Raman anisotropy in serpentine minerals, with a caveat on identification

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Abstract
The serpentine minerals lizardite, polyhedral serpentine, chrysotile, antigorite and 15-sector and 30-sector polygonal serpentine have been studied by micro-Raman spectroscopy, using selected samples, that had been previously characterized. The appropriate crystal orientations were determined by optical microscopy of petrographic sections. Oriented spectra, obtained using Nd-YAG green laser radiation (532 nm), were deconvolved, extracting wavenumber and intensity values for the peaks, possibly overlapping and forming complex bands. Relevant Raman anisotropy is common and relevant in serpentine. Depending upon the orientation of the impinging laser, significant wavenumber shifts occur (up to 10 cm⁻¹, mostly in polyhedral serpentine and lizardite). Furthermore, also, important intensity variations (up to 1 order of magnitude) occur in polyhedral serpentine, lizardite, chrysotile and antigorite as well. On the one hand, the possibly characteristic peaks have been identified and discussed. On the other hand, caution is suggested as far as the micro-Raman characterization of polyphasic, variably oriented serpentine minerals is concerned.

KEYWORDS
antigorite, chrysotile, lizardite, Raman anisotropy, serpentine

1 | INTRODUCTION

Serpentine minerals and the serpentinization process have been receiving increased attention. In fact, hydration and dehydration of mantle ultramafics have important implications on (1) the water cycle in the deep crust and upper mantle, (2) the seismic response of subducting lithosphere and (3) the control of partial melting and basaltic magma generation.¹ Because the different serpentine minerals may have significantly different stability fields, their unambiguous identification is in many respects critical.²

On the basis of structural and microstructural arrangements, five main varieties have been distinguished: antigorite (Atg), lizardite (Liz), chrysotile (Ctl), polygonal serpentine (PS) and polyhedral serpentine (PHS).² The fibrous varieties of serpentine (i.e., Ctl, PS and fibrous Atg) are of interest for their potential hazard to human health (lung cancer and mesothelioma).³ Consequently, the accurate identification of the serpentine varieties is important also in a number of environments where fibres occur, naturally or introduced by human activity.

Several analytical techniques were used,² such as infrared (IR) spectroscopy, X-ray powder diffraction (XRPD), scanning electron microscopy (SEM) with energy-dispersive spectrometry (EDS), electron microprobe analysis (EMPA) and high-resolution transmission...
electron microscopy (HRTEM). Recently, micro-Raman (µ-R) turned out to be a very promising technique for systematic studies, due to (1) high spatial resolution (approximately 1 µm), (2) short time of measurement (a few minutes) and (3) mineralogical analysis directly on the thin section (approximately 30 µm thick) used for petrographic analysis and, after carbon coating, for chemical analysis by SEM-EDS or EMPA. For such reasons, µ-R became a popular technique for the routine identification of fibrous minerals in natural and artificial matrices.[4-6]

However, identification of fibrous minerals may be hampered by the common microscopic and nanoscopic intermixing with other (even non-fibrous) phases, topotactically acquiring a similar elongated habit.[9] The resulting complex µ-R spectrum may contain the contributions of more phases. Consequently, reference spectra for pure mineral are needed. In addition, as the mineral spectrum may change significantly with the crystal orientation,[8] matching of spectra obtained at different orientations may be difficult. In this case, deconvolution techniques help the identification of underlying peaks, although possibly accepting a certain degree of subjective interpretation.

The obtainment of reference serpentine spectra under different orientations is hampered also by the absence of manageable single crystals. In fact, fibrous serpentines usually grow as fibrils a few tens or hundred nanometres wide, often growing in veins as parallel, elongated aggregates of fibrils (fibre bundles).[7,9]

The detailed µ-R analysis of tubular Ctl (claimed to be a single crystal) was previously done under different orientations using laser radiation, in the range 150-4000 cm⁻¹, with assignment of each peak to the relevant vibration mode.[8] Later, Raman spectroscopy, based on the low-wavenumber range (roughly, 190 to 1100 cm⁻¹), was proposed as a quick, simple identification tool of serpentine[9-11] (e.g., data reported in tab. 1 of reference[10]).

