-	-	
Ni-montmorillonite	Ni – O	2.056(3)	4.5(3)	0.058(4)	5(1)	16
	Ni – Al/Mg	2.97(3)	0.6(2)	-	-	
	Ni – Si	3.24(1)	2.1(3)	-	-	
	O – Ni – O	4.3(1)	6*	-	-	
	Ni – Si	4.45(2)	1.7(5)	-	-	
	Ni – Si	5.44(2)	2.3(8)	-	-	
Ni-citrate	Ni – O	2.035(5)	4.9(3)	0.063(4)	0(1)	22
	Ni – C	2.77(2)	3(1)	0.08(2)	-	
	Ni – C	3.36(2)	5(2)	-	-	
	O – Ni – O	4.2(1)	6*	-	-	
Ni-glutathione	Ni – S	2.210(4)	2.8(2)	0.051(5)	2(1)	9.3
	Ni – C	4.3(1)	4(2)	-	-	
amorphous-NiS	Ni – S	2.240(4)	3.1(2)	0.079(3)	0(1)	9.3
Ni-sorbed pyrite	Ni – S	2.284(5)	4.2(4)	0.078(4)	3(1)	43
	Ni – S	3.54(2)	1.9(6)	-	-	
	Ni – Fe	3.95(1)	4(1)	-	-	
	Ni – S	4.24(3)	3(1)	-	-	

Figure 1. Evolution of Ni concentration and speciation in mangrove sediments cores collected across the intertidal zone. Three zones are distinguished from the land to the sea: salt flat, *Avicennia* stand, and *Rhizophora* stand. The chemical profiles show the vertical changes in the normalized Ni/Ti (red lines) and normalized Fe/Ti (black lines) mole ratios in the dry sediments, calculated as $[\text{Ni}/\text{Ti}]_{\text{sample}} / [\text{Ni}/\text{Ti}]_{\text{top-layer}}$, and $[\text{Fe}/\text{Ti}]_{\text{sample}} / [\text{Fe}/\text{Ti}]_{\text{top-layer}}$, respectively. The bar plots show the quantitative Ni-speciation results obtained from LC-LS analysis of the EXAFS data (Table 2), expressed as the proportion of each Ni model compounds normalized to 100%.

Figure 2. SEM images and SEM-EDXS analyses of pyrite grains from the sample collected at 47.5 cm depth beneath the *Rhizophora* stand. The SEM image in (a) shows clustered pyrite grains with sizes ranging from few micrometers (blue) to a few hundred of nanometers (purple) and then to a few tens of nanometers (red). SEM images in (b) show two types of framboidal pyrite, one comprised of large cuboctahedral pyrites (blue) and one comprised of small spherulitic pyrites (red). The corresponding SEM-EDXS spectra are displayed in (c), with a detailed view over the 6.8 – 7.8 keV energy range in (d).

Figure 3. Three components LC-LS fits of the Ni K-edge EXAFS data of the selected mangrove sediment samples collected across the intertidal zone: (a,b) salt flat, (c,d) *Avicennia* and (e,f) *Rhizophora* stands. Experimental (black lines) and LC-LS fitting curves (red lines) are displayed as unfiltered k^3 -weighted EXAFS functions (left) and their corresponding Fast Fourier-Transforms (right). See Fig. 1 and Table 2 for quantitative Ni speciation results.

878
879
880
881
882

883
884
885
886
887
888
889
890
891
892
893
894

Figure 4. *Ab initio* Feff8.1 calculations of Ni K-edge EXAFS data for selected model compounds samples used as components in the LC-LS fitting of the mangrove sediment EXAFS data. Unfiltered k^3 -weighted EXAFS spectra (left) and their corresponding Fourier-Transforms (right) are displayed. Calculations are based on atomic clusters using parameters reported in Table 3. Experimental and calculated curves are displayed in black and red lines, respectively.

895
896
897
898
899

900
901
902
903
904
905
906
907
908
909

Figure 5. Shell-by-shell fit of the Ni K-edge EXAFS data for selected model compounds samples used as components in the LC-LS fitting of the mangrove sediment EXAFS data. Unfiltered k^3 -weighted EXAFS spectra (left) and their corresponding Fourier-Transforms (right) are displayed. Fitting parameters are reported in [Table 4](#). Experimental and calculated curves are displayed in black and red lines, respectively.

Electronic Annex

[Click here to download Electronic Annex: Noel et al_SupInfo_GCA_Rev6_GM.pdf](#)

Manuscript .docx file

[Click here to download Source or Other Companion File: Noel et al_Manuscript_GCA_Rev7.docx](#)

Tracked revisions manuscript .docx file

[Click here to download Source or Other Companion File: Noel et al_Manuscript_GCA_Rev7_track.docx](#)