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4 **Infrared spectroscopic study of the synthetic Mg-Ni talc series**

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6

7 Marc Blanchard¹, Merlin Méheut¹, Louise Delon¹, Mathilde Poirier¹, Pierre Micoud¹,8 Christophe Le Roux¹, François Martin¹

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10 ¹ Géosciences Environnement Toulouse (GET), Université de Toulouse, CNRS, IRD, UPS, 14 avenue Edouard

11 Belin, 31400 Toulouse, France

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15

16 Corresponding author: Marc Blanchard

17 E-mail: marc.blanchard@get.omp.eu

18

19 **Abstract**

20 Five talc samples ((Mg,Ni)₃Si₄O₁₀(OH)₂) covering the entire Mg-Ni solid solution
21 were synthesized following a recently developed and patented process (Dumas et al. 2013a,
22 b), which produces sub-micron talc particles replying to industrial needs. Near- and mid-
23 infrared spectra were collected and compared to infrared spectra modeled from first-principles
24 calculations based on density functional theory. The good agreement between experimental
25 and theoretical spectra allowed assigning unambiguously all absorption bands. We focused in
26 particular on the four main OH stretching bands, which represent good probes of their local
27 physical and chemical environment. The description of the vibrational modes at the origin of
28 these absorption bands and the theoretical determination of absorption coefficients provide a
29 firm basis for quantifying the talc chemical composition from infrared spectroscopy and for
30 discussing the distribution of divalent cations in the octahedral sheet. Results confirm that
31 these synthetic talc samples have a similar structure as natural talc, with a random distribution
32 of Mg and Ni atoms. They only differ from natural talc by their hydrophilic character, which
33 is due to their large proportion of reactive sites on sheet edges due to sub-micronic size of the
34 particles. Therefore the contribution on infrared spectra of hydroxyls adsorbed on edge sites
35 has also been investigated by computing the infrared signature of hydroxyls of surface
36 models.

37

38 Keywords: Talc, hydrothermal synthesis, Infrared spectroscopy, first-principles calculation,
39 DFT.

40

41 **1. Introduction**

42 Talc is a trioctahedral phyllosilicate with the structural formula $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$. A
43 representation of its structure can be found for instance in Dumas et al. (2015), where we see
44 the octahedral sheet containing Mg atoms sandwiched by two tetrahedral sheets containing Si
45 atoms. In talc, each hydroxyl group is bonded to three octahedral cations (Mg) and is oriented
46 perpendicular to the (*ab*) plane (i.e., plane defined by talc sheets).

47 Natural talc is used in many industrial applications, in particular as filler in composite
48 materials in order to reduce the production costs and possibly to improve their physical and
49 chemical properties (Claverie et al. 2017). However, natural talc has important limitations. It
50 contains minor or trace elements (Martin et al. 1999), and is often associated with other
51 minerals like chlorite, chrysotile, pyrite, graphite, calcite or amphibole. Furthermore,
52 industrial applications usually require small and homogeneous particles. This cannot be
53 achieved by grinding natural talc since the crystal structure becomes amorphized. These
54 limitations were circumvented by developing a new process to synthesize sub-micron talc
55 particles (Dumas et al. 2013a, b, 2016; Claverie et al. 2017). These syntheses produce a
56 single-phased chemically pure product from a short hydrothermal treatment (from a few
57 seconds to few hours). Providing talc products of accurately controlled chemical
58 compositions, and at the same time, an inexpensive and convenient method to verify this
59 composition would increase the industrial applications. In this aim, we investigate here the
60 Mg-Ni series by infrared spectroscopy, building on the work by Dumas et al. (2015). This
61 previous study focused on the transformation mechanism from the amorphous talc precursor
62 to crystalline synthetic talc, using samples with 50% and 100% Ni substitution.

63 We report here the infrared spectroscopic investigation of synthetic talc samples with
64 five compositions spanning the entire Mg-Ni solid solution. The measured spectra are
65 discussed in light of the modeling of the infrared spectra of Mg-Ni talcs from first-principles

66 calculations based on the density function theory. A special attention is given to the
67 absorption bands related to OH stretching vibrations in the near- and mid-infrared regions,
68 since OH groups of talc are known to be a good probe of the local chemical environment
69 (e.g., Wilkins and Ito 1967; Petit et al. 2004; Martin et al. 2006). Since the pioneer work of
70 Wilkins and Ito (1967), the four OH absorption bands observed in binary octahedral solid
71 solutions of talc are assigned to OH groups characterized by their specific cationic
72 environment. These bands can be used to derive the chemical composition of talc and to
73 discuss the distribution of the magnesium and the substituting ion between the two
74 crystallographically distinct octahedral sites. The present theoretical modeling of infrared
75 spectra provides new insights on these applications. Sub-micron talc particles are
76 characterized by a large proportion of edge surfaces with many reactive sites. This explains
77 the observed hydrophilic character of synthetic talc compared to the well-know
78 hydrophobicity of natural talc (Dumas et al. 2013c, 2016; Claverie et al. 2017). In order to
79 improve our understanding of the infrared spectra of synthetic talcs, we also modeled the
80 infrared signature of OH and H₂O adsorbed on particle edge sites.

81

82

83 **2. Materials and methods**

84

85 **2.1 Samples preparation**

86 The starting materials for the co-precipitation experiments were magnesium acetate
87 tetrahydrate ($\text{Mg}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$), nickel acetate tetrahydrate ($\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$),
88 sodium metasilicate pentahydrate ($\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$), sodium acetate trihydrate
89 ($\text{NaCH}_3\text{COO} \cdot 3\text{H}_2\text{O}$), and acetic acid. All reagents were purchased from Aldrich and used

90 without any further purification. A 1N solution of glacial acetic acid was prepared using
91 deionized water.

92 Five samples of synthetic talc (labeled Ni0, Ni25, Ni50, Ni75 and Ni100, according to
93 the mol % Ni targeted) were prepared using the process describes in patent of Dumas et al.
94 (2013a. b). Synthetic talc preparation was achieved in two steps. First, a talc precursor was
95 prepared at room temperature and atmospheric pressure with the right (Mg+Ni)/Si talc ratio
96 (Table 1). Second, a hydrothermal treatment at 300 °C and 86 bar during 6 h transformed the
97 precursor into synthetic talc. Before analysis, samples were centrifuged and rinsed to remove
98 any traces of sodium acetate salt.

99

100 **2.2 Characterization**

101 X-ray diffraction analysis (XRD) was performed on dried talc powders using the side-
102 loading procedure to minimize preferential orientations. The XRD patterns were recorded on
103 a Bruker D2 Phaser diffractometer over the 0-80°2θ CuKα₁₊₂ angular range, with a step size
104 of 0.02°2θ and a 0.5 s count time per step.

105 The Fourier transformed infrared spectroscopy in the near-infrared region was
106 recorded with 32 scans at a resolution of 4 cm⁻¹ between 4,000 and 10,000 cm⁻¹ using a
107 Thermo Nicolet 6700 FTIR spectrometer (Services Communs de Chimie, UPS, University of
108 Toulouse) with a smart NIR Integrating Sphere (CaF₂ beam splitter and InGaAs detector). No
109 specific sample preparation was needed.

110 Mid-infrared spectra were recorded with a Thermo Nicolet 6700 FTIR spectrometer
111 equipped with a DLaTGS detector using a transmission mode. The spectral conditions
112 consisted in a resolution of 4 cm⁻¹ between 400 and 4,000 cm⁻¹ using 16 scans. Sample
113 powders were diluted into KBr pellets.

114 Regions of OH stretching modes were analyzed using the Fityk program (Wojdyr
115 2010) to decompose the infrared signal into pseudo-Voigt components. The baseline was
116 defined around the two regions where vibrational modes are related to structural OH groups
117 (i.e., 6900-7300 cm^{-1} in near-infrared and 3610-3730 cm^{-1} in mid-infrared, respectively).
118 During the decomposition, the number of components was kept as minimal as possible.