More recently, µ-R adopted mapping techniques and took into account the whole spectrum, with emphasis on the high-wavenumber region, as it includes the most intense and informative peaks arising from the hydroxyl stretching modes. At present, µ-R recognizes Liz from Ctl and Atg.[3,5] On the contrary, µ-R data for PS and PHS are relatively few and perhaps contradictory.[12] As a result, Liz, PS and PHS are apparently indistinguishable by Raman spectroscopy alone, even using µ-R mapping.[4]

Therefore, we underwent the reappraisal of this issue, based on

- carefully selected Atg, Liz, Ctl, PS (both PS-15 and PS-30) and PHS samples;
- plane polarized laser radiation; and
- spot analyses, led on oriented sections, with targets selected using mapping techniques.

We focus now upon the huge anisotropic µ-R effects of serpentine minerals, studied analysing several oriented sections of the same minerals. We expect that these observations may offer the rationale for a sharper identification of these complex, difficult phases.

2 | SAMPLES DESCRIPTION

2.1 | Lizardite

Euhedral submillimetric lizardite-1T crystals occur in veins of the Monte Fico quarries (Elba, Italy), embedded within an interstitial matrix consisting of variable amounts of Ctl and minor PS.[13] Chemical compositions are

\[
\text{Mg}_{2.79} \text{Fe}^{2+}_{0.09} \text{Fe}^{3+}_{0.07} \text{Al}_{0.07} \text{Si}_{3.90} \text{O}_{5}(\text{OH})_2 \text{Σ} = 3.02 (\text{Si}_{1.91} \text{Al}_{0.09})_\Sigma = 2.00 \text{O}_{5}(\text{OH})_{3.90} \text{and}
\]

\[
\text{Mg}_{2.80} \text{Fe}^{2+}_{0.11} \text{Al}_{0.06} \text{Si}_{2.95} \text{O}_{5}(\text{OH})_2, \text{for Liz and Ctl, respectively.}[14]
\]

Subsequently, Mössbauer and Fourier transform IR data led to the improved formula[15]:

\[
\text{Mg}_{2.74} \text{Fe}^{2+}_{0.10} \text{Fe}^{3+}_{0.05} \text{Al}_{0.11} \text{Si}_{3.02} (\text{Si}_{1.94} \text{Al}_{0.05})_\Sigma = 2.00 \text{O}_{5}(\text{OH})_{3.95}.
\]

Monte Fico Liz was used as µ-R Liz reference material[10] and in high-pressure (HP) Raman investigation.[16] Two thin sections were now prepared from the original samples[13]; in particular, sections MM91A and MM91B were cut perpendicular and parallel to the lineation, respectively.

2.2 | Chrysotile

The chrysotile sample comes from the massive portions of a lizardite serpentine, quarried since the XI century as ornamental stone for religious buildings, with the trade name ‘Verde Prato’.[17] The serpentine is cut by an irregular network of discontinuous white veins of ‘cross’ chrysotile, usually less than 1 mm long. Three representative spectra were obtained from a vein cut perpendicular to the selvages, showing the chrysotile highest interference colours, corresponding to the ε-ω section; and from a vein cut parallel to the vein, showing the lowest chrysotile interference colours, corresponding to the η-ω section.

Due to the low birefringence, the desired crystal orientations were confirmed by means of the interference figures, obtained from single undeformed domains of proper sizes.

2.3 | Polyhedral serpentine

Millimetre-sized PHS spheres, visible to the naked eye on the outcrop, occur at Gew Graze, Kynance, Lizard,
Cornwall; they are composed by crystallographically controlled radial arrays of well-crystallized lizardite-1T sectors.\[^{18}\] The mineral, with composition 
\[(\text{Mg}_{2.98}\text{Fe}_{0.02}\text{Mn}_{0.005}\text{Al}_{0.004})(\text{Si}_{1.996}\text{Al}_{0.004})\text{O}_5(\text{OH})_4,\]

is very close to the Mg end-member.

Two of these spheres were now sectioned and prepared for the \(\mu\)-R investigation.

### 2.4 PS-15 and PS-30 polygonal serpentine

For sake of simplicity, we report \(\mu\)-R data for two samples only (S1283 and S491), out of the four ones studied by HRTEM and XRPD, characterized by evident PS XRPD additional reflections.\[^{19}\] However, also, S1279 and S265 produced similar results.

The samples belong to a collection of massive pale-green splintery serpentine veins, cutting across massive serpentinite bodies exposed in the ophiolites from former Yugoslavia.\[^{20}\] The veins locally show deformation features, such as kink bands and wavy extinction.

