

1 **Ni-serpentine nanoflakes in the garnierite ore from Campello Monti (Strona Valley, Italy):**

2 **Népouite, but with some pecoraite outlines.**

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10

11 **Abstract**

12 The garnierite ore at Campello Monti occurs as dark green colloform concretions covering surfaces,
13 fractures and filling veins in harzburgite rocks. The representative composition

14 $(\text{Ni}_{2.45}\text{Mg}_{0.14}\text{Cu}_{0.12}\text{Co}_{0.05})_{\Sigma=2.76}\text{Si}_{2.10}\text{O}_5(\text{OH})_4$ is consistent with a 7Å-phase, namely pecoraite or

15 népouite. Relevant chemical features are an exceptionally high Ni/Mg ratio, a significant level of

16 Cu substituting for Ni and a small content of S, possibly in tetrahedral sites.

17 Olivine and orthopyroxene in the harzburgite host rock are only partially serpentinized, do not

18 contain detectable Ni, and are almost iron free. The green coating probably originated by

19 ground-water solutions that leached nearby weathered peridotites and sulfide ores and deposited

20 less mobile elements along fractures and voids of the host peridotite, just outside their provenance

21 area.

22 Bulk techniques, such as X-ray powder diffraction and infrared spectroscopy do not confidently

23 distinguish between népouite and pecoraite, although the comparison with synthetic, implicitly

24 pure, polymorphs indicates népouite as the best matching phase. On the other hand, HRTEM
25 clearly shows that garnierite is mostly constituted by plumose aggregates made of curved crystals
26 with frayed tips, few nanometers thick along the stacks and few tens of nanometers long
27 (nanoflakes). All known lizardite stacking sequences, namely $1T$, $2H_1$, and $2H_2$, have been locally
28 observed, even though most crystals show stacking disorder.

29 The recorded nanostructure suggests possible explanations for the recurrent anomalies (low oxide
30 totals, high $^{IV}T/^{VI}M$ cation ratios, etc.) found in EMP analyses of garnierites. The small grain size,
31 the high density of defects and the structural arrangement actually intermediate between lizardite
32 and chrysotile, probably explain the ambiguities occurred during the characterization with bulk
33 techniques.

34 The results obtained in this study may have important implications in technological applications
35 involving Ni-phyllsilicates and in the development of new hydrometallurgical ore processing
36 methods.

37

38 Key words: garnierite; népouite; nanoparticles; transmission electron microscopy.

39

40 **Introduction**

41 Serpentinites originate by hydrothermal alteration of ultramafic rocks. They are abundant at mid
42 ocean ridges, where the oceanic crust forms and almost contemporarily may experience retrograde
43 metamorphism (e.g., Mével 2003), and at subduction zones, where two plates of oceanic
44 lithosphere, mostly ultrabasic in composition, converge and where a large amount of fluids circulate
45 along transform faults and “outer rise” fractures (Kerrick 2002). As corollary, considerable outcrops
46 of serpentinites occur along orogenic belts, sampled from the down going slab and exhumed by
47 tectonics after the included basin is completely recycled.

48 Serpentine minerals are hydrous magnesium silicates with ideal formula $Mg_3Si_2O_5(OH)_4$, which
49 occur in nature in four principal polymorphs, distinguished by the shape of the building TO layer.
50 Lizardite is the serpentine mineral that forms flat layers. Different polytypes with different stacking
51 of the *TO*-layers have been reported so far (e.g., Mellini and Zanazzi 1987; Brigatti et al. 1997).
52 Chrysotile adopts a cylindrical structural arrangement in which the tetrahedral sheet occupies the
53 internal position and is the main constituent of asbestos (e.g., Cavallo and Rimoldi 2013 and
54 references therein). Antigorite is based on a wave-like structure in which the tetrahedral sheet
55 periodically inverts polarity (Capitani and Mellini 2004). Different antigorite structures (polysomes)
56 are possible depending on the wavelength (Capitani and Mellini 2006, 2007). A rarer polymorph is
57 polygonal serpentine, which forms fibers with polygonal cross section, made up of flat layers in
58 sectors. The number of sectors is always either 15 or 30, with curved connections between them
59 (Mugnaioli et al. 2007).

60 Ni-serpentines are much less abundant in nature. The Ni analogue of chrysotile is pecoraite (Faust
61 et al. 1969), whereas the Ni analogue of lizardite is népouite (Brindley and Maksimović 1974). Ni-
62 analogues for antigorite and polygonal serpentine have not been reported so far. Ni-serpentines are
63 important ore minerals for Ni (e.g. Butt and Cluzel 2013; Villanova-de-Benavent et al. 2014).

64 Nickel is extracted from two principal types of ore deposits: i) sulfide ores, normally developed by
65 a magmatic concentration process, and ii) laterite ores, supergene deposits formed by the pervasive
66 chemical and mechanical weathering of parent rock, commonly peridotite. Laterite ores are further
67 distinguished in: i) oxide deposits, where Ni is mostly associated with goethite in the uppermost
68 part of the soil profile, and ii) hydrous silicate deposits, where Ni is hosted in garnierite within the
69 saprolite (Brand et al. 1988; Ridley 2013). Garnierite is the general name used to define greenish,
70 poorly crystallized, clay-like Ni ore that generally comprises an intimate mixture of Ni/Mg
71 hydrosilicates like serpentine, talc, sepiolite, smectite and chlorite (Brindley and Hang 1973;
72 Springer 1974).

73 The formation of garnierite may either result from the direct clay-like alteration olivine-rich rocks,
74 generally leading to low Ni/Mg ratio garnierite minerals, or from the weathering and leaching of Ni
75 under supergene conditions of the altered peridotite and subsequent re-precipitation of Ni-
76 serpentine (Pecora et al. 1949). In the classical *per descensum* model (e.g., Brand et al. 1998; Butt
77 and Cluzel 2013; Villanova-de-Benavent 2014), the formation of garnierite ore is related to the
78 development of a thick lateritic profile above a faulted and altered ultramafic host rock, under
79 tropical climate conditions. In this model, the Ni leached out from the oxide ore in the upper laterite
80 (which is richer in Ni than the unweathered host rock) is accumulated downward in fractures of the
81 underlying saprolite, within the structure of early formed and newly formed 1:1 and 2:1 layer
82 silicates. Recently, Fritsch et al. (2016) proposed an alternative model to explain the formation of
83 garnierite ore in New Caledonia. According to this model, the formation of hydrous Mg/Ni silicate
84 ore can be schematized by a two-step alteration process. The first step would result in the formation
85 of hydrous Mg/Ni silicates after alteration of the serpentine veins in serpentized peridotite through
86 tectonically reactivated faults. The second step would correspond to the lateritization of the
87 intensely fractured and mineralized zones of the peridotites. Unlike the *per descensum* model, in the
88 latter model would be the hydrous Mg/Ni layer silicates of the thick serpentine veins that “feed” in
89 Ni the oxide ores in the laterite horizon, and not the reverse.