119

120 **2.3 Computational methods**

121 Structural relaxations and calculation of vibrational properties were performed within
122 the framework of the density functional theory (DFT), using periodic boundary conditions
123 and the generalized gradient approximation (GGA) to the exchange-correlation functional,
124 with the PBE parameterization (Perdew et al. 1996). The ionic cores were described using the
125 latest version of ultrasoft pseudopotentials from the GBRV library (Garrity et al. 2014). Wave
126 functions and charge density were expanded in plane-waves with 40 and 240 Ry cutoffs,
127 respectively, corresponding to a convergence of the total energy better than 1 mRy/atom. For
128 the electronic integration, the Brillouin zone of the triclinic talc unit cell (space group *C-1*)
129 was sampled using a shifted $4 \times 2 \times 2$ *k*-points grid. For Ni-bearing talc, calculations were
130 spin-polarized and set up to the ferromagnetic structure. The structure relaxations and
131 vibrational mode calculations were done using the PWscf and PHonon codes of the Quantum
132 ESPRESSO package (Giannozzi et al., 2009; <http://www.quantum-espresso.org>). During the
133 relaxations, forces on atoms were minimized to less than 10^{-4} Ry/a.u. Transmission infrared
134 spectra were calculated using an electrostatic model similar to the one developed by Balan et
135 al. (2001, 2008). This approach is based on the *ab initio* calculation of the low-frequency
136 dielectric tensor, which requires the frequencies and atomic displacements of the normal
137 vibrational mode and dielectric quantities (Born effective charges and electronic dielectric
138 tensor), all computed within the harmonic approximation using the linear response theory

139 (Baroni et al. 2001) as implemented in the PHonon code. In order to avoid the divergence of
140 the low-frequency dielectric tensor at the resonance frequencies, we used a damping
141 coefficient arbitrarily fixed to 2 cm^{-1} (cf Equation 1 of Balan et al. 2001).

142 Talc unit cell contains six Mg atoms in the octahedral sheet. In order to investigate the
143 Mg-Ni series, starting from this pure Mg-talc, we substituted one, three, five or six Mg atoms
144 by Ni atoms, leading to structural models corresponding to talcs with Ni concentrations of
145 0.0, 16.7, 50.0, 83.3 or 100.0 mol %, respectively (the theoretical models were labeled Ni0,
146 Ni17, Ni50, Ni83 and Ni100, respectively).

147 In addition to the investigation of the vibrational properties of bulk Mg-Ni talcs, we
148 also explored the infrared signature of hydroxyl groups and water molecules remaining
149 adsorbed on edge sites of small talc particles even after drying of talc powders. To this aim,
150 we also built two surface models (surfaces (100) and (010)) for the two end members of the
151 Mg-Ni series. We adopted a supercell approach, in which a slab bounded by either (100) or
152 (010) surfaces was cut from the optimized bulk structure of either Mg-talc or Ni-talc. Slabs
153 were cut in a manner for preserving the tetrahedral coordination of Si atoms and the
154 octahedral coordination of Mg or Ni atoms. Protons were then added to surface O atoms in
155 order to compensate the O charge, which leads to neutral slabs containing 92 or 99 atoms for
156 the (010) or (100) surfaces, respectively. The slab surfaces were separated from their adjacent
157 images by a vacuum gap of at least 9 \AA . The four triclinic simulation cells have the following
158 X, Y, Z dimensions: 21.40 \AA , 9.27 \AA , 10.12 \AA for the (100) surface of Mg-talc, 5.35 \AA , 27.80
159 \AA , 10.12 \AA for the (010) surface of Mg-talc, 21.31 \AA , 9.24 \AA , 9.67 \AA for the (100) surface of
160 Ni-talc, and 5.33 \AA , 27.72 \AA , 9.67 \AA for the (010) surface of Ni-talc. Surface relaxation was
161 performed at constant volume and with a Brillouin zone sampling reduced to a single point in
162 the direction perpendicular to the surface. Vibrational properties were computed only for OH
163 stretching modes.

164

165

166 **3. Results and discussion**

167

168 **3.1 Structural properties**

169 X-ray diffraction patterns were collected on the five synthetic talc samples (Fig. S1).
170 Each pattern shows inter-reticular distances characteristic of 001, 003 and 02 l -11 l reflections
171 of talc structure (e.g., Dumas et al. 2015). No other mineral phase is detected. One can note
172 that 001 and 003 peaks become sharper and more intense with increasing Ni content, which
173 reflects a progressive increase in the crystallinity degree, as previously observed by Martin et
174 al. (1992).

175 Table 2 compares the experimental and DFT-optimized values of cell parameters and
176 mean bond lengths for the Mg end member of talc. In our calculations, a and b cell
177 parameters are overestimated by 1% while α , β , γ angles are slightly underestimated by less
178 than 0.4%. These trends are similar to those observed by Ulian et al. (2013). The only
179 discrepancy is the significant overestimation of the c cell parameter but this larger interlayer
180 space does not affect the interatomic bond lengths that are only 1% larger than their
181 experimental counterparts. It is well known that standard DFT does not capture accurately van
182 der Waals interactions that govern the cohesion of talc layers. However, Larentzos et al.
183 (2007) already demonstrated that first-principles calculations using DFT-GGA functionals are
184 sufficiently accurate in predicting the mineral structure and vibrational properties of talc.

185 In the solid solution of interest, Mg atoms are progressively substituted by Ni atoms in
186 octahedral sites. Because the ionic radius of Ni²⁺ (69 pm) is slightly smaller than the one of
187 Mg²⁺ (72 pm), we obtain a mean Ni-O bond length (2.07 Å in the Ni100 model) slightly
188 shorter than the mean Mg-O bond length (2.09 Å in the Ni0 model). This decrease is in

189 agreement with the values derived experimentally (2.055 Å for the Ni-talc according to the
190 EXAFS analysis of Dumas et al. 2015, and 2.071 Å for the Mg-talc according to Rietveld
191 refinement of X-ray diffraction patterns on large Mg natural talc single crystal of Perdikatsis
192 and Burzlaff 1981). Thus the Mg-Ni substitution leads to a slight contraction of the crystal
193 lattice. Cell parameters a and b decrease from 5.35 Å to 5.33 Å, and from 9.27 Å to 9.24 Å,
194 respectively (Fig. 1).

195

196 **3.2 Infrared spectra of Mg-talc and Ni-talc**

197 Experimental infrared spectra of Mg-talc (sample Ni0) and Ni-talc (sample Ni100) are
198 shown in Figure 2. The higher degree of crystallinity of Ni-talc already mentioned from the
199 X-ray diffraction patterns is also visible in infrared spectroscopy. Absorption bands are
200 sharper in Ni-talc. Above 3000 cm^{-1} , spectra are characterized by a broad band with its
201 maximum at 3438 cm^{-1} and a sharp band at higher frequency (3677 cm^{-1} in Mg-talc and 3627
202 cm^{-1} in Ni-talc). Below 1200 cm^{-1} , we can observe three groups of absorption bands at about
203 1000, 700 and 450 cm^{-1} . The striking difference between the spectra of Mg-talc and Ni-talc is
204 in the group of bands around 700 cm^{-1} . Mg-talc displays a unique band at 670 cm^{-1} while Ni-
205 talc shows two bands at 668 cm^{-1} and 710 cm^{-1} .

206 Infrared spectra have also been computed from first-principles calculations on models
207 Ni0 and Ni100, taking into account the shape of talc particles. Indeed, for particles smaller
208 than the infrared wavelength (sub-micron particles), the electric field (depolarization field)
209 induced by surface charges in the polarized particles shifts the absorption bands and affects
210 their intensity with respect to the resonances of the dielectric tensor of the bulk mineral (e.g.,
211 Balan et al. 2008a). These resonances of the dielectric tensor correspond to the spectra at the
212 bottom of Figure 2. Three particle shapes have been considered: a plate perpendicular to the
213 c^* axis, a sphere and an intermediate shape (oblate spheroid). The correspondence between

214 theoretical and experimental absorption bands is straightforward (Fig. 2). For Mg-talc, the
215 plate shape provides the best description of the bands observed at 670, 538 and 450 cm^{-1} , and
216 in particular their spacings. For Ni-talc, only the plate shape gives the right ratio of intensity
217 between the two bands at 668 and 710 cm^{-1} and in the same time, the intense and rather
218 symmetric band at 1030 cm^{-1} . This suggests that the particles of the synthetic sub-micron talc
219 samples reflect their layered structure and probably have only few talc sheets. A large stacking
220 of talc sheets relative to the lateral extension of the particle would approach the sphere model
221 instead.

