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Garnierite characterization for open mineral databases

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Abstract

The nickel laterite mining industry faces lower recovery rates related to low ore grades, multiple nickel carrying minerals, as well as lateral and vertical heterogeneities at ore deposit scale. Garnierite, a complex mixture of nickel-bearing phyllosilicates, occurs at the base of nickel laterite profiles. Samples of Ni-rich and Ni-poor phyllosilicates from garnierite and host saprolite, from New Caledonia and the Dominican Republic, were analyzed by laboratory X-ray diffractometry (XRD), Fourier Transform Infrared (FTIR) and Raman spectroscopies. These phyllosilicates are mainly composed of serpentine-, talc- and/or sepiolite-like phases. XRD allows clearly distinguishing the different phyllosilicate phases. Moreover, it shows a difference between Ni-rich and Ni-poor phases after refinement of the

31 diffractograms, in particular the (060) reflection, little exploited at present. When Ni is
32 present, the peaks are broader and the spacing corresponding to the (060) reflection tends to
33 be less than 1.534 Å. Mg substitution by Ni also cause shifts of hydroxyl bands in FTIR
34 (3500-3800 cm⁻¹ and 500-800 cm⁻¹ spectral range), and Raman spectra (3500-3700 cm⁻¹
35 spectral range). Moreover, the intensities of the bands can be correlated with the Ni content.
36 Both are reliable indicators to define the nature of garnierite. In Raman spectroscopy, the
37 substitution of Mg by Ni generates shifts on most bands, and there is a variation in intensity
38 ratios between several bands which are correlated with Ni content.
39 Our results can be applied to spectra obtained by online and handheld analytical devices, in-
40 field core scanners or XRD/X-Ray fluorescence (XRF) combined expert systems.

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42 Keywords: Garnierite; Mg/Ni substitution; X-Ray diffraction; FTIR; Raman spectroscopy

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45 **1. Introduction**

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47 Nickel (Ni) laterites represent about 70% of the Ni resources worldwide (e.g. Butt and Cluzel,
48 2013; Dalvi et al. 2004; Gleeson et al. 2003), but only about 60 % of the world's production is
49 provided by Ni laterites (McRae, 2021). One of the reasons is the low recovery rate during ore
50 processing, in particular of the “hydrous Mg silicate” and the “clay” type Ni laterites. These
51 ores are composed of Ni-rich and Ni-poor serpentine, swelling and non-swelling clay
52 minerals, and hydrotalcites in part poorly crystalline, and occur in the lower part of the laterite
53 profile. However, these phases can host up to 27% of Ni (Bish and Brindley, 1977; Brindley,
54 1980; Freyssinet et al. 2005; Cathelineau et al. 2016; Fritsch et al. 2016; Putzolu et al. 2018;
55 Putzolu et al. 2021; Tauler et al. 2017; Villanova-de-Benavent et al. 2014).

56 The Ni-rich phyllosilicates occur disseminated in the saprolite matrix, concentrated as fracture
57 and vein infillings in the upper part of the serpentinized peridotites and the saprock, or, to a
58 lesser extent (e.g. Tiebaghi), in porous silica rocks containing serpentinite clasts (Duée et al.
59 2019; El Mendili et al. 2020; Pelletier, 1983; Secchi et al. 2018, Cluzel and Vigier, 2008).
60 Garnierite, a mixture of nanocrystallites of crystalline serpentine, talc, chlorite, sepiolite
61 and/or smectite, occurring in fractures, is the main Ni ore (Brindley and Hang, 1973; Fritsch
62 et al. 2016; Villanova-de-Benavent et al. 2016; Wells et al. 2009). It was defined by Jules
63 Garnier (1867) in New Caledonia. The garnierite terminology is not recognized by the
64 International Mineralogical Association (IMA), as its mineralogical composition and colors
65 (whitish, greenish to green-blue) vary according to the evolution of the ore deposit. Garnierite
66 can be collomorphous, poorly crystalline or amorphous (e.g. Cluzel and Vigier, 2008). These
67 phases have been widely studied by laboratory analyses such as XRD, FTIR, and Raman
68 spectroscopy in order to distinguish those enriched in Ni (Bosio et al. 1975; Cathelineau et al.
69 2015; Decarreau et al. 1987; Mano et al. 2014; Villanova-de-Benavent et al. 2019). Some
70 studies identify or classify the garnierite forming minerals according to their structure and
71 their basal spacings, determined by XRD (Brindley, 1980; Brindley et al. 1977, 1979; Wells
72 et al. 2009). It was proposed to distinguished serpentine-like phases (1:1 layer type minerals -
73 7 Å), which include lizardite-népouite and chrysotile-pecoraite series; talc-like phases (2:1
74 layer type minerals - 10 Å), which include talc-willemseite and kerolite-pimelite series; and
75 sepiolite-like phases (2:1 layer type minerals - 12 Å), which consist in sepiolite-falcondoite
76 series. More details about the nomenclature can be found in the study of Brindley (1980).

77

78 At present, mining companies seek to automatize drill core logging using drill core scanners
79 composed of sensors accessing chemistry and mineralogy. These instruments are on the
80 market (e.g. Corescanner™, <https://corescan.com.au/>; Minalyzer CS™,

81 <https://minalyze.com/>; [Avaatech XRF core scanner, https://www.avaatech.com](https://www.avaatech.com); Terracore,
82 <http://terracoregeo.com>) or in pre-industrial state (e.g. SOLSA, www.solsa-mining.eu, RTM
83 mining, EIT-KIC ANCORELOG, EIT-KIC T-REX). In the SOLSA project, a combined
84 benchtop XRF-XRD-Raman instrument was developed, measuring powdered samples on
85 mine sites. All these devices contribute to more efficient mining and processing through smart
86 interpretation of the collected data. Hence, operational exploration and processing costs,
87 representing about 70% of a mining project, can be significantly reduced.

88 However, the efficiency of in-field measurements and data interpretation are highly dependent
89 on ore- deposit adapted databases.

90 Apart from Ni, these laterites may also host economic grades of cobalt (Co) and scandium
91 (Sc) (Anawati et al. 2020; Chassé et al. 2016, 2019; Kaya and Topkaya, 2016; Marsch et al.
92 2011; Orberger & Van den Ent, 2019; Putzolu et al. 2019; Teitler et al. 2019; Williams-Jones
93 and Vasyukova, 2018; Yongue-Fouateu et al. 2006). Contained in various silicates and oxy-
94 hydroxides, Co and Sc can be more efficiently extracted when systematic, reliable, at least
95 semi-quantitative, chemical and mineralogical data are smartly interpreted.

96 For mining companies, the precise determination of the mineralogy and the mineral chemistry
97 of the ores is crucial. For unambiguous identification of the complex phases, solid and robust
98 open databases are indispensable (Raman Open Database, El Mendili et al. 2019; COD,
99 Grazulis et al. 2009, 2012, Hyperspectral Open Database-(HOD) as part of the SOLSA
100 project).

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102 The goal of this paper is the specific evaluation of XRD, FTIR and Raman data on garnierites.
103 In this line, we present a comprehensive mineralogical study of three garnierite samples from
104 New Caledonia, and of two garnierite samples from the Dominican Republic, the latter
105 previously studied in Villanova-de-Benavent et al. (2014, 2016, 2019). All samples have been

106 analyzed by electron probe micro-analysis (EMPA), X-ray diffraction (XRD), Fourier
107 Transform Infrared and Raman spectroscopy. These data can be used to calibrate combined
108 XRF-XRD benchtop systems.

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111 **2. Materials and methods**

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113 **2.1. Samples**

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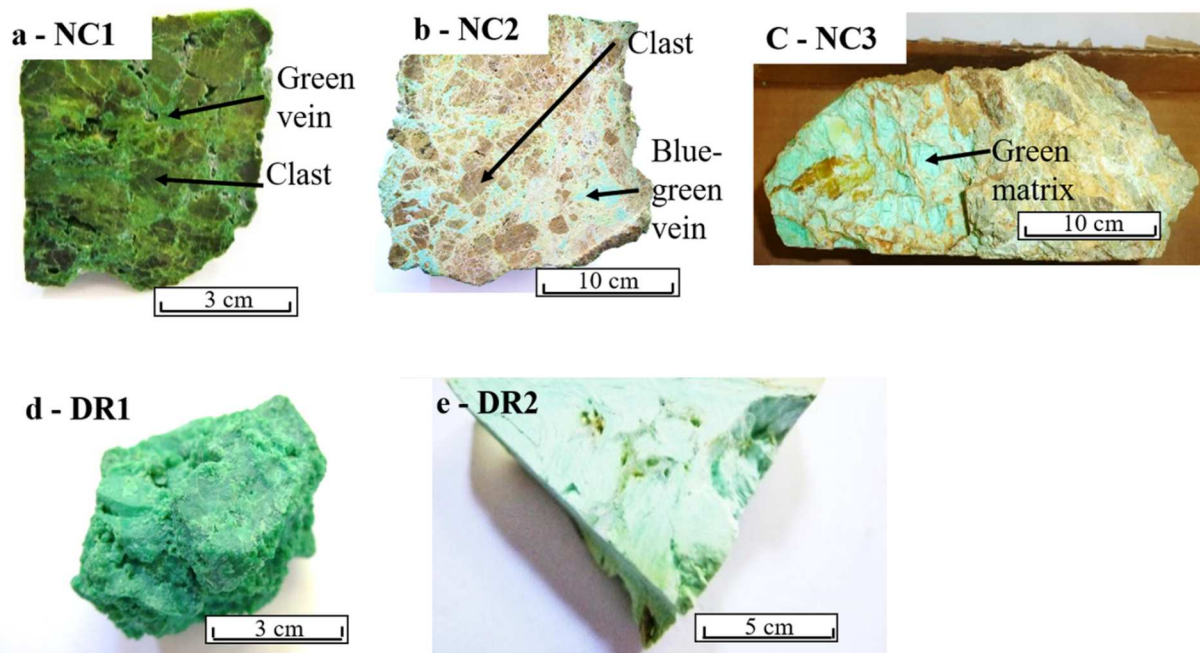
115 A set of garnierite samples, representative of different Ni laterite facies and mineralogy, were
116 investigated. Three samples, (NC1 to NC3), are from New Caledonia (Fig. 1 a-c) come from
117 the garnierite collection at BRGM set-up from numerous field campaigns and from
118 ERAMET-SLN. Two samples consist of breccias hosting saprolite clasts (dark, grey brown)
119 and garnierite veins, dark green for NC1, and blue-green for NC2. (Fig. 1a,b). The third
120 sample from New Caledonia (NC3) is composed of a blue-green “garnierite” matrix in
121 contact with saprolite (Fig. 1c).

122 Samples DR1 and DR2 are from the Falcondo mining district in the Dominican Republic,
123 and were described in Tauler et al. (2009) and Villanova-de-Benavent et al. (2014, 2016,
124 2019). Sample DR1 features bright green garnierite fragments cemented by garnierite, while
125 sample DR2 consists of pale greenish bundles of fibers.

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Figure 1. Selected samples from New Caledonia (NC1 to NC3) and from the Dominican Republic (DR1 to DR2), showing the areas sampled for this study.

2.2. Sample preparation

The samples were analyzed by EPMA, XRD, FTIR and micro-Raman spectroscopy. XRD and FTIR analyses were carried out on powders. Due to the heterogeneity of the samples, it was decided to handpick a few tens of milligrams from selected areas of each sample, in order to study the most homogeneous phases. For NC1, samples were taken from a saprolite clast (NC1_clast) and from the veins surrounding these clasts (NC1_green vein). For NC2, samples were taken on the saprolite clasts (NC2_clast) and the blue-green veins around the clasts (NC2_blue_green vein). For NC3, only the greenish part (NC3_green matrix) was sampled. For DR1 and DR2, more homogeneous, only garnierite parts were sampled. The samples were ground in an agate mortar and sieved at 63 μm. Raman spectroscopy and EPMA were performed on polished thin sections on the areas of interest.

147 2.3. Analytical methods

148 2.3.1. Electron Probe Micro-Analysis (EPMA)

149 Quantitative electron probe microanalyses were performed with a CAMECA SX FIVE
150 electron microprobe equipped with five vertical wavelength dispersive spectrometers (WDS).
151 The analyses were performed on carbon-coated (20–30 nm) polished thin sections using a 15
152 kV acceleration voltage, 20 nA probe current and 1-2 μm spot size. The system was calibrated
153 with albite for Na ($K\alpha$), periclase for Mg ($K\alpha$), Al_2O_3 for Al ($K\alpha$), andradite for Si and Ca
154 ($K\alpha$), orthoclase for K ($K\alpha$), MnTiO_3 for Mn and Ti ($K\alpha$), Fe_2O_3 for Fe ($K\alpha$), Cr_2O_3 for Cr
155 ($K\alpha$), NiO for Ni ($K\alpha$) and CoO for Co ($K\alpha$). Matrix corrections were performed with the
156 PAP computing programs of Pouchou and Pichoir (1984). For each sample, the chemical
157 composition was obtained from about ten measurements on average (varying from 9 to 19
158 measurements depending on the sample). These point analyses were acquired in areas of a
159 few square millimeters. Considering the small particle size (submicrometric) of the
160 phyllosilicates, the results give an average chemical composition that may correspond to the
161 analysis of one or more mineral phases. The structural formulae of serpentine and serpentine-
162 like minerals were calculated on the basis of 7 oxygens. For talc- and sepiolite-like phases,
163 calculations were performed using 11 and 32 oxygens, respectively.