90 Nickel usage has increased over time in parallel with the economic development. According to the
91 International Nickel Study Group (<http://www.insg.org>), the world primary nickel production has
92 recorded an annual growth rate of 5.5% in the period from 2011 to 2015. Nickel-rich laterite
93 deposits account for about 40% of the world’s Ni production, but due to the ongoing depletion of
94 sulfide ores, an increase of the Ni production from laterite deposits is expected in the future (Kesler
95 and Simon 2015). Although the metallurgical extraction of Ni from silicate and oxide minerals
96 requires significantly greater energy than extraction from Ni-bearing sulfide minerals (Ridley
97 2013), the development of new hydrometallurgical ore processing methods, including high pressure

98 acid leaching (HPAL) and atmospheric (acid) leaching (AL), makes the processing of laterite ores
99 economically more feasible than in the past (McDonald and Whittington 2008). In this respect, the
100 hydrous silicate deposits are of special interest since they show the highest Ni grades among the
101 laterite ores, ranging from 1.8 to 2.5 wt.%, and the Ni content of the garnierites can be as high as 40
102 wt.% (Soler et al. 2008). However, despite the importance of garnierites as Ni ore, significant
103 uncertainties regarding the composition, structure and nanostructure of these ill-defined phases still
104 remain.

105 In this study, for the first time we report about a garnierite ore associated with ultramafic rocks from
106 the Strona Valley (Western Alps, Italy), with the aim to contribute to a deeper knowledge of the
107 garnierite minerals in general. The detailed characterization down to the near-atomic scale, allows
108 the understanding of some common structural and compositional anomalies of garnierite minerals
109 and to envisage a positive response to acidic leaching for Ni extraction of the investigated ore, and
110 of similar ore deposits all around the world.

111

112 **Geological Context**

113 The studied samples are from Campello Monti, Strona Valley, Western Alps, Novara, Italy (Fig. 1).
114 The area has been mined for Ni-sulfides with numerous interruptions from 1865 to 1949, after
115 which the mining activity definitely ceased. The reasons that determined the closure of the mining
116 activity are both logistic and geological. The altitude, 1300-1600 m a.s.l., and the acclivity of the
117 area made difficult the mining yard operations and even the installation of the related
118 infrastructures. The lack of a mineralized dyke system, the hardness of the host rock, and the low
119 concentration of the ore mineral (2%), made the cost of the extracted Ni not competitive with that
120 coming from New Caledonia and Canada (Zanoletti 2007).

121 The mineralized rocks at Campello Monti are peridotites and olivinic pyroxenites of the “diorito-
122 kinzigitic” complex of the Ivrea Verbano Zone. This is a unit of the crystalline basement of the

123 Southern Alps, of Paleozoic age, formed by pelitic and semipelitic metasediments, subordinated
124 marbles and amphibolites, and mafic and ultramafic, highly metamorphosed, rocks (Boriani and
125 Sacchi 1973). The mineralized bodies have lenticular or irregular shapes, sometimes showing
126 stratiform arrangements. The metallic paragenesis is constituted by pyrrhothite, chalcopyrite, and
127 pentlandite, the latter sometimes transformed into bravoite. The metallic minerals are minutely
128 disseminated within the ultramafic rocks or concentrate in little veins or lenses (Zucchetti 1979).
129 The alteration of these ultramafic rocks, which are locally serpentized and talcized, and of the
130 associated sulfides, probably provided the Ni necessary for the formation of the garnierite ore object
131 of this study.

132

133 **Experimental Methods**

134 Several hand specimens from Campello Monti, all similar in macroscopic appearance, were
135 considered for this study. Both the green botryoidal coating constituting the garnierite ore and its
136 host rock were investigated.

137 Two representative specimens of the host rock were investigated by means of optical microscopy,
138 scanning electron microscopy (SEM), X-ray powder diffraction (XRPD), and energy dispersive X-
139 ray fluorescence (EDXRF) at the Department of Earth and Environmental Sciences of the
140 University of Milano-Bicocca. Petrographic investigations were carried out on standard (2.80 x 4.60
141 x 0.03 mm) polished thin sections of the host rock cross cutting the green coating. SEM
142 observations and energy dispersive (EDS) analyses were performed with a Tescan VEGA TS
143 5136XM with a tungsten filament and equipped with an EDAX GENESIS 4000XMS EDS system.
144 Operating conditions were 20 keV and 190 pA, for a probe size at the sample surface of ~50 nm
145 (see Fig. 3.8 in Reed 2005). Under these conditions, in a typical ultramafic mineral such as
146 forsterite, Montecarlo simulations of the electron/sample interaction sphere indicate a spatial
147 resolution of the probe of ~4 μm . The standardless method and the ZAF correction method were

148 used for semi-quantitative analyses. The chemical formulae of olivine, pyroxene, amphibole, spinel,
149 chlorite, carbonates, serpentine, and talc were recalculated on the basis of 8, 12, 46, 8, 28, 4, 14, and
150 22 negative charges, respectively.

151 Chemical analyses of the host rock were obtained with a PANalytical Epsilon 3^X EDXRF
152 instrument. Five grams of rock powdered in an agate mortar were mixed with 5 grams of hydrogen
153 borate and pressed at 15 tons for 1 minute. Anorthosite, basalt, diorite and norite of known
154 compositions were used as standards for quantitative analyses. Volatile components (H₂O plus CO₂)
155 were determined through the weight loss on ignition (LOI). The Fe³⁺/Fe²⁺ ratio was determined
156 through KMnO₄ redox titration.

157 For XRPD analyses, the samples were ground in an agate mortar, back loaded in aluminium holders
158 and analyzed with a PANalytical X'Pert-Pro PW3060 diffractometer, operating in Bragg-Brentano
159 specular (θ - θ) geometry and equipped with a X'Celerator position sensitive detector. Diffractometer
160 scans were recorded at 40 mA and 40 kV (CuK α radiation) in the 5-90° 2 θ range, with step size of
161 0.017° and counting time of 0.40 s per step. A Ni filter along the diffracted beam path was used to
162 filter out the CuK β radiation. The sample holder was allowed to spin horizontally during
163 measurements to improve particle statistics. The identification of major and minor phases was done
164 with the X'Pert High Score software (PANalytical) using the ICSD PDF2-2004 database.

165 Quantitative phase analyses (QPA) were performed with the Rietveld method (Hill 1991; Bish and
166 Post 1993) implemented in the GSAS/EXPEGUI (Larson and Von Dreele 2004).

167 The garnierite constituting the green botryoidal coating of the samples were investigated by wave
168 dispersive (WDS) electron microprobe (EMP) analyses, X-ray powder diffraction (XRPD), Fourier
169 transform infrared spectroscopy (FTIR), and transmission electron microscopy (TEM). For WDS-
170 EMP chemical analyses, some fragments of the green coating were embedded in epoxy resin and
171 polished. EMP data were collected at the Institute of Geosciences and Earth Resources (IGC-CNR)
172 in Florence using a Jeol JXA 8600 instrument with a W filament, operating at 15 kV and 10 nA.

173 Under this conditions, the beam size at the sample surface is ~250 nm (see Fig. 3.8 in Reed 2005).
174 Montecarlo simulations of the electron/sample interaction sphere indicate a spatial resolution of ~3
175 μm for népouite. Counting times of 15 s for peak and 5 s for background were used for Si, Al, Fe,
176 Ni, and Mg, whereas 40 s for peak and 20 s for background for S, Co, Cu and Mn. Raw data were
177 corrected using the PAP matrix correction (Pichou and Pichoir 1991) method and quantified using
178 the following standards: albite (Si), olivine (Mg), plagioclase (Al), bustamite (Mn), ilmenite (Fe),
179 celestine (S), cuprite (Cu), metallic Co and Ni (for Co and Ni, respectively). For these elements, the
180 detection limit is estimated between 0.04 and 0.07 wt. % and the relative error is below 13.8% for
181 oxide concentration above 0.5 wt. %, below 8.8% for oxide concentration above 1.0 wt. %, and
182 below 3.1% for oxide concentration above 5%.