222 Looking at the theoretical vibrational modes enables us to assign the observed
223 absorption bands. The sharp band above 3600 cm^{-1} corresponds to the stretching vibration of
224 the structural OH groups. The difference in wavenumber between calculated and observed
225 OH bands is at least partly explained by the anharmonicity. OH stretching vibrations show a
226 certain degree of anharmonicity while calculations are performed within the harmonic
227 approximation. The broad band around 3438 cm^{-1} is not related to the talc structure. It is
228 usually assigned to weakly bound water and will be discussed further. The normal mode
229 calculated at about 900 cm^{-1} (bottom spectrum of Fig. 2) corresponds to a Si-O stretching
230 mode polarized along the c^* axis while the more intense band calculated at $\sim 980 \text{ cm}^{-1}$ is due
231 to two degenerated Si-O stretching modes polarized in the (ab) plane. For the plate shape, the
232 band at $\sim 980 \text{ cm}^{-1}$ remains at the same position while the band at $\sim 900 \text{ cm}^{-1}$ shifts to higher
233 wavenumbers. The two bands become superimposed in Ni-talc, which contributes to the
234 strong intensity and symmetry of the band observed at 1030 cm^{-1} . While in Mg-talc, the mode
235 polarized along the c^* axis appears at even higher wavenumber than the modes polarized in
236 the (ab) plane, thus explaining the asymmetric shape of the band observed at 1018 cm^{-1} with a
237 shoulder at $\sim 1060 \text{ cm}^{-1}$. At lower wavenumber, the band at 670 cm^{-1} in Mg-talc and 710 cm^{-1}
238 in Ni-talc corresponds to OH libration motions. Our analysis of the theoretical data also

239 shows that in Ni-talc, even if the band observed at 668 cm^{-1} appears in the same region, the
240 vibrational mode involved is fundamentally different. This band corresponds to a lattice mode
241 polarized along the c^* axis and involving Ni, O and H atoms. In Mg-talc, the same mode
242 (involving now Mg, O, H atoms) gives rise to the band observed at 538 cm^{-1} . Finally, the
243 most intense doublet at $\sim 450, 467\text{ cm}^{-1}$ is assigned to lattice modes polarized in the (ab)
244 plane and involving all atoms.

245

246 **3.3 Infrared spectra of OH stretching bands in the Mg-Ni series**

247 Figure 3 reports the measured near-infrared and mid-infrared spectra in the range of
248 the first overtones and fundamentals OH stretching modes for the five synthetic samples.
249 Both spectra look very similar with the presence of up to four main absorption bands. The
250 decomposition of all spectra required considering, in addition to these four bands, two less
251 intense contributions on the high frequency side (at 7226 and 7206 cm^{-1} for the first
252 overtones, and at 3716 and 3687 cm^{-1} for the fundamental modes). These contributions were
253 assigned to OH groups on sheet edges by Dumas et al. (2013c). The spectra decompositions
254 can be found in supplementary information (Figs. S2 and S3), and the derived data for the
255 four main OH bands are compiled in Table 3. These absorption bands remain nearly at the
256 same wavenumbers over the entire solid solution (at $3677, 3662, 3646$ and 3627 cm^{-1} for the
257 fundamental modes). However, as reported by Wilkins and Ito (1967) for well-crystallized
258 synthetic samples, a closer look indicates that the separation between bands slightly decreases
259 when Ni content increases. This variation does not exceed 3 cm^{-1} over the entire
260 compositional range. It is possible to assess the anharmonicity of OH vibrations from the
261 wavenumbers of fundamental modes ($W_{\nu OH}$) and first-overtones ($W_{2\nu OH}$), by calculating the
262 anharmonicity constant, $X = W_{2\nu OH} / 2 - W_{\nu OH}$ (Bourdéron and Sandorfy 1973). Results are
263 given in Table 3. Considering the standard deviations, we found the anharmonicity constant to

264 be the same for all OH stretching modes and for all compositions, $X = -85.0 \pm 2.2 \text{ cm}^{-1}$ (2σ). It
265 is in good agreement with the value found by Petit et al. (2004b) for various natural and
266 synthetic talcs, $X = -86.0 \pm 2.5 \text{ cm}^{-1}$. The anharmonicity constant being independent on the
267 clay chemistry, these authors could apply this relation in order to improve the interpretation of
268 the near-infrared spectra of other phyllosilicates like smectite and kaolinite polymorphs.

269 Figure 3 also shows the theoretical spectra obtained for the talc models considered.
270 Talc unit cell contains six octahedral sites (2 M1 sites and 4 M2 sites). For the Ni17 model,
271 one Ni atom was placed in either M1 or M2 site. The two spectra are equivalent. In a similar
272 manner, the Ni83 model corresponds to one Mg atom placed in either M1 or M2 site, which
273 leads to the same spectrum. For the Ni50 model, several configurations of the three Ni atoms
274 over the six octahedral sites have been tested, and the two spectra obtained are shown in
275 Figure 3. Theoretical spectra, like measured ones, display up to four absorption bands. We
276 can already note that the distribution of the cations on the octahedral sites affects significantly
277 the infrared spectrum (number of bands and their intensities). For a given composition, the
278 limited size of the simulation cell imposes an ordered cation distribution that does not reflect
279 the distribution occurring in synthetic or natural samples. This explains the differences
280 observed between experimental and theoretical spectra in figure 3. Wavenumbers and
281 absorbances derived from the theoretical spectra are listed in Table 4. Talc unit cell contains
282 four hydroxyl groups. Due to their position perpendicular to the layers, all OH stretching
283 modes are polarized along the c^* axis. Each hydroxyl group is bonded to three octahedral
284 cations. In order to know which hydroxyl group is involved in each vibrational mode, we
285 calculated the displacement of each of these four H atoms (Table 4). Results confirm
286 unambiguously the assignment of the four mains absorption bands. From high to low
287 frequency, the four bands correspond to the stretching vibration of hydroxyl groups bonded to
288 3Mg, 2Mg1Ni, 1Mg2Ni, and 3Ni atoms. The present data also demonstrate that there is no

289 coupling between hydroxyl groups with distinct cationic environments. These conclusions
290 fully support the interpretation of Wilkins and Ito (1967).

291

292 **3.4 Water adsorption on edge sites**

293 Natural talc is known to be hydrophobic in relation with its sheet-like morphology of
294 few tens of micrometers wide (Fig. 4). Indeed the very large basal hydrophobic surface
295 dominates over the lateral surfaces (sheet edges), which display however many reactive sites
296 and a hydrophilic behavior. Talc particles synthesized here conserve their sheet-like
297 morphology but present sub-micron sizes. As illustrated in figure 4, the particles size
298 decreases drastically and concomitantly the proportion of sheet edges increases making the
299 hydrophilic behavior measurable. This is clearly evidenced by thermogravimetric analyses
300 (Dumas et al. 2013c). While natural talc has a single loss of weight around 950 °C
301 corresponding to its destabilization, synthetic sub-micron talc undertakes two additional
302 losses before 150 and 450 °C, attributed first to physisorbed water and second to silanols (Si-
303 OH) and magnesium hydroxides (Mg-OH) on the sheet edges. This previous study employed
304 spectroscopic techniques (nuclear magnetic resonance and infrared spectroscopies) to access
305 the edges contributions of synthetic sub-micron Mg-talc. In ¹H NMR spectra, two new narrow
306 and distinct peaks were interpreted as associated to physisorbed water and silanol groups. In
307 near-infrared spectra, two small contributions at 7200 and 7230 cm⁻¹ (next to the band at 7185
308 cm⁻¹ of structural OH groups) were assigned to OH groups on edge sites, i.e. Si-OH and Mg-
309 OH respectively. In order to investigate further the influence of sheet edges on the infrared
310 spectra, we built surface models with several distinct hydroxyl groups (OH bonded to one Si,
311 to one Si and one Mg, or to two Mg) and water molecules chemisorbed on a Mg site (Fig. 5).
312 These models do not consider physisorbed water molecules.