S1283 comes from Mt. Nichpur serpentinites, near the border of Albania, Northern Macedonia and Kosovo. Undeformed pale-green serpentinite veins\[^{20}\] have composition
\[(\text{Mg}_{2.93}\text{Fe}^{2+}_{0.02}\text{Fe}^{3+}_{0.03})(\text{Si}_{1.94}\text{Al}_{0.06})\text{O}_4(\text{OH})_4.\]

S491 is a compact, pale-green serpentine vein, from Kačanik (Crni Kamen), near the Kosovo–Northern Macedonia border. It is partially coated by umber limonite layers. Composition is
\[(\text{Mg}_{2.93}\text{Fe}^{2+}_{0.02}\text{Fe}^{3+}_{0.03})(\text{Si}_{1.97}\text{Al}_{0.03})\text{O}_{4.90}(\text{OH})_4.\]

HRTEM\[^{19}\] led to conclude that (1) the specimens consist of PS andCtl, with no Liz or Atg; (2) the serpentine veins consist of randomly oriented PS that becomes stress oriented close to the vein selvages; (3) oriented samples consist of PS with sectors matching the ‘magic numbers’ 15 or 30 (hereafter PS-15 and PS-30, respectively); (4) the relative contents vary from vein to vein; S1283 mostly consists of PS-15 with rare PS-30, whereas PS-30 prevails in S491; (5) Ctrl fibres occur in S491 together with large PS-30 fibres, producing a nanoporous texture; and (6) PS-15 is usually less developed and more defective than PS-30.

### 2.5 Antigorite

The antigorite sample comes from the 240-m depth in the drill core AM1 (UTM Coord: 483220.79, 492199.72) cutting massive portions of serpentinized lherzolites belonging to the Bric Boessa domain of the Voltri tectono-metamorphic unit, Ligurian Alps.\[^{21}\] Forsterite, orthopyroxene, clinopyroxene and Cr-rich spinel, which are the relics of the mantle mineralogy, during the Alpine eclogite-facies metamorphism were partly converted to antigorite, titanian hydroxyl-clinohumite and Mg-chlorite. The rock is cut by late veins of chrysotile and calcite.

### 3 MICRO-RAMAN SPECTROSCOPY AND BAND DECONVOLUTION

#### 3.1 Operating conditions

\(\mu\)-R spectra were obtained at Department of Earth Sciences, University of Turin, Italy, using a Horiba-Jobin Yvon HR800 LabRAM instrument equipped with a Nd-YAG green laser (532 nm) in N–S polarized mode, delivering 8 mW on the sample, an Olympus BX 40 optical microscope and a CCD detector cooled to −70°C by Peltier effect. The analytical conditions were 200-μm confocal hole, 100× objective (1-μm lateral spatial resolution) and 1-cm\(^{-1}\) spectral resolution with 600 grooves/mm gratings; the instrumental accuracy in determining the peak positions was \(\approx0.56\) cm\(^{-1}\). The spectrometer was calibrated to the silicon Raman peak at 520.7 cm\(^{-1}\). Raman spectra were collected in the spectral ranges of 100–1200 cm\(^{-1}\) and 3000–4000 cm\(^{-1}\). Acquisition time was 10 s, averaging over 10 accumulations per spot.

#### 3.2 Band component analysis

Band component analysis was undertaken using the Horiba-Jobin Yvon LabSpec 5 software package, which affords selection of the fitting function, as well as of variable parameters. Background was removed from the spectra before the best fitting procedure, by means of the Baseline option (type: polynomial, degree: 2) of the LabSpec5 software. Band fitting was done using a Lorentz–Gauss cross-product function with the minimum number of bands used for the fitting process. Fitting proceeded until the obtainment of reproducible results with root mean square error \(r^2\) correlations greater than 0.995. In the high-wavenumber region, where a significant band overlap occurs, the best fitting has been obtained with four bands for PHS, six bands for Liz, five bands for Ctrl, five bands for PS-30, five bands for PS-15 and seven bands for Atg.

For all the analysed spectra, the band labels reported in Figures 1–6 refer to the centroid value obtained by deconvolution. This procedure is the best way for the comparison of spectra with overlapping bands and leads to identify the low intensity peaks appearing only as
shoulders. In Figures 1–6, the convolution curves obtained from the band fitting are shown by a thick red line. The black lines representing experimental spectra are mostly hidden by the red convolution line, due to the good fitting. Each single convolution band appears as a thin black line.