183 For XRPD, fragments of the coating were detached with a scalpel from the hand specimen surface
184 and coarsely ground in agate mortar. Any possible contaminant discernible under the stereo-
185 microscope at this stage was removed with the aid of a magnet and of a needle. The enriched
186 powder was further grounded for powder X-ray analyses and loaded into a 0.3 mm glass capillary.
187 Powder diffraction patterns were collected at the University of Bari with a PANalytical Empyrean
188 diffractometer equipped with a real-time multiple strip (RTMS) PIXcel3D detector and a focusing
189 X-ray multilayer mirror. The X-ray tube ($\text{CuK}\alpha$ radiation) was operated at 40 kV and 40 mA and
190 diffraction data collected in the $5\text{-}85^\circ$ 2θ -range. In order to minimize preferred orientation, the
191 capillary was allowed to rotate during acquisition, and to improve the signal-to-noise ratio, intensity
192 data were averaged over three individual scans collected in continuous mode, with a step size of
193 $0.013^\circ 2\theta$ and a counting time of 1.40 s per step.

194 FTIR measurements were acquired at the University of Bari using a Nicolet 380 FTIR spectrometer
195 equipped with an EverGlo source, a KBr beamsplitter and a deuterated triglycine sulfate (DTGS)
196 detector. FTIR spectra were collected in transmission mode on pellets of approximately 2 mg of the
197 same powder used for XRPD diluted in 200 mg of KBr. The pellet was also dried at 110°C for at

198 least 12 hr to remove possible adsorbed water. The nominal resolution was set to 4 cm^{-1} ; 128 scans
199 over the range $400\text{-}4000 \text{ cm}^{-1}$ were averaged for both sample and background.

200 For TEM investigations, two different sample preparation methods were used. In one case, the same
201 powder used for XRPD analyses was dispersed in ethanol and ultrasonicated, then a $5 \mu\text{l}$ drop of the
202 suspension was deposited on carbon-coated Au-grids. These grids were mainly used for TEM-EDS
203 chemical analyses. Two additional samples were prepared from the largest fragments detached from
204 the green coating. These samples were embedded in epoxy resin, mechanically milled down to 30
205 μm with silicon carbide, double polished with alumina, fixed on a Cu ring, and gently ion-milled
206 down to electron transparency. Ion milling was done at the Geology Department “Ardito Desio” of
207 the University of Milan with a Gatan precision ion polishing system (PIPS). Before TEM
208 observations, these samples were carbon coated to avoid electrostatic charging within the TEM.

209 TEM observations were performed at the Department of Physical Sciences, Earth and Environment
210 of the University of Siena with a Jeol JEM 2010 operating at 200 keV and equipped with an Oxford
211 Link energy dispersive spectrometer for X-ray microanalysis (EDS) and with an Olympus Tengra
212 $2.3\text{k} \times 2.3\text{k} \times 14\text{-bit}$ slow scan CCD camera for image acquisition. To remove noise contrast due to
213 amorphous materials, high resolution (HR) TEM images were rotationally filtered (Kilaas 1998)
214 with the HRTEM filter (Mitchell 2007), as implemented in the Gatan Digital Micrograph version
215 3.9. In some cases, HR images were further filtered applying proper masks on the Fast Fourier
216 Transforms (FFT) of the image just to retain the periodic signal only, and then computing the
217 Inverse Fourier Transform (IFT). High resolution Image simulations were performed with JEMS ©,
218 a Java version Electron Microscopy Software, by P. Stadelmann (CIME-EPFL, Switzerland).

219 Finally, semi-quantitative EDS analyses were obtained with the standardless method and corrected
220 for absorption following Van Cappellen and Doukhan (1994).

221

222 **Results**

223 Petrography and mineral chemistry of the host rock

224 The garnierite collected for this study has the appearance of a thin, green coating over a dark brown,
 225 locally reddish, massive rock (Fig. 2). Under the optical microscope, the latter consists of olivine,
 226 orthopyroxene, and opaque minerals forming a coarse granular texture (Fig. 3a and b). Opaque
 227 minerals are mostly spinel with a corona texture of chlorite (Fig. 3c and d) and sulfides. Olivine and
 228 orthopyroxene may be partially altered to serpentine and talc, respectively. The alteration attacks
 229 mineral joints and rims, leaving the characteristic magnetite strings (Fig. 3e and f). Alteration
 230 products also seal veins cross-cutting the rock.

231 The chemical composition of the two host rock samples obtained by EDXRF in this study are
 232 comparable with that obtained by wet chemical analysis by Bertolani (1968) for unserpentinized
 233 peridotite from the same area (Table 1). All samples show low NiO content and quite different
 234 volatile content. Surprisingly, sample N2, with the lower LOI value, is also the most altered under
 235 the optical microscope, i.e. richer in hydrous phases. This apparent inconsistency can be at least in
 236 part explained by the higher FeO content: the weight loss due to the volatile component may be
 237 partially compensated by the oxidation of iron, which entails an increase of mass. Alternatively, this
 238 difference may reflect just the larger accidental uptake of vein material in one sample than in the
 239 other. Finally, the slightly different SiO₂/MgO ratio may suggest just different
 240 olivine/orthopyroxene proportions in the studied samples, consistently with the observations from
 241 the thin sections.

242 Average compositions obtained by semi-quantitative EDS analyses on polished thin sections for
 243 forsterite and enstatite read (Mg_{1.67}Fe_{0.33}SiO₄) and [(Ca_{0.01}Mg_{1.66}Fe_{0.29}Al_{0.04})_{Σ=2}(Al_{0.04}Si_{1.96})_{Σ=2}O₆],
 244 respectively. Minor diopside and pargasitic hornblende detected by SEM-EDS show average
 245 compositions [(Ca_{0.89}Mg_{0.92}Fe_{0.09}Al_{0.07})_{Σ=1.97}(Si_{1.98}Al_{0.02})_{Σ=2}O₆] and
 246 [(Na_{0.72}K_{0.12})_{Σ=0.84}Ca_{1.77}(Mg_{3.60}Fe_{0.65}Al_{0.59} Ti_{0.19}Cr_{0.09})_{Σ=5.13}(Si_{6.30}Al_{1.70})_{Σ=8}O₂₂(OH)₂], respectively.