313 During the structural optimization of both surfaces (100) and (010) of Ni-talc, a water
314 molecule desorbed. This molecule was removed before calculating the vibrational properties.
315 Therefore the surface relaxation differs between Ni-talc and Mg-talc. The final arrangement
316 of hydroxyl groups is different. Results analysis indicates that hydroxyl groups pointing
317 outward vibrate at a frequency close to the structural hydroxyl groups. On the contrary, Si-OH
318 groups pointing toward another talc layer or OH groups pointing toward another O atom of
319 the sheet edge vibrate at lower frequency. The stronger the hydrogen bond formed, the lower
320 the frequency of the associated absorption band. These results suggest that the observed broad
321 band centered at 3440 cm^{-1} is due not only to the physisorbed water molecules (not modeled
322 here) but also to the multitude of geometries of hydroxyls chemically adsorbed on edge sites.
323 In experimental studies investigating the infrared absorption bands related to structural OH
324 groups, the spectrum baseline is defined in such a way that the contribution of the broad band
325 is removed but small features remain on the high-frequency side. As mentioned above,
326 Dumas et al. (2013c) looked at these small bands in the near-infrared region for synthetic Mg-
327 talc. Above the structural OH band (7185 cm^{-1}), the two weak bands at 7200 and 7230 cm^{-1}
328 were assigned to Si-OH and Mg-OH respectively. It is worth mentioning that, in the mid-
329 infrared region, our calculations lead to similar features. Above the structural OH band
330 calculated at 3848 cm^{-1} , we found two weak bands at 3873 and 3885 cm^{-1} related to Si-OH
331 and $\text{Mg}_2\text{-OH}$ groups respectively.

332

333 **3.5 Quantification of the chemical composition**

334 The four main OH stretching bands are now unambiguously attributed to specific
335 structural OH groups defined by their cationic environment. For the mid-infrared region, the
336 bands at 3677 , 3662 , 3646 and 3627 cm^{-1} are related to hydroxyl groups bonded to 3Mg ,
337 $2\text{Mg}1\text{Ni}$, $1\text{Mg}2\text{Ni}$, 3Ni atoms, respectively. In order to use the relative absorbance of these

338 bands (i.e. ratio of bands areas) to quantify the concentration of each of the hydroxyl types
339 and therefore the chemical composition of the talc, one has to assume that the absorption
340 coefficients of these different hydroxyls are the same whatever the local chemistry around OH
341 groups. This is generally assumed in most experimental studies (e.g., Petit et al. 2004a).
342 However it has been shown (Balan et al. 2008b) that considering many minerals, absorption
343 coefficients of OH stretching modes globally decrease with increasing frequency. This
344 assumption of constant absorption coefficients can be checked from our theoretical study.

345 Theoretical molar absorption coefficients, K_{int} , and the relative integrated absorbances
346 for each vibrational mode (i.e. each OH band) are given in Table 4. We can note that with a
347 mean value of $K_{int} = 9071 \text{ Lmol}^{-1}\text{cm}^{-2}$, the talc OH groups have an absorption coefficient
348 similar as inner OH groups of lizardite and clinocllore (Balan et al. 2008b). Most
349 importantly, if we look at the relative absorbance of each OH band for a given sample, we see
350 variations, but these variations do not follow systematic trends. In model Ni17, both bands
351 contribute almost equally to the total absorbance. In model Ni50a, bands with lower
352 wavenumbers contribute slightly more (up to 26.8%) than bands with higher wavenumbers
353 (down to 22.4%). But this trend is opposite in model Ni83. We can consider these variations
354 either as inherent to the configurations investigated or due to the uncertainty of the calculation
355 (absorption coefficients are properties extremely sensitive to the structural optimization). To
356 clarify this point, we estimate the composition of these fully constrained models from these
357 values of relative absorbance. Table 5 shows for instance for the model Ni50a, that the
358 calculated relative absorbances lead to a composition of 52.5 mol % Ni, different from the
359 expected 50 mol % Ni that one obtains if OH band contributes equally to the total absorbance.
360 The present theoretical results suggest that the small observed variations are related to
361 computational uncertainties and therefore that the assumption of a constant absorption
362 coefficient whatever the cationic environment around the hydroxyls is correct.

363 The procedure is applied to the synthetic samples and talc compositions obtained from
364 the relative integrated absorbances of either the fundamental modes or the first-overtone
365 modes are compared (Table 6). Assuming that during the synthesis process, all nickel is
366 incorporated into the talc particles, we find that results from the near-infrared region are
367 sensibly better than those from the mid-infrared region. They provide the correct composition
368 within 2 mol %. Only sample Ni100 shows a larger difference of 6 mol % between the
369 expected composition and the one derived from infrared spectroscopy. While no magnesium
370 is used in the synthesis of this sample, both near- and mid-infrared spectra display a weak
371 band (at 7123 cm^{-1} and 3646 cm^{-1} respectively), which could be attributed, according to its
372 position, to OH groups bonded to one Mg and two Ni atoms. Note that Dumas et al. (2015)
373 already reported the presence of such weak band for the Ni end-member of a similar synthetic
374 sub-micron talc. The presence of this weak band either reflects a contamination during the
375 synthesis or a wrong assignment. An electron microprobe analysis was performed on this
376 Ni100 sample and leads to a Ni proportion of 98.8 ± 0.2 mol %, incompatible with the 94 mol
377 % derived from infrared spectroscopy. Therefore the weak band at 7123 cm^{-1} cannot be
378 explained by a Mg contamination. As suggested by the calculated spectra of surface models
379 for Ni-talc (Fig. 5), this weak band is rather related to OH groups on edge sites, like Ni-OH or
380 Si-OH. This assignment is also supported by the fact that a band located at a similar
381 wavenumber (7121 cm^{-1}) was previously observed by Christy (2010) on a silica gel surface.

382

383 **3.6 Cationic distribution**

384 The infrared spectroscopic data can also be used to discuss the distribution of cations
385 in the octahedral sheet (Petit et al. 2004a). If Mg and Ni atoms are randomly distributed, the
386 four OH bands should occur with the probabilities specified in Table 7. It is therefore possible
387 to calculate the relative integrated absorbances that one expects for a given composition and a

388 random distribution of octahedral cations. These values are compared with the relative
389 absorbances obtained by spectral decomposition in Table 7 and Figure 6. The good
390 correlation observed in Figure 6 indicates that divalent cations are randomly distributed in the
391 octahedral sheets of these synthetic sub-micron talc samples like in the various natural
392 samples investigated by Petit et al. (2004a). This conclusion is supported by our DFT
393 calculations, which predict that nickel has no preference for M1 and M2 octahedral sites. The
394 energy difference (0.3 kJ/mol) is one order of magnitude smaller than the thermal energy at
395 ambient temperature.

396

397

398 **4. Conclusion**

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400 This combined experimental and theoretical infrared spectroscopic study allowed us to
401 characterize further a synthetic talc product with potential industrial applications. Over the
402 whole range of the Mg-Ni solid solution, the sub-micron talc particles present: (i) a random
403 distribution of Mg and Ni cations in the octahedral sheets, (ii) platy shapes nicely reflecting
404 their layered structure, and (iii) an interesting hydrophilic character related to the large
405 proportion of sheet edges. The Mg-Ni substitution is also accompanied by an increase in the
406 crystallinity degree.

407 The confrontation of measured and calculated infrared spectra enabled to fix the
408 spectra interpretation to firm physical basis. Absorption bands below 1200 cm^{-1} have been
409 assigned to the corresponding vibrational modes, allowing us to understand the differences
410 observed between Mg-talc and Ni-talc. In the OH stretching region related to structural
411 hydroxyl groups, our calculations show no coupling between the stretching modes of OH
412 groups distinguishable by their cationic environment. Results thus fully support the

413 assignment made by Wilkins and Ito (1967). We have also demonstrated that absorption
414 coefficients of OH groups are constant whatever the cationic environment of these hydroxyls.
415 This validates the key assumption for quantifying the talc composition from the relative
416 absorbance of OH bands.