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165 2.3.2. X-ray diffractometry (XRD)

166 XRD analyses were performed on randomly oriented samples. For each sample, some tens of
167 milligrams of powders were set on a zero-background sample holder. The diffractograms
168 were acquired with a Bruker D8 Advance DA VINCI diffractometer equipped with a $\text{CuK}\alpha$
169 source ($\lambda = 1.5406 \text{ \AA}$), operating at 40kV and 40mA, and a LYNXEYE XE 1D detector with
170 a 3.3° opening. The XRD patterns were collected in continuous scan mode over the 4-

171 75°2 θ range with a step size and a measuring time of 0.03°2 θ and 576 seconds per step,
172 respectively.

173 As the position of the (060) reflection can be related to the Ni content in clay minerals (Baron
174 and Petit, 2016), a specific study of this reflection was carried out by recording a
175 diffractogram over the range 57-64°2 θ , with a step of 0.03°2 θ and a counting time of 576
176 seconds per step. The position of the (060) reflection and the full width half maximum
177 (FWHM) of (001) and (060) reflections were determined by fitting XRD patterns with a
178 fundamental parameter approach in the TOPAS V.6 and DIFFRAC.EVA softwares (Bruker,
179 2017).

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181 2.3.3. Fourier Transform Infrared spectroscopy (FTIR)

182 FTIR spectra were obtained using a Bruker Equinox 55 FTIR spectrometer, equipped with a
183 middle-infrared (MIR) source and a KBr beam splitter. For each sample, 30 scans in the
184 4000-400 cm⁻¹ spectral range were recorded with a resolution of 4 cm⁻¹. The analyses were
185 carried out on pellet discs consisting of a mixture of 0.5 mg of sample and 150 mg of KBr.
186 The diameter of the pellets is 13 mm. Prior to analyses, the pellets were stored at 60°C to
187 minimize the absorption of water by KBr and by the sample.

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189 2.3.4. Micro-Raman spectroscopy

190 Raman measurements were performed with a Renishaw InVIA Reflex microspectrometer,
191 coupled to a DMLM Leica microscope, equipped with Renishaw *WiRE*TM software. Three
192 different lasers were used ($\lambda_0 = 514.5$ nm; 633 nm and 785 nm). The analyses were carried
193 out on polished thin sections using the 50x or 100x objective (NA = 0.90), with a laser power
194 of around 1 mW at the sample surface. The Raman spectrometer was used in continuous

195 scanning mode with large spectral windows from 100 to 4000 cm^{-1} . Acquisition times
196 (generally over 10 seconds) and accumulations of spectra vary depending on the mineral type.

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199 **3. Results**

200

201 3.1. Mineral chemistry (EPMA)

202 The average chemical compositions with the corresponding structural formulae are given in
203 the table 1. The ternary diagram Si-Ni-(Mg+Fe) provides initial information on the nature of
204 the minerals that constitute each sample (Figure 2). Thus, it appears that the clasts present
205 compositions close to the Mg-rich serpentines. On average, these samples contain less than 10
206 wt.% of NiO and between 2 and 6 wt.% of FeO. The (Ni/(Ni+Mg)) ratio, which corresponds to
207 Mg/Ni substitution rate, is 27% and 14% in NC1_clast and NC2_clast, respectively. The
208 average structural formulae of these samples are close to the theoretical composition of a
209 serpentine ($\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$). For the clasts, the number of tetrahedral cations is between 1.95
210 and 2.05 and the octahedral occupancy is between 2.9 and 3.1. These results are similar to
211 those reported for samples from Indonesia (Golightly and Arancibia, 1979) and New
212 Caledonia (Manceau et al. 1985).

213 The composition of the garnierite veins from NC1 sample tends towards a Ni-rich serpentine.
214 This sample contains 50 wt.% of NiO, and a Mg/Ni substitution rate of 97%. In addition, it is
215 worth noting that NC1 garnierite veins are exceptionally rich in Co (0.56 wt.% of CoO), about
216 10 times higher in the veins than in the saprolite clasts (Table 1). The average structural
217 formulae shows a slight excess of Si in tetrahedral sites (2.086) and a deficiency of octahedral
218 cations (2.824). Similar observations are reported in various studies of serpentine-like
219 garnierite (Brindley and Wan, 1975; Manceau et al. 1985; Villanova-de-Benavent et al. 2014;
220 Wells et al. 2009).

221 In contrast, garnierite from the NC2 sample has a composition close to that of kerolite (talc-
222 like). This sample contains 9 wt.% of NiO, similarly to the clast of the NC1, but twofold
223 higher than the clasts from NC2. The structural formula shows that the number of tetrahedral
224 cations is slightly deficient (3.898 instead of 4) in the ideal formula of talc $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$.
225 In contrast, the number of cations in octahedral sites is in excess (3.207). The deviation from
226 the ideal formula is similar to those reported in previous studies (Brindley et al. 1979;
227 Brindley and Hang, 1973; Manceau et al. 1985; Villanova-de-Benavent et al. 2014, Wells et
228 al. 2009).

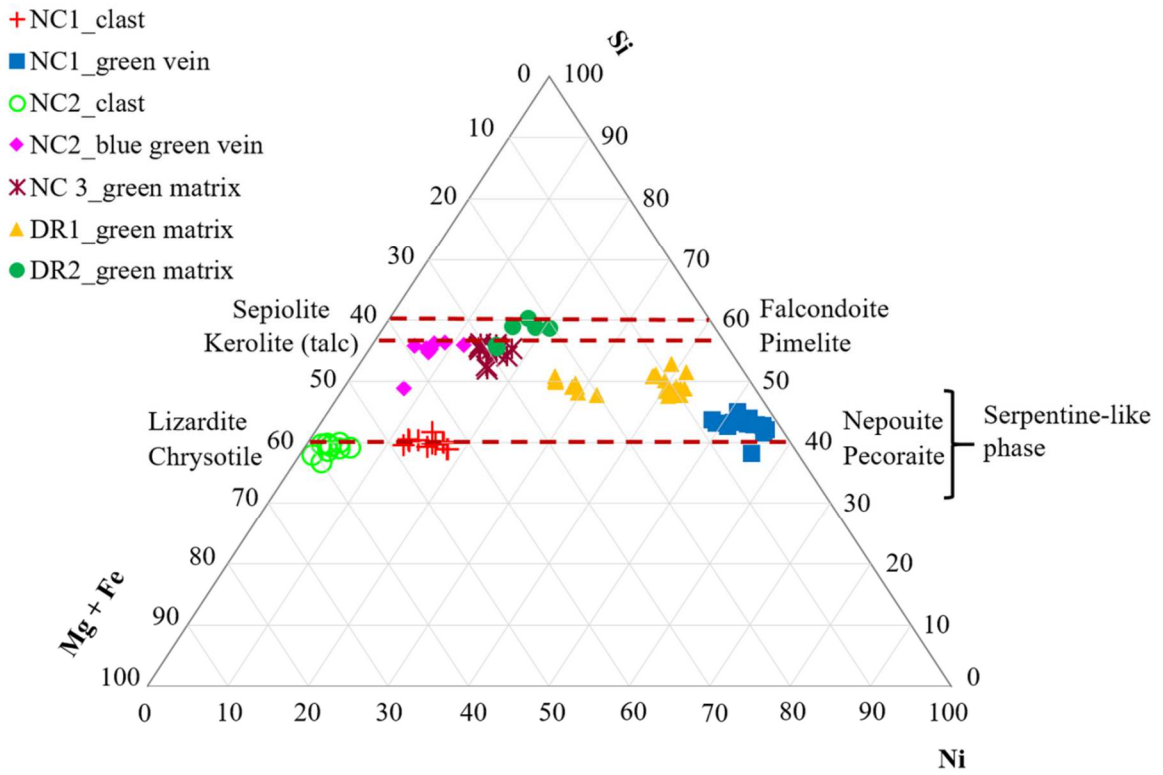
229 Among the other garnierites, sample NC3 also has a talc-like composition, but with a higher
230 Ni content than the garnierite in the NC2 sample. Its Mg/Ni substitution rate is 55% compared
231 to 33% in NC2_blue green vein. The number of cations in tetrahedral and octahedral sites is
232 equivalent to the one from NC2_blue green vein.

233 The average chemical composition of the DR1 sample shows that it is Ni-rich. Its Mg/Ni
234 substitution rate is 91%. The distribution of the analysis points in the ternary diagram does not
235 allow defining a typical mineralogy. This sample probably consists of a mixture of minerals,
236 including serpentines and talc-like minerals. Therefore, for this sample, the structural
237 formulae were calculated assuming 7 and 11 oxygens (Wells et al. 2009). On the basis of 7
238 oxygens, the results show a deviation from the ideal formula of a serpentine. There is an
239 excess of cations in the tetrahedral site (2.314 instead of 2) and a strong deficit in octahedral
240 cations (2.373 instead of 3). In contrast, the calculation based of 11 oxygens shows that the
241 number of tetrahedral cations is in deficit, while it is largely in excess in octahedral sites.

242 The DR2 sample has a chemical composition corresponding to that of sepiolite-falcondoite,
243 with 17.45 wt.% of NiO and an average Mg/Ni substitution rate of 62%. Its average structural
244 formula shows a minor deviation from the ideal formula of sepiolite
245 $(\text{Mg}_8\text{Si}_{12}\text{O}_{30}(\text{OH})_4 \cdot 12\text{H}_2\text{O})$.

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249 Figure 2. Ternary diagram Si–Ni–(Mg+Fe) (atomic proportions) showing the chemical
250 compositions of the clasts and garnierites.

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Table 1. Average composition (average of about 10 point analyses each) and structural formulae of the studied clasts and garnierites. Av: average; σ : standard deviation; Tetr.: tetrahedral site; Oct.: octahedral site.

Sample	NC1_Clast		NC1_green vein		NC2_Clast		NC2_green vein		NC3_green matrix		DR1_green matrix		DR2_green matrix	
Mineral type	Serpentine		Serpentine		Serpentine		Talc		Talc		Serpentine + talc		Sepiolite	
wt %	Av	σ	Av	σ	Av	σ	Av	σ	Av	σ	Av	σ	Av	σ
SiO ₂	40.97	0.72	33.06	1.22	37.77	1.16	50.73	2.58	54.53	1.69	40.93	1.49	47.66	7.94
Al ₂ O ₃	0.09	0.02	0.02	0.02	0.01	0.01	0.04	0.02	0.01	0.01	0.01	0.02	0.09	0.07
MgO	32.73	1.28	2.21	1.07	34.62	2.26	23.11	2.59	19.86	1.14	5.61	0.76	13.82	4.30
Cr ₂ O ₃	0.02	0.04	0.03	0.02	0.00	0.00	0.00	0.01	0.00	0.01	0.00	0.01	0.00	0.01
MnO	0.05	0.04	0.01	0.03	0.05	0.05	0.03	0.03	0.00	0.00	0.01	0.02	0.01	0.02
FeO	2.41	0.18	0.10	0.13	5.62	1.33	0.14	0.24	0.00	0.00	0.11	0.09	0.01	0.02
CoO	0.11	0.02	0.56	0.21	0.03	0.03	0.01	0.01	0.01	0.02	0.02	0.04	0.00	0.00
NiO	9.34	1.37	50.84	2.92	4.17	1.54	8.91	1.50	18.97	1.70	41.68	1.20	17.45	2.20
Total	85.73	1.50	86.91	2.60	82.32	2.76	83.06	3.78	93.52	0.73	88.52	0.85	79.17	13.75
Ni/(Ni+Mg) %	27		97		14		33		55		91		62	
Si	2.040		2.086		1.954		3.894		3.896		2.313 3.634		11.719	
Al	0.005		0.001		0.001		0.004		0.001		0.001 0.001		0.026	
Σ Tetr.	2.045		2.087		1.955		3.898		3.897		2.314 3.635		11.745	
Mg	2.430		0.208		2.670		2.645		2.115		0.473 0.743		5.066	
Cr	0.001		0.001		0.000		0.000		0.000		0.000 0.000		0.000	
Mn	0.002		0.001		0.002		0.002		0.000		0.000 0.000		0.002	
Fe ²⁺	0.100		0.005		0.243		0.009		0.000		0.005 0.008		0.002	
Co	0.004		0.028		0.001		0.001		0.001		0.001 0.001		0.000	
Ni	0.374		2.581		0.174		0.550		1.090		1.894 2.977		3.452	
Σ Oct.	2.911		2.824		3.09		3.207		3.206		2.373 3.729		8.522	
Oxygens	7		7		7		11		11		7 11		32	

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271 3.2. Mineralogy (XRD)

272 X-ray diffractograms are presented in Figures 3 and 4. They are serpentine-like, talc-like and
273 sepiolite-like phases, characterized by main peaks located at 7.3 Å, 10.2 Å and 12.1 Å,
274 respectively. The full width half maximum (FWHM) values of the (001) and (060) reflections
275 are reported in table 2.