For the selection of the main crystallographic orientations of serpentine minerals, we took advantage of the optical crystallography that links crystallographic (x, y, z directions of the unit cell) and optical parameters (the main indices ε, ω or α, β, γ of the uniaxial and biaxial indicatrices, respectively). This was performed by examining, in transmitted plane-polarized light, thin sections (about 30 μm thick) of rocks including single serpentine crystals (or bundles of iso-oriented fibres), exhibiting a clear habit. For each phase, two sections were selected: the first one having the highest (sections ε–ω or α–γ) birefringence and the second one ⊥ to the optic axis ε for uniaxial crystals (as confirmed by the centred black cross at conoscopic observations) and ⊥ to the bisector (α or γ) of the acute angle between the optical axes for negative and positive biaxial crystals, respectively (as confirmed by the relevant interference figure at conoscopic observations).

For the polygonal serpentines (PS-15 and PS-30), the inadequate optical data were supplemented by the examination of μ-R maps of appropriate sections; for the details of the procedure used, the reader is referred to the methodological paper by Cossio et al. (in preparation).

4 | RESULTS

The results of spectral deconvolution, for all the six minerals studied in the different orientations, occur in Figures 1–6, as well as in Table S1 (deconvolved wavenumber, cm⁻¹) and Table S2 (absolute intensities, cps). These data represent several different spectra in several different sites, studied by μ-R mapping, μ-R profiles and μ-R point analyses. The deconvolution results are
there reported giving one decimal digit, but the following discussions contain values truncated to the integer.

For sake of simplicity, the Raman results are presented in order of increasing spectral complexity, following the sequence PHS, Liz, Ctl, PS-30, PS-15 and Atg.

### 4.1 Polyhedral serpentine

Figure 1 shows the μ-R spectra of a sectioned PHS sphere, large enough to afford optical selection among the different sectors. The individual sectors were analysed under three different orientations; that is, from top,

1. sector cut parallel to \( \mathbf{c} \), with the optical axis \( \mathbf{e} \) oriented E–W (viz., perpendicular to the N–S polarization plane);
2. sector cut parallel to \( \mathbf{c} \), with \( \mathbf{e} \) oriented N–S (viz., parallel to the N–S polarization plane); and
3. sector cut perpendicular to \( \mathbf{c} \) (i.e., presenting the isotropic section \( \omega–\omega \)).

The pattern is sharply defined and consists of a limited number of narrow peaks. The most striking feature probably is the variation of the peak wavenumber in the different crystallographic orientations. For instance, the high-wavenumber region is characterized by a doublet; whereas the weaker peak remains at 3707 cm\(^{-1}\), the stronger one moves from 3685 cm\(^{-1}\) (Orientations 1 and 2) to 3694 cm\(^{-1}\) (Orientation 3). As a consequence, the doublet separation decreases from 22 to 13 cm\(^{-1}\). The 3685 peak (Orientation 1) is broader and slightly asymmetric, as due to the occurrence of a further contribution at 3690 cm\(^{-1}\), revealed by deconvolution; this additional peak becomes weaker in Orientation 2 and disappears in Orientation 3.

Wavenumber changes also in the low-values region. For instance, the 233-cm\(^{-1}\) peaks of Orientations 1 and

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**FIGURE 2** μ-R spectra in the low- (100–1200 cm\(^{-1}\)) and high-wavenumber (3600–3750 cm\(^{-1}\)) regions of Liz crystals from Monte Fico. From top: Section \( \epsilon–\omega \) with \( \epsilon \) oriented E–W, section \( \epsilon–\omega \) with \( \epsilon \) oriented N–S and section \( \omega–\omega \). [Colour figure can be viewed at wileyonlinelibrary.com]
2 move to 237 cm\(^{-1}\) in Orientation 3. Furthermore, the 388- and 387-cm\(^{-1}\) peaks move to 393 cm\(^{-1}\).

Depending upon orientation, peaks modify either absolute or relative intensities. Overall intensities, at both high and low wavenumbers, are definitely higher in Orientation 2 (notice the different scale factors, from 600 to 10 000 cps). More specifically, the 3685-cm\(^{-1}\) peak in Orientation 2 is more than an order of magnitude higher than in Orientation 1. Furthermore, the relative values of the two high-wavenumber peaks change, from similar to very different values (Orientations 1 and 2, respectively). Also, the low-wavenumber region shows modified relative intensities; whereas the peaks at 388 and 393 cm\(^{-1}\) are the strongest one in Orientations 1 and 3, the one at 232 cm\(^{-1}\) is the strongest one in Orientation 2 (but vanishes in Orientation 3).