247 The opaque minerals are mostly a Cr-rich spinel with average composition
 248 $(\text{Mg}_{0.51}\text{Fe}_{0.49}\text{Zn}_{0.01})_{\Sigma=1.01}(\text{Al}_{1.49}\text{Cr}_{0.42}\text{Fe}_{0.12})_{\Sigma=2.03}\text{O}_4$, altered at the borders to Cr-rich magnetite
 249 $[(\text{Fe}_{0.99}\text{Mg}_{0.03})_{\Sigma=1.02}(\text{Fe}_{1.30}\text{Cr}_{0.71}\text{Al}_{0.10})_{\Sigma=2.11}\text{O}_4]$. The reaction rim bordering spinel is clinocllore
 250 $[(\text{Mg}_{4.76}\text{Fe}_{0.27})_{\Sigma=5.03}\text{Al}_{0.93}(\text{Si}_{3.14}\text{Al}_{0.86})_{\Sigma=4}\text{O}_{10}(\text{OH})_8]$, and serpentine and talc altering olivine and
 251 orthopyroxene along joints and rims yield average compositions $(\text{Mg}_{2.74}\text{Fe}_{0.13})_{\Sigma=2.87}\text{Si}_{2.06}\text{O}_5(\text{OH})_4$
 252 and $(\text{Mg}_{2.99}\text{Fe}_{0.15})_{\Sigma=3.14}(\text{Si}_{3.83}\text{Al}_{0.13})_{\Sigma=3.96}\text{O}_{10}(\text{OH})_2$, respectively. The magnetite associated with
 253 serpentine and talc is almost pure, thus distinguished from the former spinels. Few veinlets of
 254 dolomite $[(\text{Mg}_{1.01}\text{Ca}_{0.96}\text{Fe}_{0.06})_{2.03}(\text{CO}_3)_2]$ were detected by SEM-EDS, which was also observed
 255 finely intermixed with serpentine. Finally, the scarce and corroded sulfides yield approximate
 256 compositions FeS, CuFeS₂, and FeNiS₂, consistent with pyrrhotite, chalcopyrite, and pentlandite,
 257 respectively (Fig. 3g).

258 On the basis of Rietveld refinements performed on X-ray diffractograms of two representative
 259 samples, the major mineral constituents of the host rock are: olivine (68-42%), orthopyroxene (28-
 260 36%), talc (2-9%), serpentine (1-5%), spinel (1-3%) and hornblende (0-5%). These data plot in the
 261 harzburgite field at the boundary with the olivine-pyroxenite field, both described in this area
 262 (Bertolani 1968).

263

264 Chemical composition and microstructure of garnierite

265 Under the optical microscope, garnierite consists of green, banded, botryoidal aggregates and shows
 266 first order birefringence in crossed polars, with undulose, parallel extinction. The crossed polars
 267 appearance is consistent with of parallel growth of fibers, or minute radiating crystals, elongated
 268 perpendicularly to the bands (Fig. 4a and b). The green coating is restricted to the sample surface
 269 and along fractures penetrating the host rock, and may envelope rounded saprolite fragments,
 270 mainly iron oxides and hydroxides and altered olivine (Fig. 4c and d).

271 In backscattered electron (BSE) images the green coating shows a colloform texture with concentric
272 zoning. Three main zones can be identified: 1) an inner zone characterized by small coalescent
273 spheroids with many voids and interstices; 2) a massive intermediate zone with smooth concentric
274 zoning; 3) an outer rim with fine-scale zoning and relatively darker bands. The apparent thickness
275 of these zones varies within the same sample and depends also on the cut of the sample, but is on
276 the order of one hundred of microns for the inner and intermediate zones and relatively thinner, on
277 the order of tens of microns, for the outer zone (Fig. 5a and b). As expected, the whole texture is a
278 consequence of the chemical zoning (Fig. 5c and d).

279 It turns out that most point analyses, calculated on the basis of 7 oxygens, show compositions
280 consistent with népouite and pecoraite, from apart few spot analyses from the outer zone, with
281 marked higher Cu and Al contents, which will be considered later. In Table 2, we report average
282 WDS microprobe compositions of the intermediate zone of three different mounts prepared from
283 the same hand specimen. The most notable feature is the variability in Ni and Mg, which are clearly
284 anti-correlated (Fig. 6a), as well as Ni and Cu (Fig. 6b), suggesting isomorphous substitution of Mg
285 and Cu for Ni in the octahedral site. The darker bands normally show a lower Ni/Mg ratio. In
286 addition to Si, Ni, Mg and Cu, other cations like Co, Mn, and S are detected at significant levels,
287 whereas Fe and Al are always very low or not detected at all. Higher Co and Mn contents seem
288 present in the brighter bands, while S and Cu do not show any clear preference. Co and Mn, which
289 reasonably should occupy the octahedral site, do not show any clear correlation, probably because
290 of their low concentration that makes the analytical datum inaccurate and the plot unclear.

291 Significant excess of tetrahedral cations and deficiency of octahedral cations are recorded in these
292 analyses, like in many other reports (e.g., Song et al. 1995; Brindley and Hang 1973; Brindley and
293 Wan 1975; Wells et al. 2009; Villanova-de-Benavent et al. 2014). In this case, however, it should
294 be noted that S also contributes to the tetrahedral cation summation since it has been considered as
295 S^{6+} in the calculation and attributed to the tetrahedral sites, according to the faint but significant

296 anticorrelation with Si (Fig. 6c). The averages of oxides summation (Table 2) span between ~85.3
297 and ~92.5 wt. %, which are, albeit slightly, lower and higher than expected for ideal lizardite (87.0
298 wt. %) and ideal népouite (90.5 wt. %), respectively. These values are comparable with those of
299 many other descriptions of garnierites (e.g., Faust 1966; Brindley and Hang 1973; Springer 1974;
300 Song et al. 1995; Villanova-de-Benavent et al. 2014). Finally, the measured compositions, when
301 plotted in the ternary Si-Mg-Ni system (Fig. 6d), cluster close to the népouite field and show a tail
302 towards “Ni-karpinskite”, an intermediate phase between serpentine-like and talc like-phases – not
303 accepted as mineral species by IMA – with composition $(\text{Ni,Mg})_2\text{Si}_2\text{O}_5(\text{OH})_2$. If real, i.e not due to
304 analytical artifacts such as interplay of uncounted cations, this trend could indicate either an
305 increase of octahedral cation vacancies in the Ni-serpentine, or intermixing with 2:1 layer
306 structures, with decreasing of the Ni/Mg ratio.

307 The outer zone is characterized by a general increase of the Mg, Al, and Cu contents and by a
308 decrease of Si and Ni. Al is clearly anticorrelated with Si and Cu with Ni. It should be noted that the
309 Cu peak and the Al peak are out of phase. A possible explanation is that Cu and Al belong to two
310 different phases with different abundances in the banded outer zones (Fig. 5c and d). Finally, an
311 increase of S is also recorded in the outer zone, which seems correlated with Al.

312 In Table 3 we report some selected spot analyses from the outer zone, characterized by the highest
313 contents of Mg, or Al, or Cu. It is worth reminding that the outer zone is characterized by a fine-
314 scale zoning, which is finer than the sample volume excited by the microprobe, thus the
315 composition of each individual band is difficult to obtain. Moreover, it cannot be excluded that
316 more than one single phase could be present in such bands. As a consequence, most analyses cannot
317 be straightforwardly recalculated on the basis of known phases – although, for the sake of
318 comparison, the same base of 7 oxygens as for Ni-serpentine is maintained – with the exception of
319 some spot analyses, which can be still attributed to Ni-serpentine, even if richer in Mg than the Ni-
320 serpentine detected in the intermediate zone (cfr. Table 3 with Table 2). Finally, few spot analyses

321 from the inner zone can be attributed to Ni-serpentine, analogous to that present in the intermediate
322 zone (cfr. Table 3 with Table 2).