276 In the saprolite clasts (NC1-, and NC2-clasts), serpentine is a major component. This is in
277 agreement with the chemical analyses (Figure 2). In sample NC2, this mineral is associated
278 with quartz (26.6°2 θ , 3.34 Å). This may explain a higher SiO₂ content in this sample than in
279 the NC1-clast sample. It should also be noted that for both samples, a small amount of a talc-

280 like phase is detected, by a low intensity, broad peak centered at 10.2 Å. Although the two
281 samples have a similar chemical and mineralogical composition, the study of the (060)
282 reflection reveals a difference. The distance d_{060} is slightly longer in the sample NC2_clast
283 (1.537 Å), than in sample NC1_clast (1.534 Å). Also, it appears that the peaks are slightly
284 broader for NC1_clast than for NC2_clast. The FWHM of the 001 reflections are $0.430^\circ 2\theta$
285 and $0.204^\circ 2\theta$, respectively (Table 2).

286 The garnierite veins of the NC1 sample are mainly composed of Ni-rich serpentine. In this
287 sample, the serpentine-like phase is characterized by broader peaks (FWHM (001) =
288 $0.897^\circ 2\theta$) and a shorter d_{060} distance (1.530 Å) compared to those observed in the saprolite
289 clasts.

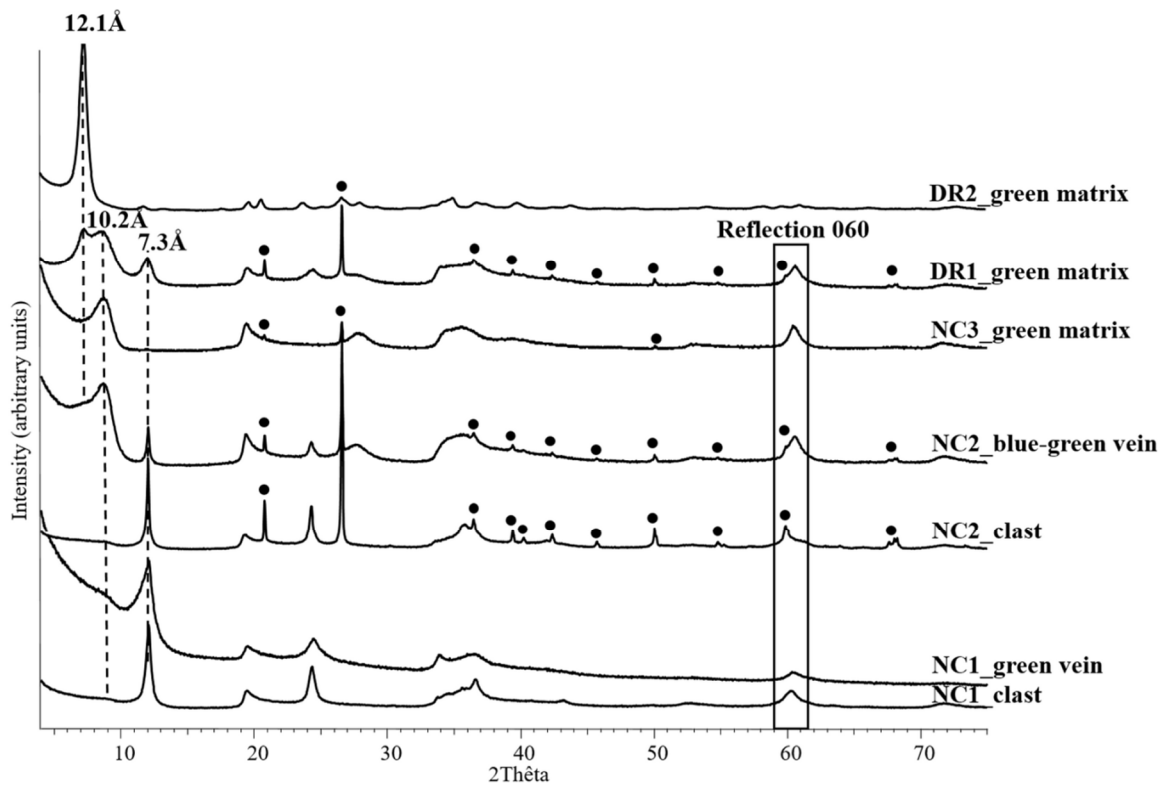
290 The garnierite veins of the NC2 sample are composed of a mixture of serpentine-, talc- and
291 sepiolite-like phases and quartz. This composition is more complex than that expected from
292 chemical analyses (kerolite–Mg-rich talc-like phase). The serpentine-like phase is defined by
293 a narrow (FWHM (001) = $0.243^\circ 2\theta$) and well-defined peak at 7.3 Å. Compared to the clasts
294 and garnierite composed of Ni-rich serpentine, this characteristic indicates that the serpentine-
295 like phase is rich in Mg. The peaks of the talc- and sepiolite-like phases are relatively broad
296 and centered at 10.2 Å and 12 Å, respectively. Then, although this sample is composed of a
297 mixture of phyllosilicates, the deconvolution of the (060) reflection does not allow
298 distinguishing spacings corresponding to serpentine- or talc-like phases (for sepiolite, the
299 (060) reflection is around $19.7^\circ 2\theta$, which corresponds to 4.50 Å). Only a peak corresponding
300 to a spacing d_{060} of 1.527 Å has been defined. As the serpentine-like phase has similar
301 characteristics to those of the clasts, one might expect to have a peak around 1.535 Å.
302 However, this is not the case. The observation of a single peak at 1.527 Å may be related to a
303 predominance of talc-like phase in the sample.

304 In sample NC3, the talc-like phase is predominant. This result is in agreement with the
305 chemical analyses. The talc-like phase is defined by a broad basal peak at 10.2 Å and a (060)
306 reflection centered at 1.529 Å. This reflection is close to the one from the garnierite veins of
307 the NC2 sample.

308 The sample DR1 presents a mineralogy close to that observed for NC2 green vein sample. It
309 is composed of a mixture of serpentine-, talc- and sepiolite-like phases associated with quartz.
310 However, as indicated by the chemical analyses, this sample is much richer in Ni than the
311 NC2 garnierite (Table 1). This results in a broad basal peak, which characterizes all
312 phyllosilicates, in contrast to the garnierite of the sample NC2. It is possible that Ni is present
313 in the structure of all the minerals that characterizes DR1.

314 As expected with the chemical analyses, the DR2 sample is composed solely of a sepiolite-
315 like mineral. It is characterized by a main peak centered at 12.1 Å.

316

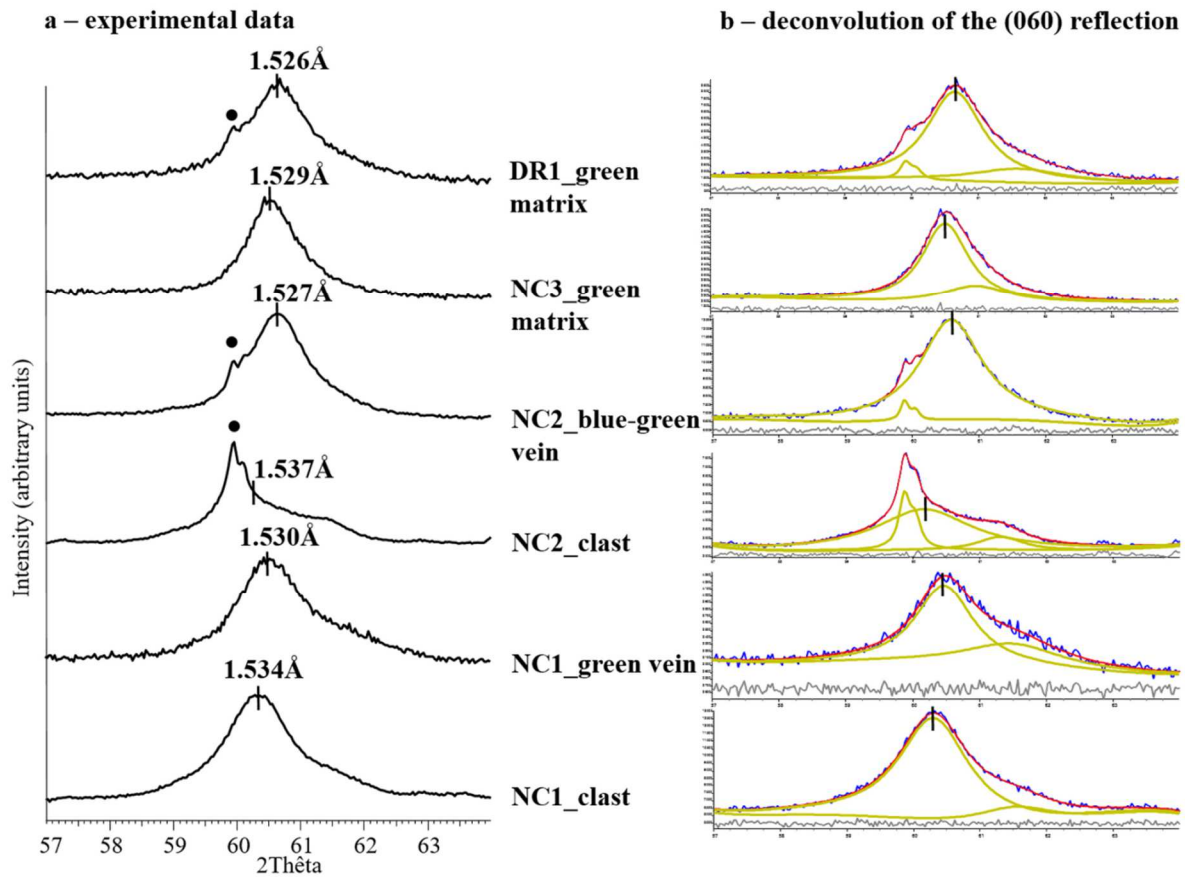


317

318 Figure 3. X-ray diffractograms of the samples selected for this study, with the main basal
 319 spacings of serpentine-like, talc-like and sepiolite-like phases at 7.3Å, 10.2Å and 12.1Å,
 320 respectively. Black circles correspond to quartz peaks.

321

322



323

324 Figure 4. X-ray diffractograms of the (060) reflections of serpentine-like and talc-like phases
 325 present in NC1, NC2, NC3 and DR1 samples, and their profile refinement: experimental
 326 pattern in blue; calculated pattern in red; difference in grey.

327

328

329 **Table 2. Full width half maximum (FWHM) values of the main reflections observed by**
 330 **XRD for the seven samples. The values are expressed in °2θ.**

Sample	FWHM – (001) reflection			FWHM – (060) reflection
	12.1 Å	10.2 Å	7.3 Å	
NC1_clast	-	1.149	0.430	0.913
NC1_green vein	-	1.168	0.897	1.062
NC2_clast	-	0.834	0.204	0.729
NC2_blue green vein	1.703	1.347	0.243	1.086

NC3_green matrix	-	1.345	-	0.931
DR1_green matrix	1.043	1.633	0.903	1.060
DR2_green matrix	0.700	-	-	-

331
332 Table 3 summarizes the mineralogical characteristics obtained from XRD of the different
333 types of minerals of this study. The three types of minerals (serpentine-like, talc-like and
334 sepiolite-like) are highlighted by distinct basal distances located at 7.3 Å, 10.2 Å and 12.1 Å,
335 respectively. In the case of serpentine, the shape of the peaks as well as the position of the d_{060}
336 reflection are indicators of the presence of Ni within this type of phase. In the presence of Ni,
337 the peaks are broader (FWHM (001) lower than $0.430^\circ 2\theta$ for Ni-poor serpentine and close to
338 $0.900^\circ 2\theta$ for Ni-rich serpentine) and the distance corresponding to the (060) reflection tends
339 to be less than 1.534 Å.