417 The surface models considered here suggest that the infrared signatures of hydroxyls
418 adsorbed on the reactive sites of sheet edges fall in the same wavenumber range as the broad
419 band assigned to physisorbed water molecules (band observed between 3000 and 3700 cm^{-1}).
420 In more details, the bands related to the most weakly hydrogen-bonded OH surface groups are
421 located in the same range as the bands attributed to OH structural groups. This observation
422 might hinder the accurate determination of talc composition. However absorption bands
423 related to OH surface groups have relatively weak intensities and do not affect the infrared-
424 derived composition by more than a few percent.

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426

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430 their help in XRD, IR, and EMP measurements, respectively.

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506 Table 1: Starting materials used for the preparation of talc precursors.

Sample	sodium metasilicate pentahydrate	magnesium acetate tetrahydrate	nickel acetate tetrahydrate	acetic acid	sodium acetate trihydrate
Ni0	0.10 mol	0.075 mol	0.000 mol	50.0 ml	50.0 g
Ni25	0.10 mol	0.056 mol	0.019 mol	50.0 ml	50.0 g
Ni50	0.10 mol	0.038 mol	0.038 mol	50.0 ml	50.0 g
Ni75	0.10 mol	0.019 mol	0.056 mol	50.0 ml	50.0 g
Ni100	0.10 mol	0.000 mol	0.075 mol	50.0 ml	50.0 g

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511 Table 2: Calculated (this study) and experimental (Perdikatsis and Burzlaff 1981) cell
512 parameters and mean bond lengths of Mg-talc.

	Calc.	Exp.
a (Å)	5.349	5.290
b (Å)	9.268	9.173
c (Å)	10.116	9.460
α (°)	90.35	90.46
β (°)	98.28	98.68
γ (°)	90.01	90.09
Si-O (Å)	1.642	1.623
Mg-O (Å)	2.090	2.071
O-H (Å)	0.977	-

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522 Table 3: Infrared-active OH stretching modes of Mg-Ni talc samples: wavenumber (W in cm^{-1})
523 ¹) and relative integrated absorbance (A) for the fundamental (νOH) and first overtone bands
524 ($2\nu\text{OH}$), anharmonicity constant calculated as follow $X = W_{2\nu\text{OH}}/2 - W_{\nu\text{OH}}$ (Bourdéron and
525 Sandorfy 1973). Data derived from the spectra decomposition shown in supplementary
526 information (Figs S2 and S3).

Sample	$W_{\nu\text{OH}}$	$A_{\nu\text{OH}}$	$W_{2\nu\text{OH}}$	$A_{2\nu\text{OH}}$	X
Ni0	3677	1.00	7184	1.00	-85
Ni25	3676	0.52	7184	0.43	-84
	3662	0.33	7154	0.35	-85
	3646	0.15	7119	0.19	-86.5
	-	-	7077	0.03	-
	3676	0.17	7185	0.18	-83.5
Ni50	3662	0.41	7156	0.34	-84
	3646	0.33	7121	0.34	-85.5
	3625	0.10	7078	0.14	-86
	3676	0.03	7183	0.05	-84.5
Ni75	3662	0.25	7157	0.14	-83.5
	3647	0.43	7122	0.30	-86
	3625	0.28	7079	0.51	-85.5
	3646	0.20	7123	0.17	-84.5
Ni100	3627	0.80	7080	0.83	-87

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538 Table 4: Theoretical infrared-active OH stretching modes of talc models: wavenumber (W in
539 cm^{-1}), normalized displacement (a.u.) of each of the four H atoms of the simulation cell
540 defined by their cationic environment, integrated molar absorption coefficient (K_{int} in Lmol^{-1}
541 cm^{-2}) and contribution of each mode to the total absorbance (%).

Model	W	Norm. displ. and neighbor cations				K_{int}
Ni0	3848	3Mg	3Mg	3Mg	3Mg	8117
		0.49	0.49	0.48	0.48	100%
Ni17	3849 3826	3Mg	3Mg	2Mg1Ni	2Mg1Ni	8958
		0.69	0.69	0.03	0.03	49.7%
		0.03	0.03	0.69	0.69	50.3%
Ni50a	3851 3828 3799 3762	3Mg	2Mg1Ni	1Mg2Ni	3Ni	9327
		0.97	0.02	0.01	0.01	22.4%
		0.02	0.97	0.02	0.01	24.5%
		0.01	0.02	0.97	0.01	26.3%
		0.01	0.01	0.01	0.97	26.8%
Ni50b	3827 3797	2Mg1Ni	2Mg1Ni	1Mg2Ni	1Mg2Ni	9778
		0.81	0.53	0.01	0.01	47.5%
		0.01	0.01	0.74	0.63	52.5%
Ni83	3800 3762	1Mg2Ni	1Mg2Ni	3Ni	3Ni	9377
		0.69	0.69	0.01	0.01	52.6%
		0.01	0.01	0.69	0.69	47.4%
Ni100	3765	3Ni	3Ni	3Ni	3Ni	8868
		0.49	0.49	0.48	0.48	100%

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543

544 Table 5: Ni proportions in theoretical models estimated from the relative integrated
545 absorbances and compared to the exact value.

Model	mol % Ni from A	Exact mol % Ni
Ni17	16.77	16.67
Ni50a	52.50	50.00
Ni50b	50.83	50.00
Ni83	82.47	83.33

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548 Table 6: Ni proportions in synthetic samples estimated from the relative integrated absorbances of the fundamental and first overtone OH bands.

Sample	mol % Ni from ν OH	mol % Ni from 2ν OH
Ni0	0	0
Ni25	21	27
Ni50	45	48
Ni75	66	75
Ni100	93	94

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551 Table 7: Relative integrated absorbances for the fundamental (ν OH) and first overtone (2ν OH) OH bands, calculated assuming a random
 552 distribution of octahedral cations (rand). In that case, we used the sample composition derived from infrared spectroscopy and the probabilities of
 553 occurrence of each OH band that are specified in the Table. Results are compared to the ones obtained by spectral decomposition (dec).

OH group	Probability	Ni25 ν OH		Ni25 2ν OH		Ni50 ν OH		Ni50 2ν OH		Ni75 ν OH		Ni75 2ν OH		Ni100 ν OH		Ni100 2ν OH	
		rand	dec	rand	dec	rand	dec	rand	dec	rand	dec	rand	dec	rand	dec	rand	dec
Mg ₃ OH	[Mg] ³	0.49	0.52	0.39	0.43	0.17	0.17	0.14	0.18	0.04	0.03	0.01	0.05	0.00	0.00	0.00	0.00
Mg ₂ NiOH	3[Mg] ² [Ni]	0.39	0.33	0.43	0.35	0.41	0.41	0.39	0.34	0.23	0.25	0.14	0.14	0.01	0.00	0.01	0.00
MgNi ₂ OH	3[Mg][Ni] ²	0.10	0.15	0.16	0.19	0.33	0.33	0.36	0.34	0.44	0.43	0.42	0.30	0.18	0.20	0.15	0.17
Ni ₃ OH	[Ni] ³	0.01	0.00	0.02	0.03	0.09	0.10	0.11	0.14	0.29	0.28	0.43	0.51	0.81	0.80	0.84	0.83

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556 **Figure captions**

557 Figure 1: DFT optimized cell parameters of talc as a function of the Ni molar concentration.
558 Angles ($\alpha = 90.35^\circ$, $\beta = 98.28^\circ$, $\gamma = 90.01^\circ$) remain nearly constant over the Mg-Ni series.

559

560 Figure 2: Experimental (top) and theoretical mid-IR absorption spectra of Mg-talc (sample
561 and model Ni0) and Ni-talc (sample and model Ni100). Spectra have been computed for three
562 particle shapes: a plate perpendicular to the c^* axis, a sphere and an intermediate shape. The
563 trace of the imaginary part of the dielectric tensor computed for an infinite crystal (bottom)
564 serves as reference and indicates the frequency of normal modes in absence of the
565 depolarization field occurring in small particles.

566

567 Figure 3: Experimental IR spectra of Mg-Ni synthetic talcs (in the regions of fundamental
568 modes and first overtones of OH stretching vibrations) compared to theoretical spectra of
569 fundamental modes. Vertical dashed lines are guides for the eye.