Therefore, the PHS \(\mu\)-R spectra show anisotropic features, affecting both peak positions and peak intensities. We remark that overall intensity is higher for Orientation 2 (\(\mathbf{c}\) parallel to the N–S polarization plane); this is the direction of the \(\mathbf{c}\) unit-cell axis, corresponding to the direction of the PHS OH bonds.

### 4.2 | Lizardite

Figure 2 reports the \(\mu\)-R spectra of euhedral Liz crystals, collected under the same orientations used in Figure 1 for PHS; that is, from top,

1. crystal cut parallel to \(\mathbf{c}\), with \(\mathbf{c}\) oriented E–W;
2. crystal cut parallel to \(\mathbf{c}\), with \(\mathbf{c}\) oriented N–S; and
3. crystal cut perpendicular to \(\mathbf{c}\) (i.e., presenting the isotropic section \(\omega–\omega\)).

Liz spectra strongly match PHS, either as regards the variable peak positions and the variable absolute and relative intensities, with limited differences.
Once more, the most striking feature probably is the discontinuous variation of the peak wavenumber with orientation. In the high-wavenumber region, whereas the sharp 3707-cm\(^{-1}\) peak does not move, the strongest peak shifts from 3678 cm\(^{-1}\) (Orientations 1 and 2) to 3688 cm\(^{-1}\) (Orientation 3). The doublet separations expand, from 22 and 13 in PHS, to 29 and 19 cm\(^{-1}\) in Liz. The 3678-cm\(^{-1}\) peak (Orientations 1 and 2) is broad and overlaps two further contributions at 3670–3668 and 3696–3695 cm\(^{-1}\), revealed by deconvolution; they almost disappear in Orientation 3.

Similarly to PHS, in the low-wavenumber region, the 235-cm\(^{-1}\) peak of Orientations 1 and 2 moves to 242 cm\(^{-1}\) in Orientation 3; furthermore, the 388-cm\(^{-1}\) peak moves to 394 cm\(^{-1}\).

Here again, overall intensities, at both high and low wavenumbers, are definitely higher in Orientation 2 (notice again the different scale factors); more specifically, the 3678-cm\(^{-1}\) peak is eight times stronger than in Orientation 1. Another major feature, similar to PHS, is associated with the different relative intensities at low wavenumber; whereas the peak close to 388 cm\(^{-1}\) is the strongest one in Orientations 1 and 3, the peak close to 235 cm\(^{-1}\) is the strongest one in Orientation 2 (but vanishes in Orientation 3).

Therefore, also, the oriented, Liz \(\mu\)-R spectra reveal anisotropic effects, affecting both peak positions and peak intensities. Similar to PHS, overall intensity is maximal for Orientation 2, with \(\epsilon\) (as well as the \(\epsilon\) cell axis and the OH bonds) parallel to the N–S laser polarization plane.

### 4.3 Chrysotile

Figure 3 reports the \(\mu\)-R spectra ofCtl pseudo-crystals (viz., bundles of parallel fibres) under three representative orientations; that is, from top,

1. fibre bundle cut parallel to \(\epsilon\) (i.e., the bundle elongation), oriented E–W;
2. fibre bundle cut parallel to \( \mathbf{e} \), oriented N–S; and
3. fibre bundle cut perpendicular to \( \mathbf{e} \).

Compared with PHS and Liz, the Ctl high-wavenumber region presents a broad, poorly resolved band in the range 3680–3701 cm\(^{-1}\). Higher wavenumber peaks (such as the 3707-cm\(^{-1}\) peak of PHS and Liz) are absent. Deconvolution reveals embedded peaks at relatively constant values close to 3694 and 3701 cm\(^{-1}\), plus a weaker contribution that moves from 3684 to 3680 and 3673 cm\(^{-1}\).

Ctl systematically shows a sharp peak at 1105–1107 cm\(^{-1}\). This peak was absent in Liz, yielding weak peaks at 1040 and 1070 cm\(^{-1}\) in Orientations 1 and 2, but absent in Orientation 3. PHS showed variable peaks, moving from 1088 to 1079 and to 1104 cm\(^{-1}\).