340
341

342 Table 3. Main characteristics of the different types of clay minerals

CLAST	GARNIERITE		
	Ni-rich serpentine <i>NC1_green vein</i>	Talc-like <i>NC2_blue green vein</i> <i>NC3_green matrix</i>	Sepiolite-like <i>DR2_green matrix</i>
$d_{001} = 7.3 \text{ \AA}$ (narrow peak; FWHM = $0.2 - 0.4^\circ 2\theta$) $d_{060} > 1.534 \text{ \AA}$	$d_{001} = 7.3 \text{ \AA}$ (broad peak; FWHM = $0.9^\circ 2\theta$) $d_{060} < 1.534 \text{ \AA}$	$d_{001} = 10.2 \text{ \AA}$ $d_{060} = 1.529 \text{ \AA}$	$d_{001} = 12.1 \text{ \AA}$

343
344
345

3.3. FTIR measurements

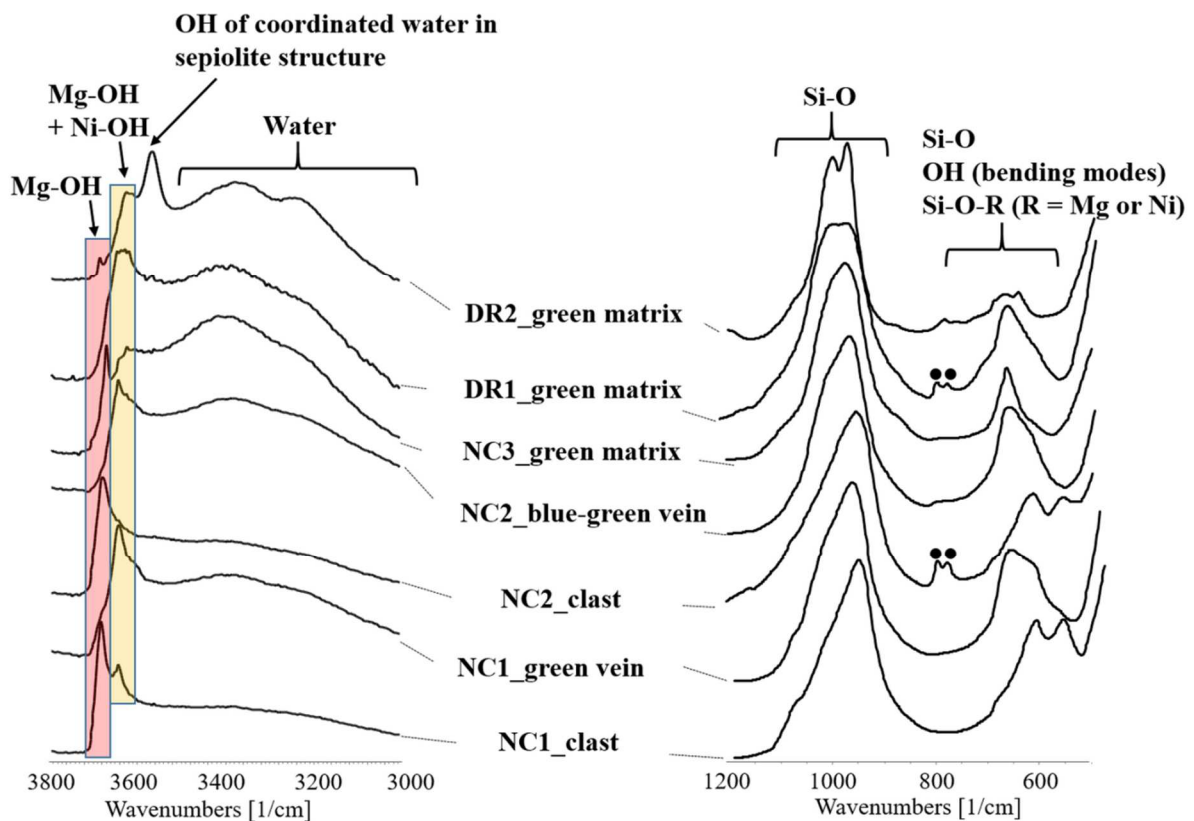
346 The spectra obtained by FTIR (spectral ranges of $3000-3800 \text{ cm}^{-1}$ and $500-1200 \text{ cm}^{-1}$), are
347 shown in figure 5. Each spectrum shows three series of absorption bands; the first between

348 3500 and 3750 cm^{-1} , the second between 800 and 1200 cm^{-1} and the third between 500 and
349 700 cm^{-1} .

350 The 3500-3700 cm^{-1} range is characteristic of the vibrations of hydroxyl groups associated
351 with R-(O,OH) octahedra (where R = Mg or Ni) (Balan et al. 2002, Baron and Petit, 2016;
352 Bishop et al. 2002). The 800-1200 cm^{-1} range corresponds to the stretching vibration modes
353 of Si-O bonds (Balan et al. 2002). The 500-700 cm^{-1} range is assigned to bending vibration
354 modes of OH groups bonds as well as Si-O and Si-O-R (where R = Mg or Ni) bonds (Balan et
355 al. 2002; Bishop et al. 2002; Hofmeister and Bowey, 2006; Yariv and Heller-Kallai, 1975).

356

357



358

359 Figure 5. Infrared spectra of the selected samples, in the 3000-3800 cm^{-1} and 500-1200 cm^{-1}
360 spectral ranges. Black circles correspond to quartz bands.

361

362

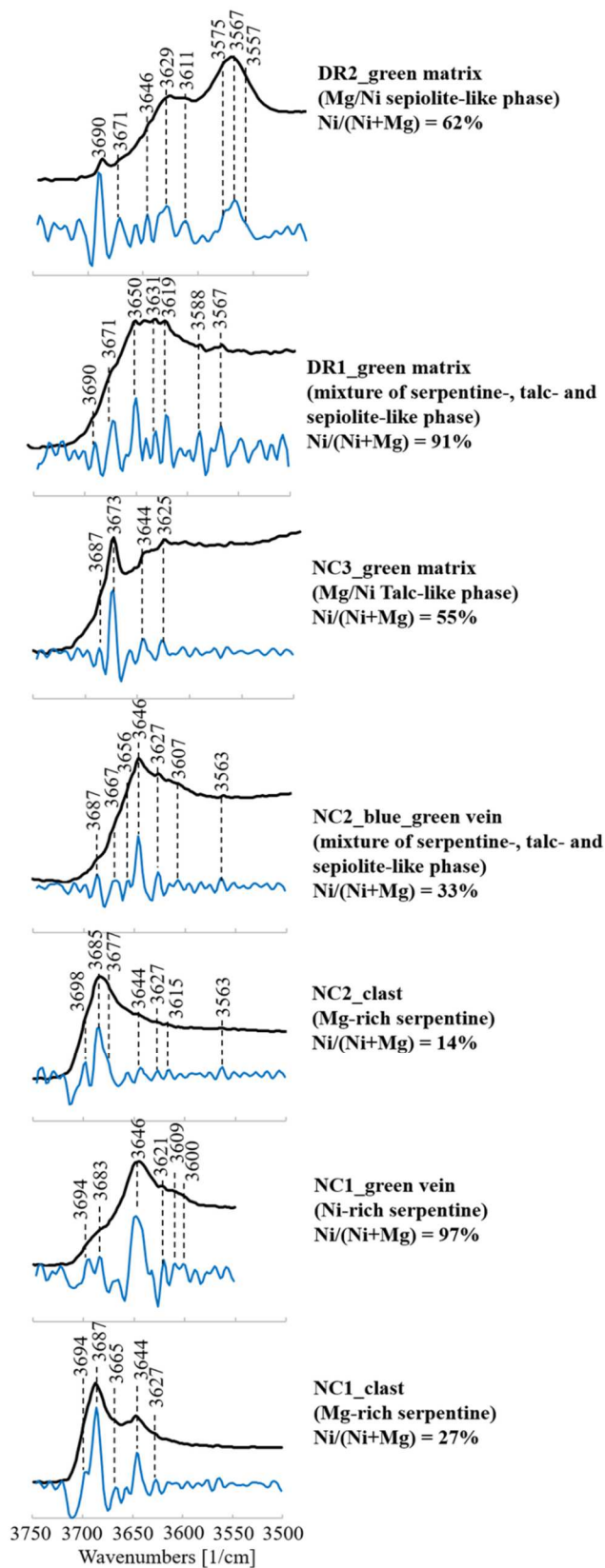
363 3.3.1. The 3500 – 3750 cm^{-1} region.

364 In this region there are one or more bands around 3600 cm^{-1} . However, since the absorption
365 bands are relatively broad and complex, a second derivative treatment was performed for each
366 spectrum in order to separate overlapping bands, and to determine the position of the main
367 bands (Figure 6). The derivative has been calculated by a numerical method such as the one
368 described by Savitzky and Golay (1964). This method is based on the derivative preceded by
369 smoothing. Smoothing allows reducing the noise due to the derivative, which is amplified in
370 the spectrum. In the present case, smoothing (using seven smoothing points) was applied
371 using the Savitzky-Golay algorithm.

372 The saprolite clasts from NC1 and NC2, mainly composed of Ni-poor serpentine, are
373 characterized by a main band centered at 3687 cm^{-1} with a shoulder between 3694 cm^{-1} and
374 3698 cm^{-1} . Secondary bands with variable intensities are also visible around 3680 cm^{-1} and
375 3615 cm^{-1} . The positions of these bands are in accordance with observations by Baron and
376 Petit (2016), and Jovanoski and Makreski (2016).

377 The garnierite composed of Ni-rich serpentine (NC1_green vein), differs from the Ni-poor
378 serpentine from the saprolite by its main band at 3646 cm^{-1} . This band has shoulders at 3683
379 cm^{-1} , 3694 cm^{-1} and between 3600 cm^{-1} and 3620 cm^{-1} . These bands have similar positions as
380 those observed in the saprolite clasts, but the intensity of the bands varies with the Ni content.

381



382

383 Figure 6. Infrared spectra of the selected samples in the 3500-3750 cm^{-1} region (black line)

384 and their second derivative (blue line).

385

386 Regarding the talc-like ROI in the NC3 green matrix sample, the results are different from
387 those of ROIs mainly composed of serpentine. In the present case, the main band is at 3675
388 cm^{-1} . This band is accompanied by other bands located at 3658 cm^{-1} , 3644 cm^{-1} and 3627 cm^{-1} .
389 Interestingly, this spectrum has a relatively high baseline between 3660 cm^{-1} and 3500 cm^{-1} .
390 This effect is due to the presence of water molecules absorbed onto the surfaces of the layers
391 of the talc-like structure (Figure 5) (Brindley et al. 1979).

392 For the sepiolite-like ROI, in the DR2_green sample, the spectrum differs from those obtained
393 in garnierite composed of serpentine-like or talc-like phases. There is a main band centered at
394 3567 cm^{-1} , accompanied by bands around 3690 cm^{-1} and 3631 cm^{-1} . The second derivative
395 also reveals numerous bands located at positions equivalent to those detected in serpentine-
396 like and talc-like ROIs (for example, the bands at 3671 cm^{-1} and 3646 cm^{-1}). However, XRD
397 analyses only identified sepiolite-like phase. These results suggest that there are
398 crystallographic similarities around the hydroxyl groups between these minerals.

399 For the samples with a more complex mineralogy, such as NC2_blue-green vein and
400 DR1_green matrix, poorly or not well-resolved absorption bands characterize the spectra in
401 the 3500-3750 cm^{-1} range. However, some positions of the main detected bands in the second
402 derivative, can be assigned to serpentine-, talc- and sepiolite-like minerals, comparing with
403 the previous spectra. Thus, for NC2_blue green vein ROI, the band at 3688 cm^{-1} reflects Ni-
404 poor serpentine; the band at 3648 cm^{-1} can be ascribed to both Ni-rich serpentine and a talc-
405 like phase, the band at 3629 cm^{-1} can be assigned to both talc-like and sepiolite-like phases.
406 The last band at 3565 cm^{-1} can be attributed to a sepiolite-like phase. For the DR1_green
407 matrix ROI, the presence of a talc-like phase is characterized by the band located at 3675 cm^{-1} .
408 The band at 3652 cm^{-1} can be attributed to Ni-rich serpentine while the bands located at
409 3569 cm^{-1} , 3633 cm^{-1} and 3690 cm^{-1} correspond to sepiolite-like phases.

410

411 3.3.2. The 800 – 1200 cm⁻¹ region.

412 In this region (Figure 7), except for the sepiolite-like ROI (DR2_green matrix), all the ROIs
413 are characterized by a broad and asymmetric band with a maximum located around 950-975
414 cm⁻¹, and shoulders between 1000 and 1100 cm⁻¹. These bands are characteristic of the
415 stretching vibrations of SiO₄ groups present in the structure of serpentine, talc and sepiolite
416 (Balan et al. 2002; Frost et al. 2001; Hofmeister and Bowey, 2006).