570

571 Figure 4: Scanning electron microscope images taken at the same scale of a natural talc (A)
572 and a talc synthesized using the present protocol (B) (images from F. Martin's library). C.
573 Schematic representation of a talc particle (left) and the same particle split in four (right),
574 highlighting that the basal surface remains constant in both cases while lateral surfaces are
575 doubled. This explains why the hydrophilic character of talc increases when the size of talc
576 particles decreases.

577

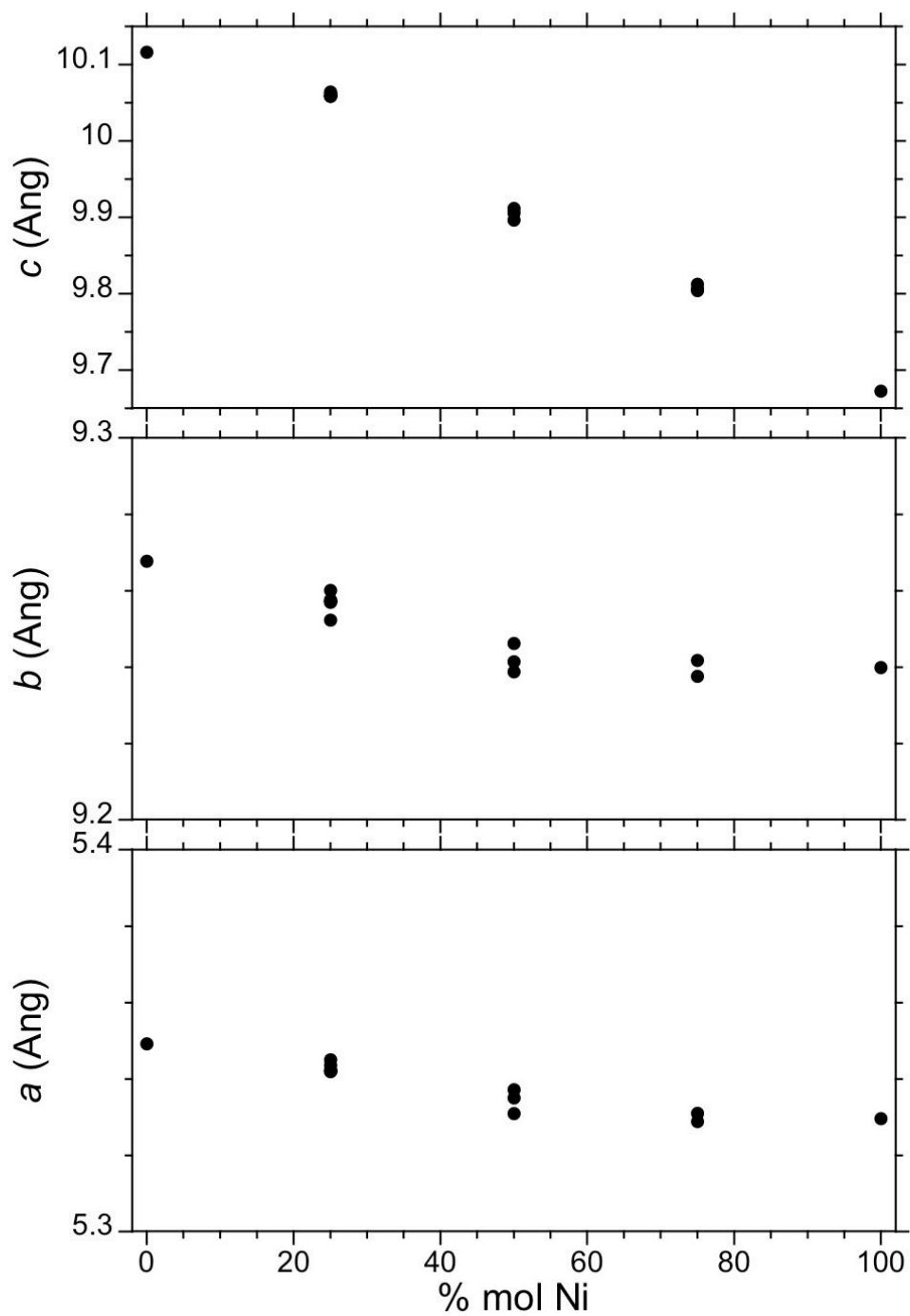
578 Figure 5: Structural models of the (100) and (010) surfaces of Mg-talc (left) and Ni-talc
579 (right), with the corresponding theoretical IR spectra of OH and H₂O groups. Experimental IR
580 spectra in the 4000 – 2700 cm⁻¹ range are shown for comparison (top).

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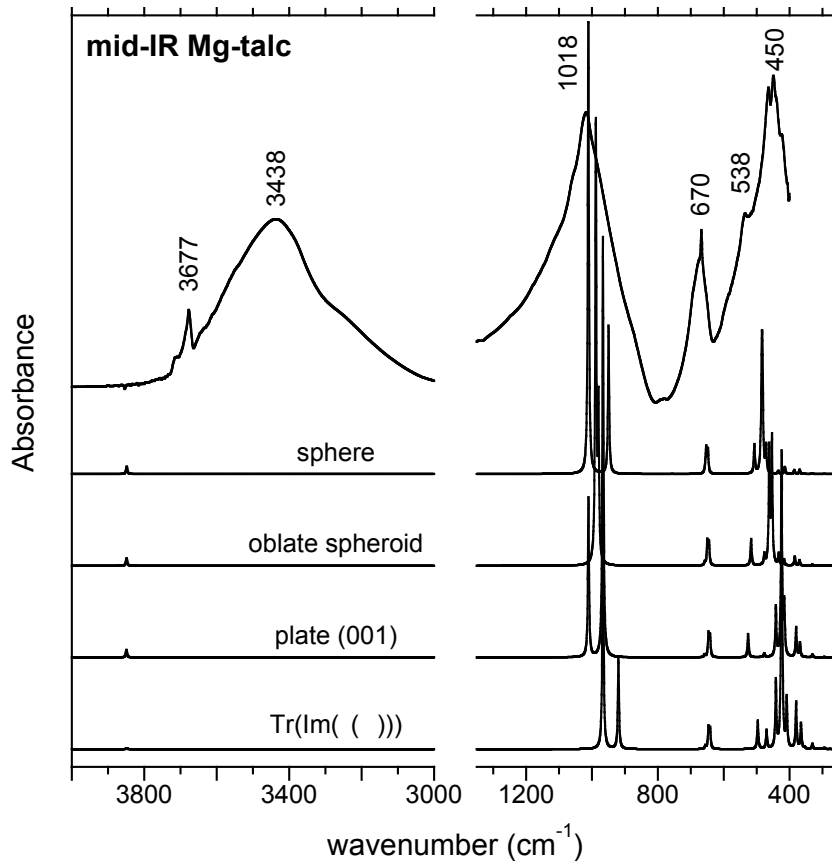
582 Figure 6: Comparison of relative integrated absorbances calculated assuming a random
583 distribution of octahedral cations and obtained by spectral decomposition. Solid and open
584 symbols correspond to fundamental and first overtone OH bands, respectively.