323

324 Crystallography of the Ni-serpentine

325 The XRPD pattern of garnierite from Campello Monti shows six relatively sharper peaks and three
326 broader peaks at 42.25 , 53.35 , and $71.73^\circ 2\theta$, which look like shoulders or smooth bulges rather
327 than real peaks, suggesting that the sample lacks of perfect long range order and/or it is very fine
328 grained (Fig. 7). Probably because of the poor crystallinity, mineral identification is ambiguous. In
329 fact, as evidenced in Figure 7, where the pattern of the Ni-serpentine from Campello Monti is
330 compared with those of pecoraite and népouite from Kwangcheon, Korea (Song et al. 1995), the
331 main difference between pecoraite and népouite is that the chrysotile-type mineral has only one
332 strong peak at 1.53 \AA ($60.5^\circ 2\theta$), while lizardite-type mineral has two distinct lines at 1.53 and 1.50
333 \AA (Milton et al. 1983; Song et al. 1995). The Ni-serpentine from Campello Monti actually shows
334 only one single peak at 1.53 \AA , although a shoulder in the right side suggests that it could be
335 convoluted with the at 1.50 \AA .

336 The powder diffraction data of the garnierite from Campello Monti are shown in Table 4 and
337 compared with those of pecoraite and népouite. It should be noted that the first peak (at $\sim 7.60 \text{ \AA}$),
338 tied to the c -axis length and thus to the interlayer spacing, occurs at a significantly lower 2θ
339 position than expected according to the pecoraite and népouite structures. This deviation
340 (quantifiable in $\sim 0.24 \text{ \AA}$) is probably an artifact that arises from the high background occurring at
341 low 2θ . However, the possibility of a slightly expanded cell should not be completely discarded,
342 since, as it can be inferred from the peak profile of the current diffractogram, the crystallite size of
343 the investigated material is very small, i.e. in the nanoparticle range, and it is well known that

344 nanoparticles show slightly expanded cells with respect to the corresponding bulk specimen (e.g.,
345 Reynolds 1968; Zhang et al. 2002).

346 The unit cell refinement starting from the pecoraite $2M_{c1}$ parameters leads to the following unit cell
347 parameters: $a = 5.27(2)$, $b = 9.18(1)$, $c = 14.76(3)$ Å, $\beta = 92.16^\circ$. Refinement in the $P31m$ népouite
348 $1T$ structure gives comparatively worse results (compare RM_s deviations in Table 4) and the
349 following cell parameters: $a = 5.28(1)$, $c = 7.36(2)$ Å. This result, however, should be taken with
350 caution since the small number of reflections and their flat profile make the refinement very prone
351 to errors.

352 The same powder analyzed with XRPD was also analyzed by FTIR. The resulting spectrum is
353 plotted in Figure 8 along with reference spectra of natural népouite and pecoraite from the literature,
354 and the vibrational frequencies of the observed bands are shown in Table 5. FTIR data for the
355 garnierite of Campello Monti appear to agree better with the literature data for synthetic népouite
356 than for synthetic pecoraite and natural pecoraite and népouite. In particular, the inner surface O-H
357 stretching bands at 3646 and 3610 cm^{-1} (Balan et al. 2002) and the Ni-OH libration band at 673 cm^{-1}
358 (Farmer 1974) are discriminant in this comparison.

359

360 Nanostructure of the Ni-serpentine

361 TEM observations were focused in the wide intermediate zone, where microprobe analyses indicate
362 Ni-serpentine with slightly varying Ni/Mg ratio. The average composition from 11 TEM-EDS spot
363 analyses randomly taken on the investigated areas, expressed on the basis of 14 positive charges,
364 reads: $(\text{Ni}_{2.11}\text{Mg}_{0.15}\text{Co}_{0.07}\text{Cu}_{0.31})_{\Sigma=2.64}\text{Si}_{2.17}\text{O}_5(\text{OH})_2$, which is consistent, within the experimental
365 error, with the microprobe analyses.

366 A bright field (BF) image and a lattice fringe image from an ion-milled sample of the Ni-serpentine
367 are shown in Figures 9a and 9b, respectively. These images clearly show that the Ni-serpentine

368 forms plumose aggregates of crumpled particles no longer than few tens of nanometers and no
369 ticker than few nanometers. Particles have flat structure (nanoflakes) as lizardite and népouite,
370 though bent and frayed, and not a cylindrical shape as chrysotile and pecoraite. The interplanar
371 distance measured on HR images is about 7.3 Å, consistent with one-layer serpentine.

372 A selected area electron diffraction (SAED) pattern taken on the plumose aggregate of Figure 9a is
373 shown in Figure 9c along with the related radial profile (Fig. 9d). The SAED pattern contains few
374 continuous and diffuse rings typical of randomly oriented nanoparticles, and is entirely consistent,
375 within the experimental error, with the XRPD pattern, although less resolved and with a much
376 higher background. With reference to the refined XRPD pattern, the (110) and the (003) peaks are
377 convoluted into one large peak at 2.57 Å (Fig. 9d); the (002) peak at 3.61 Å is present as large
378 shoulder on the flank of the (010) peak (4.54 Å); the (001) peak at 7.43 Å is almost completely
379 hidden by the huge background around the transmitted beam (towards the center of the
380 diffractogram); the diagnostic (300) peak occurs at 1.56 instead of 1.53 Å. Other detected peaks are:
381 a shoulder on the right side of the (003) peak at 2.18 Å; a small, flat peak at 1.75 Å; a relatively
382 sharper peak at 1.35 Å. These peaks were detected also in the X-ray powder diffractogram, although
383 at slightly higher angle, and indexed after refinement as (112), (210), and (220), respectively. Other
384 high angle diffuse rings (at 1.01 and 0.91 Å) could not be indexed with certainty because of the
385 many close-spaced reflections potentially occurring at higher Bragg angles.

386

387 *TO* stacking sequence and disorder

388 To decipher the stacking of népouite, as for any sheet-silicate, two-dimensional HR images are
389 required. In most cases, observations of the same area along two non-equivalent directions
390 perpendicular to the stacking direction are required (e.g., Kogure 2002; Fregola et al. 2009; Capitani
391 et al. 2016). However, because of the quick amorphization of beam-sensitive phyllosilicates, often

392 one-dimensional lattice fringe images only are obtained, as that of Figure 5b, which are not enough
393 to distinguish different polytypes.

394 Notwithstanding, in the present investigation, two dimensional information was obtained making
395 use of low dose operation and improving the image quality through Fourier filtering. To help
396 interpreting two-dimensional HR experimental images, we made use of HR image simulation of
397 népouite. For this purpose, the crystal structures of the three different known polytypes of lizardite,
398 $1T$ (Mellini 1982), $2H_1$ (Mellini and Zanazzi 1987) and $2H_2$ (Brigatti et al. 1997) were taken and
399 modified by substitution of the octahedral cations (Mg and Fe) by Ni. It turns out that with the
400 current instrumental conditions only the $\langle 110 \rangle$ directions allow a two-dimensional view of the
401 structure and thus the possibility to simulate the stacking sequence. All the other directions, namely
402 $\langle 120 \rangle$, rotated 30° apart around the c -axis, require higher resolution to distinguish structural features
403 within the layer and thus lead to (001) lattice fringe only. $\langle 110 \rangle$ HR images for the three polytypes
404 were then simulated for defocus values between the optimal Scherzer (35 nm) and the extended
405 Scherzer (42.5 nm) and for thicknesses between 2 and 10 nm. The results are shown in Figure 10,
406 for a sample thickness of 4 nm and a defocus of 42.5 nm. It should be noted that népouite $1T$ and
407 $2H_1$ cannot be distinguished in this projection, since they show analogous contrast with the same
408 “straight” sequence. They would be distinguished in $\langle 120 \rangle$ projections if higher resolution were
409 possible, since along that projection népouite $1T$ shows a straight sequence, whereas népouite $2H_1$ a
410 “zig-zag” sequence. On the other hand, népouite $1T$ and $2H_1$ can be distinguished from népouite
411 $2H_2$ on $\langle 110 \rangle$ HR images, since the latter shows a “zig-zag” sequence.