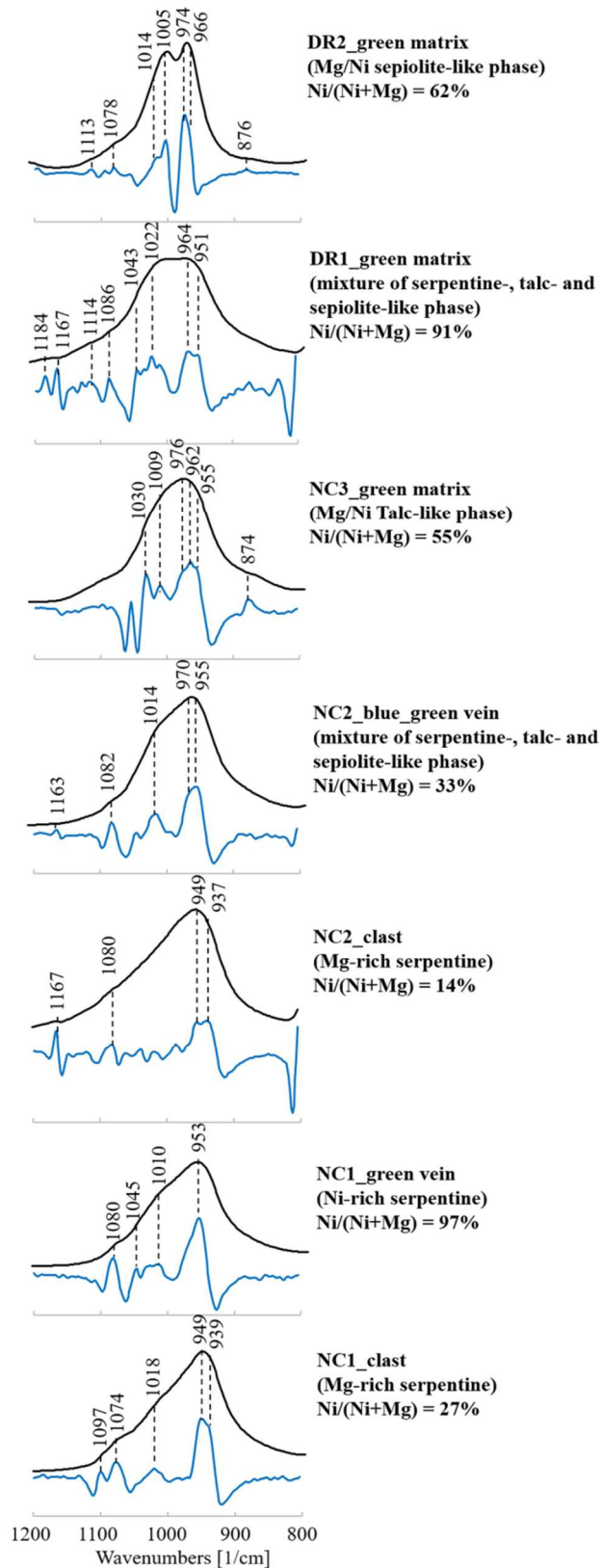
417 Comparison of the characteristic spectra of serpentine-like ROIs (in NC1 clast, NC1_green
418 vein and NC2 clast) shows that the band around 1010-1020 cm⁻¹ is more pronounced in the
419 Ni-rich ROI (NC1_green vein) than in the Ni-poor ROI (NC2_clast). A slight shift of the
420 main band from 953 cm⁻¹ for Ni-rich to 949 cm⁻¹ for Ni-poor ROI is observed.

421 The talc-like phase spectrum, as shown in the NC3_green matrix ROI, has a wide band. It is
422 more symmetrical than that of serpentine. However, the second derivative reveals that the
423 positions are similar. Only variations in intensities are observed.

424 The sepiolite-like spectrum differs from that of serpentine- and talc-like ROIs by two well-
425 defined bands centered at 1005 cm⁻¹ and 974 cm⁻¹. These bands have similar intensities.

426 For samples consisting of mixed phases (NC2_blue-green vein and DR1_green matrix), the
427 bands are more or less symmetrical. The intensity of the different bands, detected from the
428 second derivatives, is variable and probably related to the proportion of each phase within the
429 samples.

430



431

432 Figure 7. Infrared spectra of the selected samples in the 1200-800 cm⁻¹ region (black line) and
433 their second derivative (blue line).

434

435 3.3.3. The 500 – 700 cm^{-1} region.

436 The spectra obtained over this region, as well as their second derivatives, are shown in Figure
437 8. In general, the spectra are characterized by one or two main bands. For Ni-poor serpentine
438 from the saprolite clasts (NC1 and NC2_clasts), these bands are around 610 cm^{-1} and 554 cm^{-1} .
439 The band at 610 cm^{-1} is wide and has shoulders towards high wavenumbers (625 cm^{-1} , 667
440 cm^{-1} and around 690 cm^{-1}).

441 In addition to band widening, the presence of Ni in serpentine-like phase causes a significant
442 difference in the intensity of the bands around 655-670 cm^{-1} , 610 cm^{-1} and 550-560 cm^{-1} . This
443 difference is visible in the spectrum of the NC1_green vein ROI, characteristic of a Ni-rich
444 serpentine. The band around 655-670 cm^{-1} becomes more intense with increasing Ni content.
445 In contrast, the band at 550-560 cm^{-1} tends to disappear.

446 The spectrum of the talc-like ROI (NC3_green matrix) is characterized by a main band
447 centered at 667 cm^{-1} . Remarkably, in contrast to serpentine-like phases, the bands around 610
448 cm^{-1} and 560 cm^{-1} are almost non-existent.

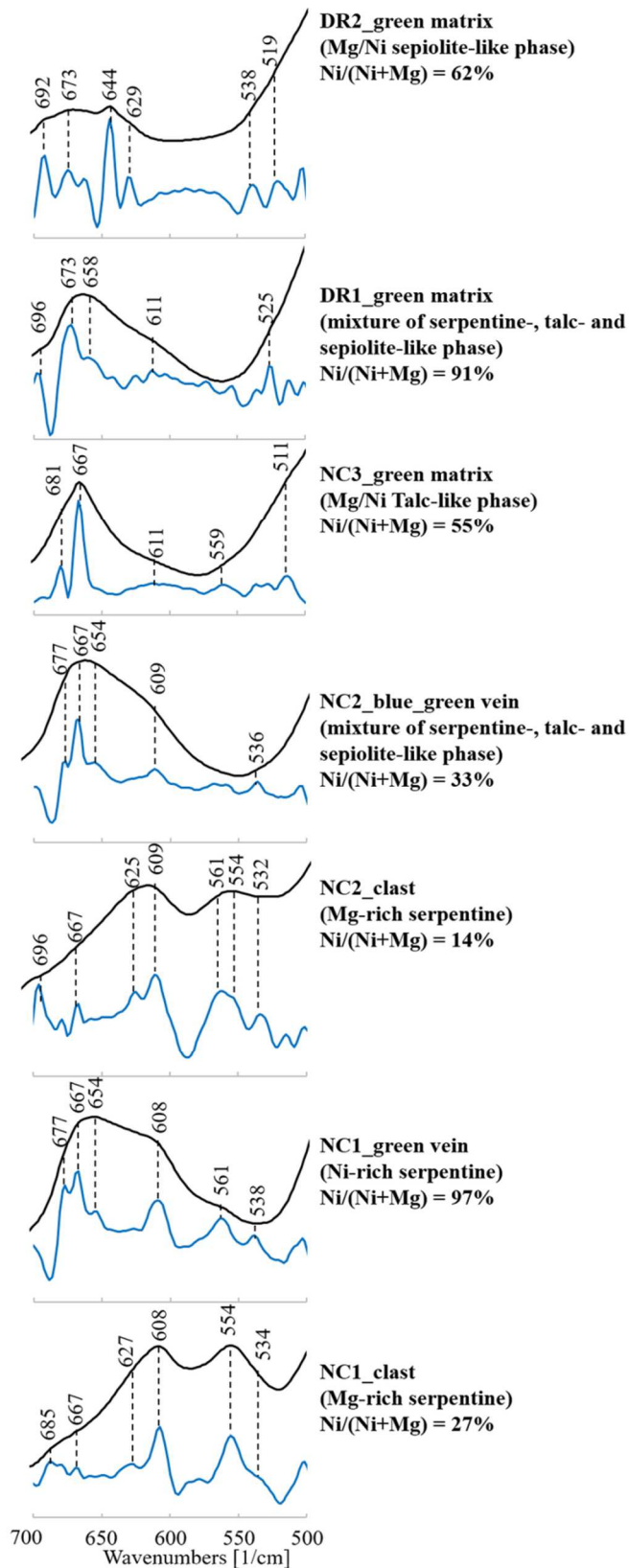
449 Unlike for serpentine- and talc-like phases, this region does not contain large and intense
450 bands in sepiolite-like phase (DR2_green matrix). The spectrum of sepiolite-like ROI differs
451 from the others by the absence of bands between 550 and 620 cm^{-1} , but is characterized by a
452 band centered at 644 cm^{-1} .

453

454

455

456



457

458 Figure 8. Infrared spectra of the selected samples in the 700-500 cm⁻¹ region (black line) and
459 their second derivative (blue line).

460

461 The spectra of ROIs consisting of a mixture of serpentine-like, talc-like and sepiolite-like
 462 phases (NC2_blue green vein and DR1_green matrix) show similar signatures. The spectra of
 463 NC2_blue green vein and DR1_green matrix have a larger band at 610 cm⁻¹, suggesting the
 464 presence of serpentine within the ROIs. In addition to that, the spectra show a contribution
 465 linked to a talc-like phase by a band at 667 cm⁻¹ and 673 cm⁻¹, in NC2_blue-green vein and
 466 DR1 green matrix, respectively.

467
 468 Table 4 presents a summary of the characteristic bands of the different types of minerals
 469 occurring in the studied samples. Each mineral group is characterized by distinct bands in the
 470 3500 - 3700 cm⁻¹ and 500-1000 cm⁻¹ domains. In the serpentine spectra, the presence of Ni
 471 generates new bands, at 3646 cm⁻¹ and 660 cm⁻¹ which are not, or only slightly visible in Ni-
 472 poor serpentine. These bands can be used as indicators for the presence of Ni-rich serpentine.
 473 Concerning talc-like and sepiolite-like phases, the present data does not allow the
 474 identification of differences in the spectra that can be attributed to the Ni content.

475
 476 Table 4. Summary of the main IR bands (in cm⁻¹) of the different types of phyllosilicates
 477 found in the studied ROIs.
 478

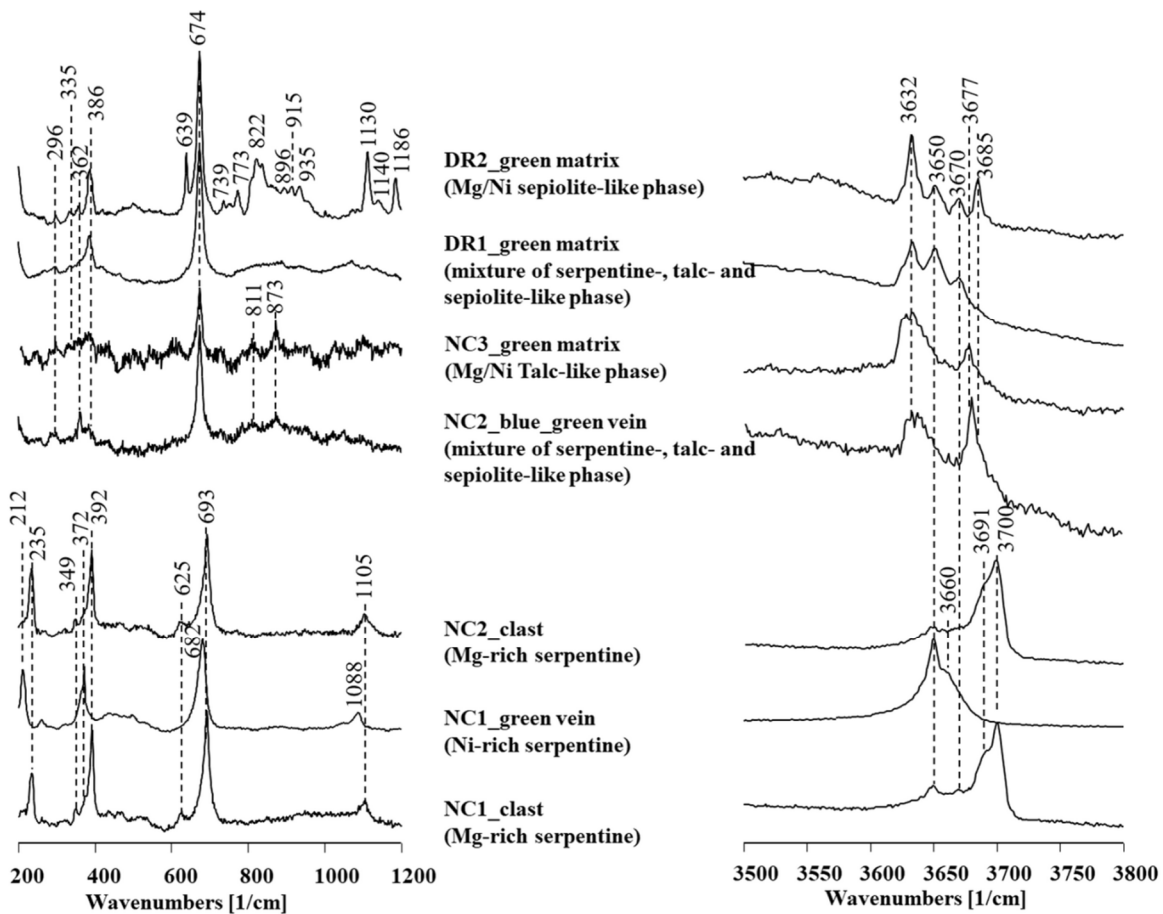
CLAST	GARNIERITE		
	Ni-rich serpentine <i>NC1_green vein</i>	Talc-like <i>NC2_blue green vein</i> <i>NC3_green matrix</i>	Sepiolite-like <i>DR2_green matrix</i>
3687	3646	3673 3625	3690 3673 3577 3567
608	660	667	692
554	608	554	644

479
 480

481 3.4. Raman spectroscopy

482 As well as FTIR analyses, Raman spectroscopy allows distinguishing the different
483 phyllosilicates. The Raman spectra of the seven samples are shown in Figure 9. Each sample
484 was analyzed over two regions. The first region, between 200 and 1200 cm^{-1} , corresponds to
485 lattice and internal vibration modes, such as O-H-O vibrations and Si-O-Si vibrations
486 (Auzende et al. 2004; Groppo et al. 2006). The second region, between 3500 and 3800 cm^{-1} ,
487 corresponds to the vibrations of the OH groups (e.g. Cathelineau et al. 2015, Villanova-de-
488 Benavent et al. 2019).