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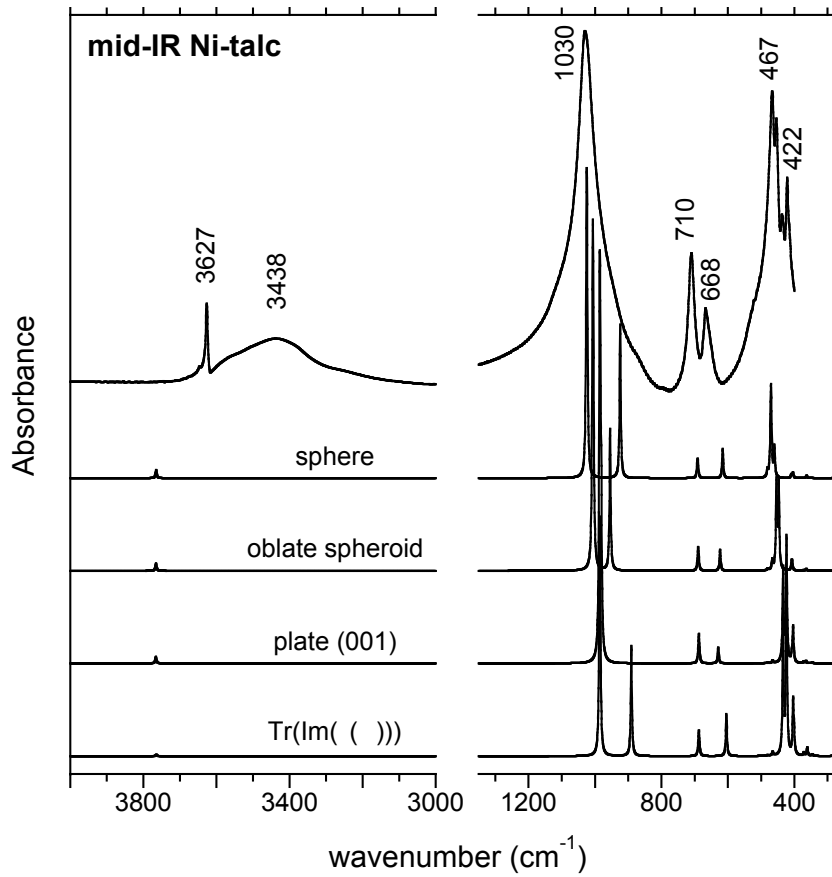
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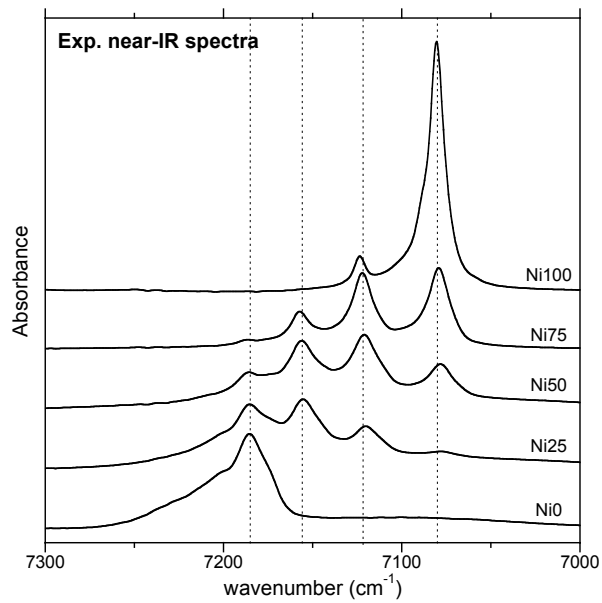


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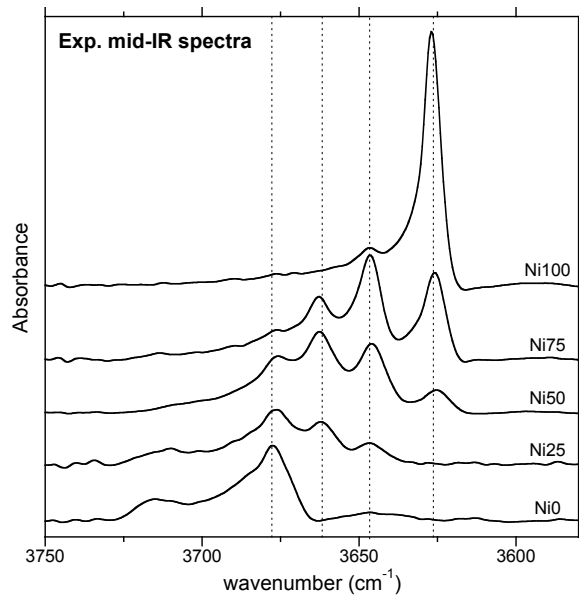


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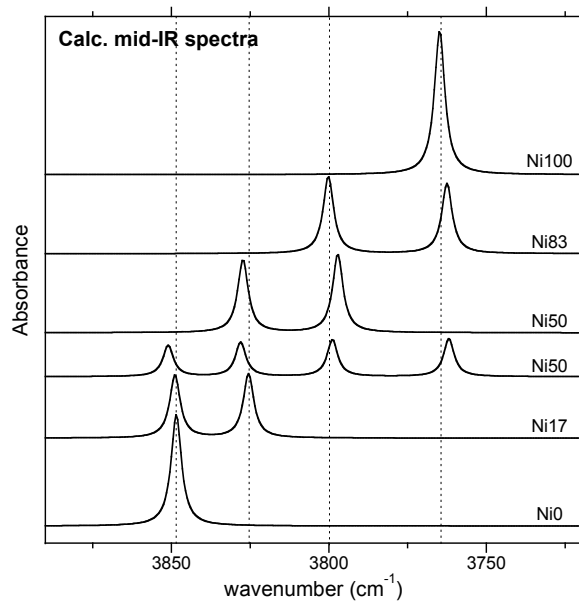
594 Figure 3:



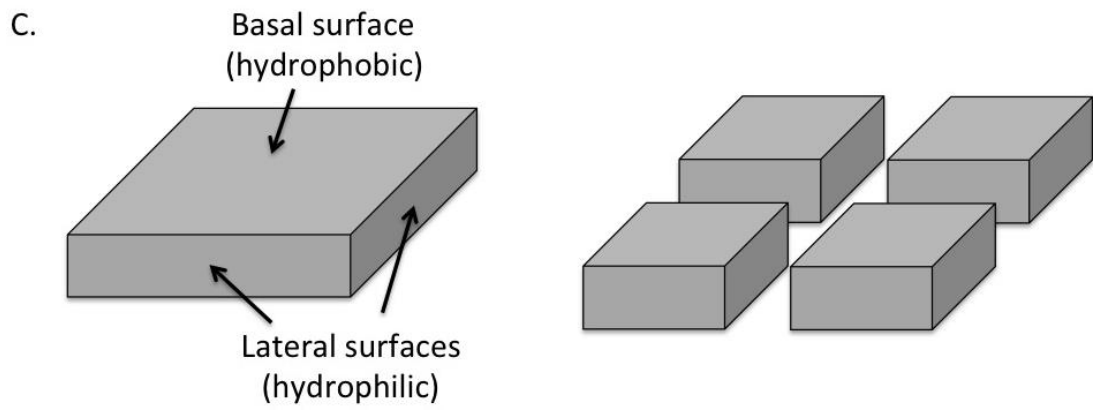
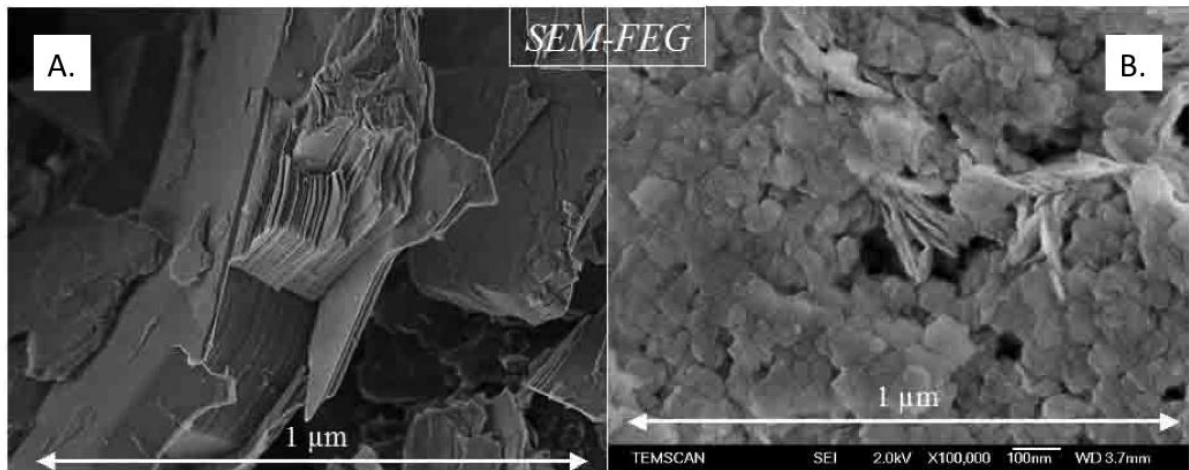
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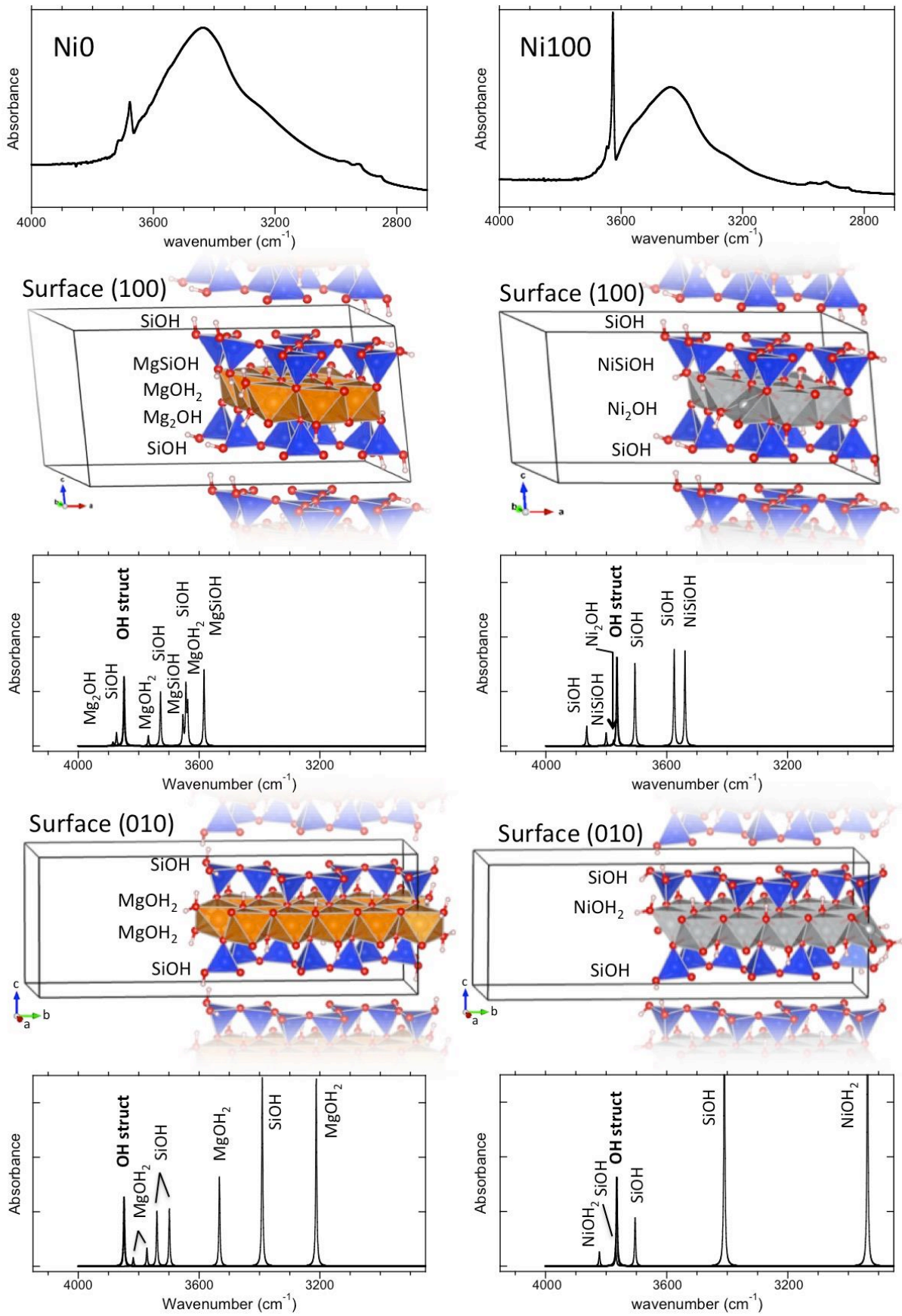
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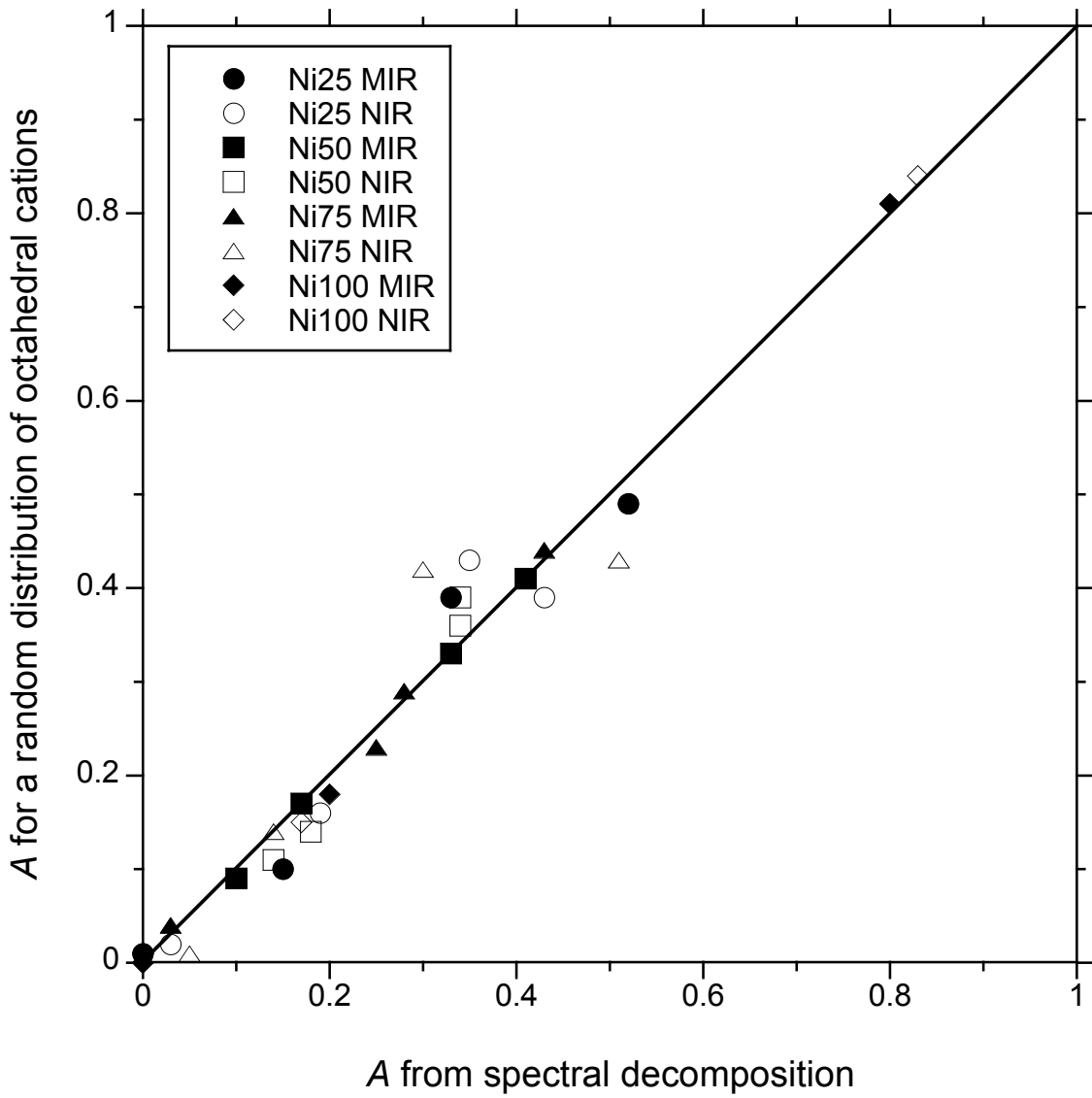
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611 Figure 5:

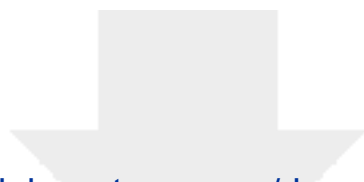


613 Figure 6:



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