412 The results show that népouite nanoflakes possess both ordered straight sequences as in lizardite $1T$
413 and $2H_1$ (Fig. 11a) and ordered zig-zag sequences as in the lizardite $2H_2$ polymorph (Fig. 11d),
414 although ordered stacking sequences involve crystal thickness of just few unit cells. Moreover, most
415 crystals show disordered sequences and dislocation-like defects (Fig. 11b and 12). These

416 observations make the concept of “long range order” quite feeble for this mineral, confirming the
417 first impression given by XRPD and SAED.

418

419 **Discussion and Conclusions**

420 Crystal chemistry of népouite

421 Garnierite from Campello Monti, at least with regard to the widespread dark green colloform
422 concretions found in peridotite fractures and veins, is constituted mostly by népouite, with the
423 following chemical features: i) high Ni content, which is anti-correlated with Mg; ii) significant
424 amount of Cu, apparently substituting for Ni (and Mg); iii) excess of tetrahedral cations and
425 deficiency of the octahedral ones; iv) highly variable oxide totals often lower than expected; v)
426 presence of S, possibly in tetrahedral position.

427 The Ni-serpentine described in this paper is among the richest in Ni (2.074-2.570 a.p.f.u.) ever
428 reported in the literature (compare Fig. 6d with Fig. 12d of Villanova-de-Benavent et al. 2014), and
429 contains significant amounts of Cu (0.060-0.150 a.p.f.u.), which apparently is in solid solution with
430 Ni and Mg in the octahedral site. The high Ni and Cu contents probably derive from efficient
431 leaching of these elements in the parent peridotite, present either as minor elements in olivine or in
432 Ni-Cu sulfides.

433 The anti-correlation of Ni and Mg reaffirms the solid solution between népouite and lizardite
434 (Brindley and Hang 1973; Brindley and Wan 1975; Baron and Petit 2016). In the studied Ni-
435 serpentine, however, the entry of Mg in the octahedral site is accompanied by a shift towards more
436 silicic, talc-like compositions. This trend has already been observed (e.g. Suárez et al. 2011), but
437 apparently contradicts reports on garnierites from other localities where 7-Å and 10-Å phases
438 coexist in the same sample and the 10-Å phase is always richer in Ni than the 7-Å one (Esson and
439 Carlos 1978; Poncelet et al. 1979; Soler et al. 2008; Villanova-de-Benavent et al. 2016).

440 Slow scan diffractograms taken in the 3-30° 2 θ region on oriented samples do not show any
441 additional peak relating to any 10-Å phase, and XRPD patterns recorded after ethylene glycol
442 treatment do not show any significant shift of the (001) peak (supplementary material S1), whose
443 occurrence, according to Choulet et al. (2016), would indicate the presence of interstratified
444 serpentine-like and smectite-like phases. Accordingly, lattice fringes with periodicity other than 7-Å
445 were not observed in the studied samples at the TEM, either as single phase or as intergrowths in
446 népouite. A possible explanation of the observed shift towards more silicic compositions is that the
447 Mg for Ni substitution is accompanied by an increase in octahedral vacancies.

448 According to previous interpretations (Brindley and Hang 1973; Brindley 1980), the excess of
449 tetrahedral cations coupled with deficiency of octahedral ones in microprobe analyses are related to:
450 i) the presence of colloidal silica within the analyzed volume; ii) intergrowths of silica richer
451 phases; iii) leaching of octahedral cations at the edges of the clay particles. In the present study, the
452 most plausible mechanism seems the latter, which would remove the soluble M²⁺ cations and OH⁻
453 from the edges, leaving a silica residue (Brindley 1980; Suárez et al. 2011). The curved crystals
454 with frayed tips observed at the TEM actually suggest altered crystal chemistry at the border of the
455 crystals. Given the very small grain size and the consequent high surface/volume ratio, it is very
456 probable that such altered crystal chemistry could arise in microprobe analyses. Moreover, among
457 the népouite nanoflakes, an amorphous matrix is observed in HR images, which could easily
458 resemble residual silica. Unfortunately, the presence of a pure silica matrix could not be confirmed,
459 because the alternation of nanoflakes and amorphous matrix occurs at a scale that is finer than the
460 TEM-EDS probe size.

461 The highly variable oxide totals and, as a consequence, the calculated H₂O contents, are common of
462 Ni-serpentine from other localities analysed by electron microprobe (Springer 1974; Song et al.
463 1985; Villanova-de-Benavent et al. 2014). In the present case, the poor crystallinity and the porous
464 microstructure make the samples less dense than the standard used for calibration (metallic Ni).

465 This oddness can potentially generate uncorrected matrix effects, which in turn can be responsible
466 for the low totals.

467 Finally, the Ni-serpentine from Campello Monti shows detectable amounts of S (up to 0.047
468 a.p.f.u.), which seems anti-correlated with Si, and thus occupying the tetrahedral site. The presence
469 of S may be related to the leaching of this element out of the parent rock, which contains pyrrhothite,
470 chalcopyrite, and pentlandite (Zucchetti 1979). Its incorporation into garnierite minerals, however,
471 has never been reported before.

472

473 Crystal morphology and structural state of the Ni-serpentine

474 Ni-serpentine usually give poorer diffraction patterns than the corresponding Mg analogues
475 because of their smaller grain size and poorer crystallinity (Brindley and Wan 1975; Brindley 1980)
476 and, unsurprisingly, are even more sensitive to electron beam damage. It has been recognized that
477 the substitution of Ni for Mg causes the structure to be less stable (Brindley and Hang 1973;
478 Poncelet et al. 1979), and has been observed that the substitution of Ni for Mg in chrysotile gives
479 rise to non-tubular, but also not well-formed platy crystals (Roy and Roy 1954).

480 The Ni-serpentine from Campello Monti forms plumose aggregates made of curved crystals with
481 frayed tips, few nanometer thick along the stacks and few tens of nanometer long (nanoflakes). This
482 description actually is intermediate between that of lizardite-like and chrysotile-like phases, even if
483 closer to the lizardite-like one. With regard to polytypism, within the limit of the observation of
484 such beam sensitive material, all the possible lizardite stacking sequences have been observed,
485 although most crystals show stacking disorder. The small grain size, the high density of defects and
486 the intermediate character between lizardite-like and chrysotile-like phase, probably explain the
487 ambiguities occurred during the characterization of this material. On the contrary, as explained
488 below, it seems plausible that the high Ni content could be responsible for the crystal morphology,
489 i.e. a flat rather than cylindrical habit and a poor crystallinity (high density of defects).