489

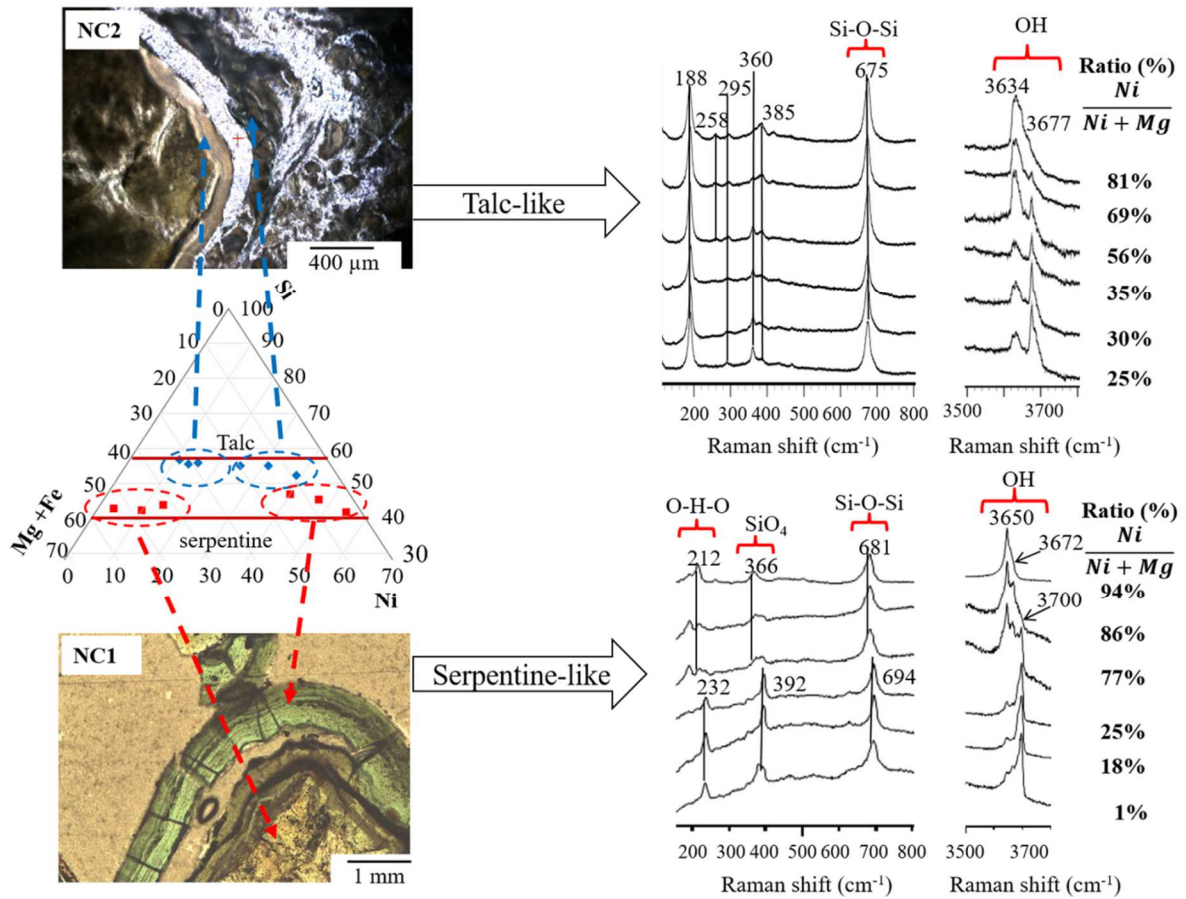


490

491 Figure 9. Raman spectra of the selected samples in the 200-1200 cm^{-1} and 3500-3800 cm^{-1}
492 regions.

493

494 As the samples NC1 and NC2 present variations in the chemical composition at the
 495 micrometric scale (determined by EPMA), analyses were performed in different areas in order
 496 to study the influence of the Ni content on the Raman spectra of serpentine-like and talc-like
 497 phases. Analyses were carried out for Ni/(Ni+Mg) compositions ranging from 1 to 94% in the
 498 case of serpentine-like ROIs, and from 25 to 81% in the case of talc-like ROIs. The Raman
 499 spectra, linked to the corresponding chemical compositions are presented in Figure 10. The
 500 sepiolite-like ROI (DR2_green sample) has a more homogeneous Ni content, and therefore it
 501 was not considered for this part of the study.



502
 503 Figure 10. Optical photomicrographs (transmitted, parallel light) of the talc-like and the
 504 serpentine-like garnierites in samples NC2 and NC1, respectively, and their chemical
 505 composition, compared to their corresponding Raman spectra

506

507 3.4.1. The 200-1200 cm^{-1} region.

508 In this region Ni-poor serpentine (NC1 and NC2_clast, in figure 9) is characterized by five
509 main bands located around 232 cm^{-1} , 392 cm^{-1} , 625 cm^{-1} , 694 cm^{-1} and 1105 cm^{-1} . Bands with
510 similar positions are reported by Petriglieri et al. (2015) for lizardite and chrysotile. The band
511 at 232 cm^{-1} is assigned to the O-H-O vibrations, the band at about 625 cm^{-1} to the OH-Mg-OH
512 vibrations, while those at 392 cm^{-1} , 694 cm^{-1} and 1105 cm^{-1} involve the SiO_4 tetrahedral
513 group (Auzende et al. 2004; Groppo et al. 2006; Petriglieri et al. 2015; Rinaudo et al. 2003).

514 The same bands are observed in Ni-rich serpentine (NC1_green vein), but with shifted
515 positions towards shorter wavelengths. This shift as a function of the Ni content is also
516 observed in Figure 10.

517 In the samples mainly composed of talc-like phases or mixtures of phases (NC2_blue green
518 vein, NC3_green matrix and DR1_green matrix), the Raman spectra are characterized by two
519 main bands located around 385 cm^{-1} and 675 cm^{-1} . Similar data were reported by Villanova-
520 de-Benavent et al. (2019) for a garnierite composed mainly of kerolite-pimelite. Figure 10
521 shows that the Ni content has no influence on the band at 675 cm^{-1} in contrast to the band at
522 385 cm^{-1} . It turns out that when the mixture is Ni-poor, this same band is around 360 cm^{-1} .
523 The Ni decrease in the mineral structure shifts progressively the intensity ratios between the
524 bands at 360 and 385 cm^{-1} (I_{360} / I_{385}). By analogy with talc, these bands are located at 365
525 cm^{-1} and 675 cm^{-1} (Fumagalli et al. 2001; Wang et al. 2015) and are attributed to vibrations of
526 Mg-OH bonds, and vibrations of Si-O-Si deformations, respectively (Fumagalli et al. 2001;
527 Rosasco and Blaha, 1980). Also, it should be noted that the band located at 675 cm^{-1} varies in
528 intensity from one analysis point to another (Figure 10). This variation may be due to the size
529 and orientation of the grains analyzed (Sharma et al. 2000).

530 It is also noted that unlike talc, the samples from this study show a more or less wide and not
531 intense band between 800 and 900 cm^{-1} . This band may be related to vibrations of
532 deformation of Ni-OH bonds (Frost et al. 2008).

533 The DR2_green matrix ROI has a Raman signal that is relatively close to that of the previous
534 samples. It is characterized by the presence of bands at 386 cm^{-1} , 640 cm^{-1} , 675 cm^{-1} , between
535 750 and 850 cm^{-1} and above 1100 cm^{-1} . The main and only difference is the variable intensity
536 of some bands, depending on the talc-like or serpentine-like phases. Only McKeown et al.
537 (2002) indicate that peaks below 700 cm^{-1} involve the deformation vibrations of SiO_4
538 tetrahedra and $\text{M}(\text{O},\text{OH})_6$ octahedra, (where $\text{M}=\text{Mg}, \text{Ni}$), and those above 700 cm^{-1} , only of
539 SiO_4 tetrahedra.

540

541 3.4.2. The 3500-3800 cm^{-1} region.

542 As expected and in agreement with infrared spectroscopy, the region involving hydroxyl
543 groups shows many differences across the samples.

544 These differences are related both to the nature of the mineral phases analyzed (serpentine-,
545 talc- and sepiolite-like) and to the influence of the presence of Ni in the octahedral position.

546 This last point is particularly visible in figure 10, when comparing the Ni-poor serpentine or
547 talc with the Ni-rich ones. In the case of serpentine-like samples, Ni-poor serpentines are
548 characterized by a main band at 3700 cm^{-1} with a shoulder at 3690 cm^{-1} , and lower intensity
549 bands centered at 3650 cm^{-1} and 3665 cm^{-1} . Comparison of these positions with data from the
550 literature (Fritsch et al. 2016; Petriglieri et al. 2015; Tarling et al. 2018) on serpentine group
551 minerals (lizardite, chrysotile, antigorite) indicates that NC1 and NC2 clasts are most likely
552 composed of chrysotile.

553 The substitution of Mg by Ni in a serpentine-like structure results in relatively significant
554 changes. This goes through a broad and complex signal for a Ni/(Ni+Mg) ratio of 77% where

555 three main bands are found at 3650 cm^{-1} , 3672 cm^{-1} and 3700 cm^{-1} . These bands are attributed
556 to the vibrations of the $\text{Ni}_3\text{-OH}$, $(\text{Ni,Mg})\text{-OH}$ and $\text{Mg}_3\text{-OH}$ bonds, respectively (El Mendili et
557 al. 2019). Then, the band at 3700 cm^{-1} disappears to give place to a main band centered at
558 3650 cm^{-1} with a shoulder around 3672 cm^{-1} , as observed in Ni-rich serpentine (NC1_green
559 vein). In the present study, the effect of Ni caused a shift of the main band of about 50 cm^{-1} .

560 The Raman spectra of samples NC2 blue green vein and NC3 green matrix can be
561 distinguished from serpentine-dominated samples by main bands centered at 3634 cm^{-1} and
562 3677 cm^{-1} . These bands have shoulders around 3640 cm^{-1} and 3686 cm^{-1} . Between these two
563 main bands, the Raman spectrum of the NC3 green matrix ROI shows a band of low intensity
564 centered at around 3660 cm^{-1} . All these results are consistent with those of Cathelineau et al.
565 (2015) on Ni-Mg kerolite solid solutions.

566 In the sepiolite-like phase (sample DR2_green matrix), the Raman signal has four distinct
567 bands. They are located at 3633 cm^{-1} , 3651 cm^{-1} , 3670 cm^{-1} and 3686 cm^{-1} . Their position is
568 relatively close to those observed in more or less Ni-bearing individual serpentine-like and
569 talc-like phase analyzed in this study.

570 Table 5 lists the main bands that differentiate between the analyzed Mg- and Ni-
571 phyllosilicates. Each mineral group is distinguished by several characteristic bands, and
572 within the same group (except sepiolite), Ni generates significant variations. All these
573 differences make Raman spectroscopy a technique that can identify the presence of Ni in
574 phyllosilicate ores.