One more discriminating feature regards the overall absolute intensities (Table S2), now constant as regards the low-wavenumber region, but definitely lower for Orientation 2 at high wavenumber that produced stronger peaks in PHS and Liz. This different behaviour depends again upon the OH orientation, peculiar in the case of the Ctl fibres. Here, these bonds partially coincide with the electric field, associated with the laser N–S polarization plane, either when the bundle lays E–W or, alternatively, when the bundle is vertical.

The most significant relative intensity variations affect the 233-cm\(^{-1}\) peak only, with minimal intensity in Orientation 2.

Anisotropic effects, appearing as intensity variations, were already observed, for polarized Ctl Raman spectra under different orientations.\[^{[8]}\]

### 4.4 | Polygonal serpentine PS-30

Figure 4 reports the \( \mu \)-R spectra of PS-30 S491; that is, from top,
1. ‘crystal’ cut parallel to \(c\), with \(\epsilon\) oriented E–W (viz., perpendicular to the N–S polarization plane); 
2. ‘crystal’ cut parallel to \(c\), with \(\epsilon\) oriented N–S; and 
3. ‘crystal’ cut perpendicular to \(c\) (i.e., presenting the isotropic section \(\omega\–\omega\)).

At difference from PHS and Liz, the \(\mu\)-R spectra of PS-30 ‘crystals’ (actually, fibre bundles, possibly intermixed with Ctl) reveal a less anisotropic spectral behaviour, characterized by relatively constant wavenumber values. Such a behaviour reflects into overall intensities that approach, but do not reach, the pattern present in Ctl, still producing lower values for Orientation 2.

For instance, four peaks systematically occur in the high-wavenumber region: a strongest peak at 3682 cm\(^{-1}\), a shoulder at 3687–3688 cm\(^{-1}\), another peak at 3696–3697 cm\(^{-1}\) (that shows the most significant intensity
variation) and a low but sharp peak at 3702–3706 cm$^{-1}$; the four peaks produce quite a distinctive multiplet. Similarly, the low-wavenumber peaks do not significantly change.

A possibly distinctive feature here occurs in the range 1092–1098 cm$^{-1}$, with weak peak that has no correspondence in Liz, PHS or Ctl.

### 4.5 Polygonal serpentine PS-15

Figure 5 reports the $\mu$-R spectra of PS-15 S1283; that is, from top,

1. ‘crystal’ cut parallel to $c$, with $e$ oriented E–W (viz., perpendicular to the N–S polarization plane);
2. ‘crystal’ cut parallel to $e$, with $e$ oriented N–S; and
3. ‘crystal’ cut perpendicular to $e$ (i.e., presenting the isotropic section $\omega$–$\omega$).

As already observed for PS-30, and at difference from PHS, Liz and Ctl, PS-15 ‘crystals’ (actually, fibre bundles possibly intermixed with Ctl) yield $\mu$-R spectra characterized by similar wavenumber and similar absolute intensity values under the different orientations (viz., a nearly isotropic behaviour).

A four-peak multiplet occurs in the high-wavenumber region, with the 3697- to 3699-cm$^{-1}$ peak being the most intense one and masking the weak 3702–3705 cm$^{-1}$ (visible after deconvolution); two other peaks occur on the low-wavenumber side of the multiplet band. The wavenumber values do not differ from PS-30; notwithstanding, the four-peak multiplet of PS-15 has a different overall shape, resulting from the different intensities distribution, capable to discriminate it from PS-30. In particular, the strong band at 3682 cm$^{-1}$ in PS-30 is replaced by a strong peak at 3697 cm$^{-1}$ in PS-15, producing left- and right-oriented envelopes, respectively.

In the low-wavenumber region, the peak positions do not significantly change. Intensities are almost constant from pattern to pattern, with a limited difference only, regarding the 233 cm$^{-1}$, that yields minimal values for Orientation 2.

A possibly distinctive feature derives from the 1103- to 1107-cm$^{-1}$ peaks (1107 cm$^{-1}$ in Orientation 2 and moving to 1103 cm$^{-1}$ in Orientations 1 and 3). These values differ from PS-30, Liz and PHS and are similar to Ctl.