490 It is generally accepted that that the misfit between the smaller parameter of the tetrahedral sheet
491 and the larger parameter of the octahedral one is the main cause of the cylindrical habit of chrysotile
492 (Bailey 1988), although other authors give different explanations (e.g., Viti and Mellini 1997).
493 Perbost et al. (2003) found a correlation between the curvature of serpentine layers and the misfit
494 between the tetrahedral and octahedral sheets, and thus a dependence with the cation size in the
495 tetrahedral and octahedral positions. Since the ionic radius of $^{[VI]}\text{Ni}^{2+}$ (0.69 Å) is lower than that of
496 $^{[VI]}\text{Mg}^{2+}$ (0.72 Å) (Shannon 1976), a lower structural mismatch for Ni-serpentine than for Mg-
497 serpentine can be predicted, explaining the absence of cylindrical structures in the Ni-rich
498 serpentine from Campello Monti.

499

500 Origin of Ni-serpentine at Campello Monti

501 The garnierite ore at Campello Monti is extremely rich in Ni, whereas primary minerals and their
502 alteration products in the parent rock, which is only partially serpentinized, do not contain Ni at
503 detectable levels, and Ni-bearing sulfides are sparse.

504 It is generally accepted that the low content of iron – the Ni-serpentine from Campello Monti is
505 almost iron free – confirms the supergene origin of garnierite, since iron is largely not soluble under
506 common weathering conditions (Pelletier 1983, 1996; Galí et al. 2012 and references therein).
507 Moreover, the alteration of peridotite is a necessary, but not a sufficient condition for the formation
508 of garnierite: high Ni-contents, as those of the studied népouite, are possible either as result of
509 continual chemical reaction of ground water on earlier-formed garnierite (Pecora et al. 1949) or
510 recrystallization of phases able to release a large amount of Ni, such as secondary goethite and
511 hematite (Pelletier 1983).

512 All these observations point to the supergene origin of the Ni-serpentine of Campello Monti. The
513 green coatings have probably been deposited by ground-water solutions derived from material
514 subjected to a leaching process. This material cannot be represented by the peridotite on which the

515 Ni-serpentine has been deposited since it does not contain appreciable amount of Ni (0.10-0.32 wt.
516 % of NiO, Bertolani 1968; 0-34-0.44 wt. %, Table 1, this study) and does not show signs of farther
517 serpentinization. The most possible scenario is thus that late fluids scavenged Ni from nearby
518 altered peridotites and sulfide ores and deposited less mobile elements along fractures and voids of
519 the host peridotite just outside their provenance area. Since serpentine and serpentine-népouite s.s.
520 are stable with respect to talc and kerolite-pimelite s.s. at higher $\log[a_{\text{Mg}^{2+}} + a_{\text{Ni}^{2+}}/a^2_{(\text{H}^+)}]$ and lower
521 $\log[a_{\text{SiO}_2}]$ conditions (Bricker et al. 1973; Back et al. 2004; Galí et al. 2012), it is very possible that
522 at Campello Monti a high Ni/SiO₂ activity ratio in the fluids led to the precipitation of népouite
523 instead of a talc-like phase.

524

525 **Implications**

526 Fundamental research on Ni-bearing hydrous silicates has attracted great attention in the scientific
527 community during last years (e.g., Wells et al. 2009; Suárez et al. 2011; Villanova-de-Benavent et
528 al. 2014, 2016), probably because it provides a spin-off for the many technological applications of
529 Ni-phyllsilicates and because of their importance of the latter as ore for Ni.

530 Sivaiah et al. (2011) used serpentine-like and talc-like Ni-phyllsilicates as catalyst precursors for
531 processing greenhouse gases such as CO₂ and CH₄. Yang et al. (2011) synthesized Ni-serpentine
532 nanotubes (analogous to pecoraite) with tunable magnetic properties. Moreover, this material
533 showed promising transport kinetics and discharge capacity when used as anode in Li-ion batteries.
534 Alencar et al. (2014) synthesized organophilic talc-like Ni-phyllsilicates for the removal of blue
535 dye from textile industry wastewater.

536 In our study, we report an unprecedented chemical and structural characterization down to the near-
537 atomic scale of a natural Ni-serpentine, which may be very useful for the design of new
538 technological applications, since it may represent a reference for the synthetic analogues. Moreover,

539 our study also suggests that natural Ni-phyllsilicates may be directly used as catalyst precursor or
540 starting material for the synthesis of functionalized devices.

541 Nickel is extensively used in stainless steel production, in metal plating, in NiMH batteries, coins,
542 etc. and this usage has increased over time connected with economic development. The continual
543 growth of Ni demand paralleled by the ongoing depletion of sulfide ores, ask for an increase of the
544 Ni production from laterite deposits in the future (Kesler and Simon 2015).

545 Hydrometallurgical ore processing methods, such as acidic leaching, are traditionally used for the
546 extraction of Ni from laterites. However, speed and percentage recovery of Ni have proven to be
547 variable among different ore bodies, depending on the mineralogy and reactivity of Ni laterites (for
548 a review see McDonald and Whittington 2008). The data indicate that Ni is more readily leached
549 from clay-like ores than limonitic ores. The reason relies on the kinetics and mechanism of acid
550 leaching of laterite minerals. For instance, serpentine minerals dissolve incongruently by partial
551 decomposition of the structure, quickly releasing octahedral cations and leaving a hydrate silica
552 residue, so that the total dissolution of the serpentine is not required for complete Ni extraction.
553 Conversely, in goethite, where small amounts of Ni (up to 7%) can substitute for iron, substantial
554 extraction requires complete dissolution of the goethite grains (Soler et al. 2008; McDonald and
555 Whittington 2008 and references therein).

556 The development of new hydrometallurgical ore processing methods, more effective and
557 economically feasible, requires a greater understanding of the mineralogy, morphology and texture
558 of the nickel-bearing minerals. Indeed, isomorphic substitutions, crystallinity and particle size also
559 affect the leaching kinetics of laterite minerals. For instance, chromium and aluminum substitutions
560 stabilize goethite against proton attack (Schwertmann 1991) and mechanical activation (grinding) of
561 laterite ore increases the rate of Ni extraction (Sanchez et al. 1997; Kim and Chung 2002). In
562 particular, dry grinding of garnierite ore induces structural changes that convert serpentine (and
563 other limonitic material) from crystalline to amorphous, which may have beneficial effects on metal
564 extraction, but detrimental effects, i.e. worse settling properties, on downstream processing.

565 This study reveals that the garnierite ore from Campello Monti is among the richest in Ni ever
566 reported. TEM observations suggest that Ni can be easily extracted by acid leaching from
567 octahedral sites at the edges of the curved clay particles with frayed tips. Moreover, the very fine
568 grain size and the high density of defects of the Ni-serpentine offer high surface-to-volume ratio
569 and high reactive sites, which should promote fast acid leaching even without mechanical
570 activation, thus reducing downstream treatment problems. This implies that similar hydrous silicate
571 deposits all around the world may be favourably treated with modern hydrometallurgical methods
572 and thus to represent a possible answer to the continual growth of the Ni demand. The nanoscale
573 approach used here may be extended to other base metals such as Zn, which may be abundant in
574 phyllosilicates forming similar textures (e.g., Buatier et al. 2016).

575 Overall, it seems that fundamental studies on Ni-bearing hydrous silicates, and specially
576 characterization of these minerals down to the near-atomic scale, may have important implications
577 for the development of new technological applications and new and more efficient ore processing
578 methods, which is required by the continual growth of the Ni demand and of other base metals, in
579 general.

580

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586 greatly benefited of the careful revision by two anonymous referees.