575

576

577

578

579

580

581 Table 5. Main Raman bands (in cm^{-1}) of the different types of phyllosilicates in the studied
 582 ROIs

CLAST	GARNIERITE			
	Ni-rich serpentine <i>NC1_green vein</i>	Mg-rich talc-like <i>NC2</i> <i>NC3_green matrix</i>	Ni-rich talc-like <i>NC2</i>	Sepiolite-like <i>DR2_green matrix</i>
3700	3650	3677	3634	3686
				3670
				3651
				3633
694	681	675	675	> 1100
392	366	360	385	750-850
232	212	295	295	640
		188	258	386
			188	

583

584

585 4. DISCUSSION

586

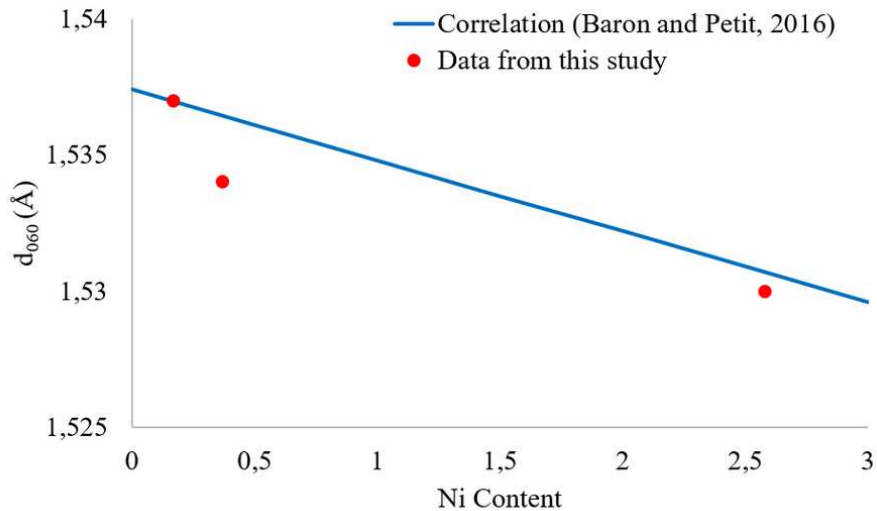
587 4.1. Influence of Ni on the shape and position of X-ray diffraction peaks

588 The X-ray diffractograms obtained in the present study are characterized by relatively broad
 589 peaks. This effect seems to be related to a difference of crystallinity caused by the presence of
 590 Ni within the structure of the minerals. It is particularly visible when comparing the
 591 serpentine-like phases encountered in samples NC1 and NC2 ROIs. The peaks, especially the
 592 main peak at 7.3 \AA , broaden with the Ni content. This observation was also made by Brindley
 593 and Wan (1975) in their study of lizardite-népouite system, where broader peaks are due to
 594 small coherent domains and structural disorders caused by the presence of Ni in octahedral

595 sites. Similar broadening was observed at the 10.2 Å peak, characteristic of talc-like phases,
596 by Brindley et al. (1977, 1979), Cathelineau et al. (2015), Martin de Vidales et al. (1991) and
597 Villanova-de-Benavent et al. (2014).

598 The substitution of Mg by Ni in the octahedral position has also an effect on the position of
599 the (060) reflection. This is directly related to the crystallographic parameter *b*. In the present
600 study, this effect is visible in the diffractograms of serpentine-dominated samples, where the
601 (060) reflections are located at 1.537 Å, 1.534 Å and 1.530 Å for NC2_clast, NC1_clast and
602 NC1_green vein, respectively. As indicated by Baron and Petit (2016), the variation observed
603 for the (060) reflection is due to the atomic radii difference between Mg and Ni in the
604 octahedral coordination. In their study on the lizardite-népouite series ((Mg_{3-x}Ni_x)Si₂O₅(OH)₄), these authors established a correlation between the position of the (060)
605 reflection and the Ni content. This can be written as follows: d_{060} (Å) = -0.0026x + 1.5374, for
606 x between 0 (lizardite) and 3 (népouite). From this relationship, it can be estimated that Ni in
607 the structural formula is of 0.15, 1.31 and 2.85 atoms per formula unit for NC2_clast,
608 NC1_clast and NC1_green vein, respectively. From the chemical analyses (EPMA), the
609 values of x are 0.17, 0.37 and 2.58 for the same samples. These results are reported in figure
610 11 and compared to the data by Baron and Petit (2016). Except for NC1_clast, the comparison
611 shows that the results are relatively close to the correlation proposed by Baron and Petit
612 (2016). It confirms that the position of the (060) reflection is an indicator of the presence of
613 Ni in serpentine-like phases. For sample NC1_clast, there is a deviation from the correlation.
614 However, due to lack of data, it is difficult to know if this deviation is related to the nature of
615 the sample (synthetic in Baron and Petit (2016) and natural in this study), or to the chemical
616 composition of the sample. In our case, the composition is based on point analyses and not on
617 the bulk sample. In addition, it is important to mention that amorphous compounds rich in Ni
618 can also be associated with garnierites (Cluzel and Vigier, 2008) and are not detected by
619

620 XRD. The chemical composition of the material may be influenced by this association and
621 generate a deviation between the position of the (060) reflection peak and the Ni content. In
622 the present case, more statistics are needed.



623
624 Figure 11. Comparison between d_{060} position and Ni content in serpentine-like samples.

625
626
627 Samples containing talc-like phases such as NC2_blue green vein, NC3_matrix and
628 DR1_matrix, display a (060) reflection with a position varying between 1.526 Å and 1.529 Å.
629 These positions are similar to those observed by Brindley et al. (1979) on five kerolite-
630 pimelite samples. The observed variations may be related to different Ni contents, but also to
631 the presence of serpentine-like phases in the NC2 and DR1 samples.
632 For sepiolite-like phases, substitution of Mg by Ni forms a series of solid solutions between
633 Mg end-member, sepiolite and Ni-end member, falcondoite. Tauler et al. (2009) showed that
634 there are little differences among diffractograms of various sepiolite-falcondoite solid-
635 solutions. From a structural point of view, they mainly noted an influence on the cell
636 parameter a , which tends to decrease with the Ni content. In this study, there is not sufficient
637 data to confirm this statement.

638

639 4.2. FTIR – influence of Ni on the position of the characteristic bands

640

641 4.2.1. Ni effect on the hydroxyl groups bands

642 The characteristic bands of the stretching and bending vibration modes of the hydroxyl groups
643 are located in the 3500-3750 cm^{-1} and 500-700 cm^{-1} ranges, respectively (Balan et al. 2002;
644 Baron and Petit, 2016; Brindley et al. 1979; Frost et al. 2001; Yenyol, 2014). As the hydroxyl
645 groups are linked to cations in octahedral positions, the position of these bands is influenced
646 by the substitution of Mg by Ni.

647 For serpentine-like phases, this substitution generates a significant difference in the position
648 of the main bands. They are at 3685 cm^{-1} , 610 cm^{-1} and 554 cm^{-1} in Ni-poor serpentine (NC2
649 clast) and at 3646 cm^{-1} , 667 cm^{-1} and 608 cm^{-1} in Ni-rich serpentine (NC1_green vein). Baron
650 and Petit (2016) obtained similar results in the lizardite-népouite series. They assigned the
651 band at 3685 cm^{-1} to the stretching vibrations of Mg-OH. The band at 3646 cm^{-1} corresponds
652 to the stretching vibrations of Ni-OH. In the present study, these two bands were detected in
653 the three samples that are mainly composed of serpentine-like phases. However, they display
654 different intensities. Baron and Petit (2016) observed that the intensity of the band at 3646
655 cm^{-1} increases progressively with the Ni content, while the intensity of the band at 3687 cm^{-1}
656 decreases. This finding is particularly important as it shows that the intensity of the 3646 cm^{-1}
657 band is indicative for the presence of Ni. The intensity of this band is low in NC2_clast and
658 significant in NC1_green vein. Based on the chemical composition, coherent with the
659 estimation of Ni content by XRD, the NC1_clast has an intermediate composition between
660 Ni-poor (NC2_clast) and Ni-rich serpentine-like phases (NC1_green vein). In particular, this
661 sample shows that both bands (3687 cm^{-1} and 3646 cm^{-1}) are relatively well defined. As

662 expected, the intensity of the band at 3646 cm^{-1} is higher than in NC2_clast but lower as in the
663 NC1_green vein.

664 In the $500\text{-}700\text{ cm}^{-1}$ region, the band around $655\text{-}670\text{ cm}^{-1}$ is characteristic of Ni-(O,OH) bond
665 vibrations in Ni-rich serpentines (Baron and Petit, 2016; Brindley et al. 1979). The equivalent
666 (Mg-(O,OH)) bond appears at $550\text{-}560\text{ cm}^{-1}$ for Ni-poor serpentine. Our results are in
667 agreement with these assignments, since they highlight that the $550\text{-}560\text{ cm}^{-1}$ band tends to
668 disappear, while the band at $655\text{-}670\text{ cm}^{-1}$ increases with Ni content (NC1_green vein).

669 For talc-like phases, four bands are reported in the $3500\text{-}3750\text{ cm}^{-1}$ region, at 3687 cm^{-1} , 3675
670 cm^{-1} (main band), 3644 cm^{-1} and 3625 cm^{-1} . These positions are in accordance with published
671 data (Gerard and Herbillon (1983), Hofmeister and Bowey (2006), Jovanoski and Makreski
672 (2016)). They correspond to four different environments of hydroxyl groups (variable
673 distances of the R-OH groups, with R = cation in octahedral position) within the talc structure
674 (Gerard and Herbillon, 1983). According to these authors, the substitution of Mg by Ni
675 influences the intensity of these bands, particularly those located at 3675 cm^{-1} and 3625 cm^{-1} .
676 The intensity of the band at 3675 cm^{-1} decreases as the Ni content increases. The opposite
677 phenomenon occurs for the band at 3627 cm^{-1} . This is similar to the effect observed in the
678 serpentine-like phase with the bands at 3687 cm^{-1} and 3646 cm^{-1} . The observation by Gerard
679 and Herbillon (1973) suggests that the intensity of the band located at 3625 cm^{-1} may be an
680 indicator of the presence of Ni in a sample with high amounts of talc-like phases.

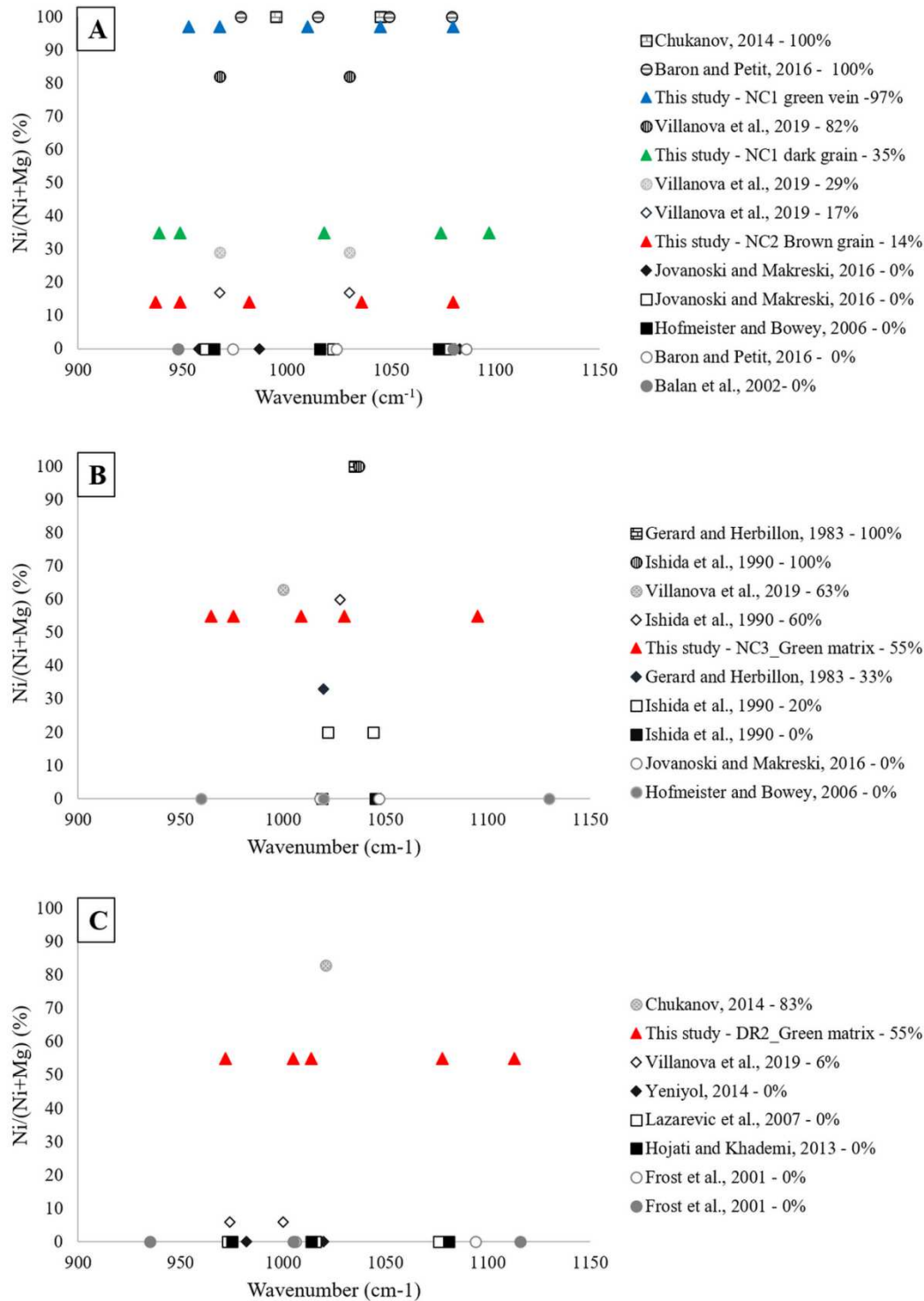
681 In the $500\text{-}700\text{ cm}^{-1}$ region, the band at 667 cm^{-1} is well resolved and corresponds to both the
682 Mg-OH bending vibrations and the Si-O bond vibrations present in the Mg-rich talc-like
683 phase (Gerard and Herbillon, 1973; Brindley et al., 1979). According to Wilkins and Ito
684 (1967), the equivalent band occurs in higher frequencies ($670\text{-}690\text{ cm}^{-1}$) in Ni-rich talc. This
685 suggestion allows us to propose that the band detected at 681 cm^{-1} in the NC3_green matrix
686 sample can be attributed to the presence of Ni.