### 4.6 Antigorite

Owing to the lower symmetry, Atg required four different orientations (Figure 6); that is, from top,

1. $\alpha$–$\gamma$ section (z and y directions of the unit cell, respectively), with $\alpha$ oriented N–S;
2. $\alpha$–$\gamma$ section (z and y directions of the unit cell, respectively), with $\gamma$ oriented N–S;
3. $\beta$–$\gamma$ section (x and y directions of the unit cell, respectively), with $\beta$ oriented N–S; and
4. $\beta$–$\gamma$ section (x and y directions of the unit cell, respectively), with $\gamma$ oriented N–S.

Throughout the four spectra, almost no peak shift occurs; the only detectable difference regards the 3671-cm$^{-1}$ peak of the $\alpha$–$\gamma$ section, moving to 3674 cm$^{-1}$ in the $\beta$–$\gamma$ section.

The absolute intensities are maximal for the section $\alpha$–$\gamma$ with $\alpha$ oriented N–S, approximately by a factor 4 at low wavenumber and by a factor 10 at high wavenumber. Notwithstanding the different symmetries, this orientation corresponds to the section $e$–$\omega$ with $e$ oriented N–S of Liz and PHS, from both the optical and structural points of view.

Relative values change at high wavenumber, with inversion; whereas the 3671-cm$^{-1}$ peak is stronger than the 3700-cm$^{-1}$ peak in the two orientations of the $\alpha$–$\gamma$ section, the latter becomes the stronger one in the two orientations of the $\beta$–$\gamma$ section. Relative intensities change also at low wavenumber, with the 230-cm$^{-1}$ peak being the strongest one for $\alpha$–$\gamma$ with $\alpha$ oriented N–S, decreasing in $\alpha$–$\gamma$ with $\gamma$ oriented N–S and almost disappearing in the two orientations of the $\beta$–$\gamma$ section.

Deconvolution shows also the presence of minor contributions within the high-wavenumber doublet, with weak peaks between 3658 and 3696 cm$^{-1}$, slightly variable in positions and intensity.

### 5 DISCUSSION AND CONCLUSIONS

The $\mu$-R study of the different serpentine minerals, led using common conditions (laser, Raman equipment and software) on previously documented samples, offers the rationale for the reappraisal of their spectrometric data.

#### 5.1 Anisotropy

The Raman anisotropic behaviour of Ctl was previously reported,$^8$ pointing out that the intensities of all the OH bands were strongly dependent on the crystal orientation with respect to the polarization plane. We extend now their observation to PHS (Figure 1), Liz (Figure 2) and Atg (Figure 6). Anisotropy arises because the OH bonds are sharply oriented perpendicular to the octahedral
Mg–O and tetrahedral T–O sheets (c direction of PHS, Liz and Atg); therefore, the vibrations occur in well-defined directions and produce the strongly anisotropic spectra with intensity variations. Furthermore, μ-R anisotropy means also wavenumber jumps, with peaks disappearing and being replaced by new ones (e.g., from 3678 to 3688 cm\(^{-1}\) in Liz and from 3684–3685 to 3694 cm\(^{-1}\) in PHS). Conversely, the circular distribution of OH bonds in PS-30 and PS-15 removes any Raman anisotropy.

Variable intensity values give another evidence of the Raman anisotropy. For instance, the overall spectral intensities of Liz and PHS are approximately 1 order of magnitude higher when crystals are cut parallel to c, with the elongation directions (corresponding to the optic axis c) parallel to the N–S polarization plane. Furthermore, as several peaks change their intensity (either increasing or decreasing), their relative heights become modified and also possibly inverted. Examples may be found in the low-wavenumber portions of both Liz and PHS.

We expect that not-oriented sections or unpolarized spectra of Liz, PHS and Ctl produce variable, complex patterns. These patterns result as weighted averages of spatially resolved wavenumber, merged according to the actual textural features and producing poorly resolved envelopes. Merging effects will be even more dramatic in the case of polymineralic, misoriented aggregates (that is quite common for serpentine minerals).

### 5.2 Merging effects

From the point of view of crystal physics, the use of large, selected specimens and plane polarized light is definitely an advantage for the determination of accurate spectral properties. However, these accurate values may be poorly transferable to real samples, where major merging effects occur.