587

588

589

590 Caption to Figures and Tables

591

592 Figure 1. Geological map of the Strona Valley (modified after Bertolani 1974).

593 Figure 2. Left: hand specimen of garnierite from Campello Monti used in this study (sample ~13 cm
594 wide); right: stereomicrograph of the green, thin coating separated from the hand specimen
595 (micrograph side ~0.5 mm).

596 Figure 3. Optical and electron microscopy images of peridotite (scale bar 0.5 mm if not differently
597 specified): a) crossed polars image and (b) backscattered electron (BSE) image of olivine (Ol),
598 orthopyroxene (Opx), and spinel (Spl) forming a coarse granular texture. Note the magnetite strings
599 (Mag) along fractures possibly produced by incipient serpentinization; c) crossed polars image and
600 (d) BSE image of altered spinel grains with a corona texture of chlorite (Chl) and a rim of Cr-rich
601 magnetite (Cr-Mag). The orthopyroxene embedding spinel and chlorite is partially substituted by
602 serpentine (Srp) and magnetite (Mag). A small clinopyroxene grain (Cpx), complete the local
603 mineral association; crossed polars images of orthopyroxene (e) partially replaced along fractures
604 by talc (Tlc), and (f) olivine and spinel partially altered to serpentine and chlorite, respectively; g)
605 BSE image (Pn) and pyrrhotite (Po) rimmed by Fe-oxides (Fe-Ox) within partially serpentinized
606 harzburgite (black).

607 Figure 4. Optical micrographs of garnierite (scale bar 0.5 mm): a) parallel light image and (b)
608 crossed polars image of the green coating; c) parallel light image of a cross section through the
609 garnierite coating (green) and the host rock (lower part). The opaque minerals are mostly iron
610 oxides (black) and hydroxides (reddish); d) single polar image of a garnierite vein intruding the host
611 rock. Note the colorless Mg-serpentine (Srp) bordering the vein and altering the surrounding olivine
612 (Ol).

613 Figure 5. BSE images of two selected areas from sample GC1 (a) and GC3 (b) analyzed at the WDS
614 microprobe. Dotted lines limit three different zones, indicated by numbers 1, 2, 3, characterized by
615 different microstructure/composition (for explanation see text). L-L' lines represent the traces of the

616 major element intensity profiles shown in (c) for sample GC1 and in (d) for sample GC3. Spot
 617 analyses were acquired in EDS mode at steps of $\sim 0.18 \mu\text{m}$ using a counting time of 5 s per step.
 618 Figure 6. Binary plots showing the compositional correlations in Ni-serpentine from Campello
 619 Monti: a) Mg vs. Ni; b) Cu vs. Ni; c) S vs. Si and (d) ternary Mg-Si-Ni diagram. Dashed lines
 620 represent compositional trends. Lz = lizardite $[(\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4]$, Nep = népouite $[(\text{Ni}_3\text{Si}_2\text{O}_5(\text{OH})_4]$,
 621 Krp = “karpinskite” $[\text{Mg}_2\text{Si}_2\text{O}_5(\text{OH})_2]$, Ni-Krp = “Ni-karpinskite” $[\text{Ni}_2\text{Si}_2\text{O}_5(\text{OH})_2]$, Tlc = talc
 622 $[\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2]$, Wil = willemseite $[(\text{Ni}_3\text{Si}_4\text{O}_{10}(\text{OH})_2]$, Sep = sepiolite $[\text{Mg}_4\text{Si}_6\text{O}_{15}(\text{OH})_2 \cdot 6\text{H}_2\text{O}]$,
 623 Fal = falcondoite $[\text{Ni}_4\text{Si}_6\text{O}_{15}(\text{OH})_2 \cdot 6\text{H}_2\text{O}]$.

624 Figure 7. X-ray powder diffractogram of Ni-serpentine from Campello Monti (left), to be compared
 625 with the Ni-serpentine from Kwangcheon, Korea (inset, Song et al. 1995). Note the presence of
 626 only one strong peak in the region $1.50\text{-}1.54 \text{ \AA}$ ($61.8\text{-}60.0^\circ 2\theta$), unlike the diffractogram of
 627 dimorphous népouite that shows two intense peaks in this “critical” region.

628 Figure 8. Infrared spectrum of the Ni-serpentine from Campello Monti in comparison with the
 629 spectrum of népouite from Petea Mine (Soroako, Sulawesi Island, Indonesia) and that of pecoraite
 630 from Loma Peguera (Bonaio, Dominican Republic), taken as reference (Chukanov and Chervonnyi
 631 2016).

632 Figure 9. a) Low magnification TEM image of népouite; b) Lattice fringe image of the same area
 633 showing nanoflakes with one-layer periodicity. Note the close resemblance of Fig. 9a with Figure
 634 5c of Villanova-de-Benavent et al. (2016), although they refer to two different phases, namely a 7\AA -
 635 phase and a 10\AA -phase, respectively; c) SAED pattern of (a) and related radial profile (d) with
 636 indication of the measured interplanar distances.

637 Figure 10. HR image simulation along $\langle 110 \rangle$ of three népouite polytypes derived from the three $1T$,
 638 $2H_1$ and $2H_2$ lizardite polytypes. Relevant Blochwave simulation parameters: atomic potential =
 639 Bethe; atomic form factors = PRDW (Peng-Ren-Dudarev-Whelan); n. of strong reflections = 50;
 640 sample thickness = 4 nm; defocus = 42.5 nm; spherical aberration = 0.5 mm; chromatic aberration =

641 1 mm; convergence semi-angle = 1 mrad; defocus spread = 3.5 nm; energy spread = 1.40 eV;
642 objective aperture = 5.2 nm⁻¹.

643 Figure 11. HR filtered (average background subtracted) images of népouite crystals: a) and (b) refer
644 to the same TEM image, as well as (c) and (d); only a drawing of the direct lattice has been added to
645 (b) and (d) to emphasize the stacking. Note the local straight sequence to the left and the presence
646 of a dislocation-like defect in the bent region to the right (b) and the local zig-zag sequence (d).

647 Figure 12. a) HR filtered (average background subtracted) image of népouite showing many
648 nanoflakes with preserved two-dimensional information; b) and (c) enlargement of the square
649 regions indicated in (a), further filtered in the Fourier space using a periodical mask, and with
650 drawings to emphasize the stacking. Note the disordered sequence in (b) showing stacking to the
651 left (l), straight (s), and to the right (r) in short succession. In (c) the closure gap to the lattice circuit
652 probably disclose a dislocation-like defect.

653

654 Table 1. EDXRF bulk analyses of the garnierite ultramafic host rock.

655 Table 2. WDS-EMP analyses of Ni-serpentine from Campello Monti (averages and ranges) carried
656 out on the intermediate zones (zone 2 in Fig. 5) of three different samples and distinguished
657 according to their backscattered electron (BSE) contrast (analyses calculated on the basis of 7
658 oxygens).

659 Table 3. WDS-EMP spot analyses referring to Ni-serpentine from the inner and outer zones (zone 1
660 and zone 3 in Fig. 5, respectively) and to the most deviating compositions found in the outer zone
661 (analyses calculated on the basis of 7 oxygens).

662 Table 4. XRPD data and crystallographic parameters of the Ni-serpentine from Campello Monti as
663 compared with pecoraite and népouite from Kwangcheon, Korea (Song et al. 1995).

664 Table 5. Positions (cm⁻¹) and proposed assignment for peaks observed in the FTIR spectra of the
665 Ni-serpentine from Campello Monti.