687 For the sepiolite-like phase (DR2_green matrix), the main bands which involve the vibration
688 of hydroxyl groups, are at 644 cm^{-1} , 3567 cm^{-1} , 3629 cm^{-1} and 3690 cm^{-1} . These data are
689 consistent with those of Frost et al. (2001) from sepiolite of various origins. They observed
690 band positions around 649 cm^{-1} , 3565 cm^{-1} , 3620 cm^{-1} and 3690 cm^{-1} , in addition to bands
691 centered at around 3430 cm^{-1} and 3230 cm^{-1} , which are attributed to the vibrations of the
692 water molecules (the two latter bands are not shown in the present study). In the case of
693 falcondoite, Chukanov (2014) reports three bands centered at 3677 cm^{-1} , 3628 cm^{-1} and 3575
694 cm^{-1} . Our findings show that the second derivative of the spectrum reveals similar bands at
695 3673 cm^{-1} , 3631 cm^{-1} and 3577 cm^{-1} . On the base of the comparison with the literature, we
696 propose the bands located at 3673 cm^{-1} and 3577 cm^{-1} to be characteristic for the presence of
697 nickel within the structure (vibrations of the Ni-OH bonds) while the bands at 3567 cm^{-1} and
698 3690 cm^{-1} are characteristic of the presence of Mg (vibrations of the Mg-OH bonds). The
699 3629 cm^{-1} band can be attributed to both Mg and Ni, in the case of an intermediate
700 composition within sepiolite-falcondoite solid-solution, as in our study.

701

702 4.2.2. Nickel effect on silicate bands (FTIR)

703 For the seven samples, the same absorption bands are generally found around 950-960 cm^{-1} ,
704 1000-1030 cm^{-1} or around 1090 cm^{-1} . All samples have vibration bands of the Si-O bonds of
705 serpentine, talc and sepiolite, making the mineral identification difficult (Figs. 12 A, B and
706 C). This observation is supported by data from the literature, all displayed in figure 12.
707 Although our study indicates an effect of the presence of Ni on the intensity of the band
708 around 1010 cm^{-1} , literature data show that for the same type of phase, there is no relationship
709 between the bands observed and the substitution of Mg by Ni.



710

711 Figure 12. Positions of the vibration bands in the 900-1150 cm^{-1} range observed in this study,
 712 compared with those from the literature, for serpentine-like phases (A), talc-like phases (B)
 713 and sepiolite-like phases (C). The percentage indicated next to the authors corresponds to the
 714 Ni/(Ni+Mg) ratio calculated from the chemical composition or the structural formulae
 715 mentioned in the published articles.

716 These variations can have several origins. It may be due to the nature of the mineral within
717 the same mineral group, such as lizardite, chrysotile, antigorite (serpentine group), and/or, its
718 origin (natural/synthetic, various formation conditions). Moreover, as in our study, quartz is
719 also detected (NC2_clast) having absorption bands between 900 and 1100 cm⁻¹ (Liang et al.
720 2006).

721 An important point to mention is the influence of data processing on the higher precision on
722 band number and positions obtained. Indeed, some studies mention only the maximum
723 intensities observed (Balan et al. 2002; Gerard and Herbillon, 1983; Ishida, 1990), while
724 others have carried out deconvolution or mathematical treatments such as second derivatives
725 (Frost et al. 2001; Baron and Petit, 2016; Jovanosky and Makreski, 2016). Our study clearly
726 shows that mathematical data treatments bring higher resolution on a spectral area giving
727 information that is more precise.

728

729 4.3. Raman spectroscopy – influence of nickel on the position of the characteristic bands

730 The substitution of Mg by Ni generates shifts on most bands. These shifts can be important,
731 especially for those involving hydroxyl groups (mainly in the 3500-3800 cm⁻¹ range), but also
732 for those characterizing the vibrations of SiO₄ groups. This is observed in the case of
733 serpentine with a shift towards lower wavenumbers of about 15 to 20 cm⁻¹.

734 This shift can be attributed to the Ni-enrichment mechanisms of serpentine in the NC1 sample
735 (Majumdar et al. 2014; Putnis, 2009). Such shifts are reported for various mineral
736 replacements (Hövelmann et al. 2010; Niedermeir et al. 2009; Putnis et al. 2007) and may be
737 associated with dissolution-precipitation mechanisms (Putnis, 2009). One consequence is
738 probably the modification of the environment of SiO₄ tetrahedra (Wang et al. 2015).

739 According to Hooke's law equation, which relates the wavenumber ν to the force constant k ,

740 according to the following equation $\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$, which relates the wavenumber ν to the force

741 constant k , and where μ is the reduced mass, the weaker the force constant, the lower the
742 wavenumber. In the present case, the fact that the Raman bands of the Ni-rich serpentine
743 decrease indicates weaker Si-O bonds. However, in our study, the observed shift only
744 concerns the Ni-rich serpentine from sample NC1. Depending on the origin and the
745 mechanisms involving the formation of the Ni-rich serpentine, the shift may not be observed.
746 This may also be one of the reasons why no correlations are observed from the FTIR data on
747 the characteristic bands of SiO_4 (Figure 12).

748 For bands involving hydroxyl groups, the nature of the cation in the octahedral position
749 (Mg^{2+} , Ni^{2+}) generates a relatively large shift, which can reach 50 cm^{-1} . Because of a
750 difference in bond lengths (Ni-OH is longer than Mg-OH), the metal-hydroxyl bond has a
751 lower force constant when Ni is present.

752 In addition to band shifts, we noted variations in intensity ratios between several bands, which
753 tends to correlate with the Ni content. This is particularly the case for talc-like phases,
754 between the bands at 360 cm^{-1} and 385 cm^{-1} (I_{360}/I_{385}) and between 3636 cm^{-1} and 3677 cm^{-1}
755 (I_{3634}/I_{3677}) (Figure 9), in agreement with those reported by Cathelineau et al. (2015). They
756 showed that the bands located between 3620 and 3660 cm^{-1} tend to increase with the Ni
757 content, while those above 3675 cm^{-1} tend to decrease. In our study, the intensity ratio of the
758 two main bands (I_{3634} / I_{3677}) is higher with a higher Ni content.

759 For sepiolite, the Raman spectra obtained do not allow determining a possible influence of
760 nickel. There is no precise attribution for each band and there are few or no Raman spectra of
761 sepiolite or falcondoite in literature (Frost et al. 2001; Villanova-de-Benavent et al. 2019). It
762 can only be noted that the characteristic bands of this series are relatively close to those
763 observed in serpentines and talc-like phases. This can be explained by similar environments
764 around Mg^{2+} and Ni^{2+} cations although their crystallographic structure is different.

765

766 **5. Implications for Ni-laterite deposit mineral library databases used for in-field**
767 **analyses**

768

769 In recent years, more and more projects are concerned with developing expert systems
770 combining mineralogical, chemical and textural analyses (Duée et al. 2019; El Mendili et al.
771 2019). In the case of Ni mining exploration, studies focus on the characterization of various
772 garnierites in order to determine indicators of the presence of Ni-bearing phases. Figure 13 is
773 a summary of the main results obtained in this study. It highlights the characteristic signs of
774 each compound analyzed and shows the value of combining several analytical techniques to
775 identify the mineralogy and phases of interest. Indeed, in the present case, this study showed
776 that XRD allows to easily differentiate clay mineral families by the 001 peak, but this
777 technique is limited to give an indication of the presence of Ni within the samples.
778 Conversely, vibrational spectroscopies show similar characteristics from one clay mineral
779 family to another, by the presence of more or less large bands on domains of similar wave
780 numbers. However, these techniques have a sensitivity on the substitutions which can take
781 place within a mineral by shifts of the characteristic bands of the M-OH bonds, with M = Mg
782 or Ni. The combination of these techniques, summarized in Figure 13, therefore offers the
783 advantage of unambiguous mineral identification. The serpentine-like phases are
784 characterized by a basal distance d_{001} located around 7.3 Å and the presence of Ni evidenced
785 by the presence of FTIR and Raman bands centered around 3650 cm^{-1} . Talc-like phases are
786 characterized by XRD with a peak around 10.2 Å. The presence of Ni is detected by FTIR
787 and Raman bands centered respectively around 3625 cm^{-1} and 3634 cm^{-1} . In the presence of
788 Mg, these bands are shifted at around 3670 cm^{-1} . Finally, sepiolite-like phases are
789 distinguished by a basal distance of about 12.1 Å. Data obtained by FTIR suggest that the
790 presence of Ni can be detected by bands around 3673 cm^{-1} and 3577 cm^{-1} . However, for this

791 type of compounds, further investigations are needed to provide further signals characteristic
 792 of the presence of Ni.
 793 The development of on-line mineralogical and chemical analysis systems, with existing
 794 databases such as the Crystallography Open Database (COD), and the Raman Open Database
 795 (ROD) integrating these results, is a real opportunity to identify on site and in near real time
 796 the areas of interest for mineral exploration.

Serpentine-like Mg	Serpentine-like Ni	Talc-like Mg	Talc-like Ni	Sepiolite-like Mg	Sepiolite-like Ni
XRD					
$d_{001} = 7.3 \text{ \AA}$ $d_{060} = 1.537 \text{ \AA}$	$d_{001} = 7.3 \text{ \AA}$ $d_{060} = 1.530 \text{ \AA}$	$d_{001} = 10.2 \text{ \AA}$	$d_{001} = 10.2 \text{ \AA}$	$d_{001} = 12.1 \text{ \AA}$	$d_{001} = 12.1 \text{ \AA}$
IR (main bands in cm^{-1})					
3687	3646	3673	3625	3690	3673
950-960	950-960	960-980	960-980	3567	3577
608	660	667	667	1005	1005
554	608	554	554	972	972
				644	644
Raman (main bands in cm^{-1})					
3700	3650	3677	3634		3686
694	681	675	675		3670
392	366	360	385		3651
232	212	295	295		3633
		188	258		
			188		

797
 798 Figure 13. Main characteristics of the different minerals analyzed in this study.

799
 800 **6. Conclusions**

801 This study focused on the characterization of garnierite facies of different colors, mineralogy,
 802 chemical composition and spectral features. Our data can feed open databases which are
 803 useful for in-field analyses during exploration and mining of Ni-laterites. The characteristic
 804 signals allow: 1) the identification of Ni-rich phases and their nature (serpentine, talc and
 805 sepiolite) and 2) an estimation of the Ni content. These data find particular application using

806 the XRD-XRF benchtop systems (e.g. Equinox, Thermofisher), which are used on mine sites
807 or processing plants.

808 This study on Ni-rich and Ni-poor phyllosilicates from garnierite and the host saprolite shows
809 that the presence of Ni has a significant impact on the crystallographic structure and
810 crystallinity of phyllosilicates. It can be observed in the XRD diffractograms and FTIR and
811 Raman spectra. From an XRD point of view, this results in a widening of the main peaks and
812 a shift of the d_{060} reflection, visible in the serpentine. From a vibrational spectroscopic point
813 of view, the substitution of Mg by Ni generates shifts in the characteristic bands of the bonds
814 involving the relatively large OH groups (of the order of 50 cm^{-1}). Moreover, Raman analyses
815 also showed that as a function of the Ni and Mg content, the intensity ratio of Mg-OH/Ni-OH
816 bands decreases progressively with the Ni content, in serpentine-like as well as talc-like
817 phases.

818 Finally, this study shows the importance of combining the different analytical techniques to
819 unambiguously interpreting the data. In the case of Ni laterite exploration, the combined use
820 of these techniques connected to databases including detailed information on Ni mineralogy
821 offers encouraging prospects for improving and facilitating in-field analysis.

822 Finally, smart mathematical data treatment allows higher resolution of single spectral regions.

823

824

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829

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