For instance, the size of our μ-R spot was in the order of 1 μm, capable to excite volumes probably larger and deeper than 1000 nm. This volume is definitely larger than the usual Ctl diameter (30 nm), larger even of our selected PS (less than 250 nm), comparable with the size of individual PHS spheres previously studied. Therefore, during routine μ-R identification, we may expect relevant merging effects, resulting from the association of different phases (e.g., Liz + Ctl) or different orientations. In the case of largely heterogeneous samples, merging over phases and directions will lead to poorly resolved bands; in the case of pure phases with heterogeneous orientation distributions, this leads to variable wavenumber. As matter of speculation only, we may wonder whether a possible example of this latter behaviour may be found in tab. 3 of reference\(^9\) that reports the variable values 388, 380, 388 and 386 cm\(^{-1}\) for (unfortunately different) Liz samples.

Another case may be associated with PS-15 and PS-30. We know from HRTEM characterization that even the best available PS samples actually consist of several PS fibres, pointing in different directions; intermixed with Ctl fibres, they are also pointing in different directions. Therefore, the PS μ-R spectra may represent a complex mixture of more phases in more orientations. However, based on the XRPD-HRTEM results\(^1\) as well as on our study of many μ-R spectra, we estimate PS contents greater than 80%.

These merging effects may limit the definition of archetypal reference spectra and their use in routine identification work.

### 5.3 Interlaboratory data reproducibility

The Raman spectrum of Monte Fico Liz was previously determined, in the low-wavenumber region and using random powder orientation.\(^1\) The strongest bands of that Figure 4 (690, 388 and 233 cm\(^{-1}\)) match the present data (691–692, 388–394 and 235–242, for sections parallel and perpendicular to c, respectively), with better agreement with our parallel section. For the same spectral region, using razor cut Monte Fico samples,\(^1\) values were 695, 393 and 238 cm\(^{-1}\). In the high-wavenumber region, two intense peaks at 3703 and 3688 cm\(^{-1}\), to be compared with our 3707 and 3688 cm\(^{-1}\), were found.\(^1\) Among the three different data sets, the differences may be as large as 5 cm\(^{-1}\). It is not clear whether they are due to uncalibrated, differently resolving spectrometers or different experimental details (powders, crystal sections, diamond-anvil cell and orientations).

### 5.4 Fingerprints in the low-wavenumber region

In the low-wavenumber region, the unambiguous distinction among the four serpentine phases may be difficult. The most informative region occurs at 1040–1110 cm\(^{-1}\).

In particular, Ctl systematically shows a sharp band at 1106–1107 cm\(^{-1}\). Similar values occur also in PS-15 (1103–1107 cm\(^{-1}\)). PS-30 shows a peak in the 1092–1098 range, at wavenumber variable with the different orientations. Depending again upon orientation, PHS shows an evident peak, variable from 1088 to 1080 and 1104 cm\(^{-1}\). This peak was absent in Liz, replaced by very low intensity distribution. Finally, Atg produces a sharp peak at 1045–1046.
Therefore, in this region, some confusion occurs between PHS and PS-30, as well as between PS-15 and Ctl.

5.5  |  Fingerprints in the high-wavenumber region

The high-wavenumber region mostly results from the OH stretching vibrations. As OH bonds are sharply oriented perpendicular to the octahedral Mg–O and tetrahedral T–O sheets, the vibrations occur in defined directions and give arise to the strongly anisotropic spectra. These spectra are characterized from recognizable features:

- multiplet in the 3640–3710-cm\(^{-1}\) range. It is based on two main peaks (3678 plus 3707 cm\(^{-1}\), and/or 3688 plus 3707 cm\(^{-1}\)) (depending on orientation) in Liz. The same pattern occurs quite similarly in PHS (3685 plus 3707 cm\(^{-1}\), and/or 3694 plus 3707 cm\(^{-1}\));
- more complex multiplet in PS-30 (four peaks between 3682 and 3705 cm\(^{-1}\), with maximal emission at 3682), comparable but different from PS-15 (four peaks between 3684 and 3705 cm\(^{-1}\), with maximal emission at 3697). Therefore, PS-30 is climbing to the left, whereas PS-15 is climbing to the right;
- poorly resolved 3680–3706 cm\(^{-1}\) envelope in Ctl, with deconvolved maximal emissions at 3694–3692 and 3699–3701 cm\(^{-1}\); and
- sharp peak at 3707 cm\(^{-1}\), strongly evident in Liz and PHS, but vanishing in PS-30 and PS-15, and absent in Ctl.

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of this article.

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