Raman characteristics of Alpine–Himalayan serpentine polymorphs: A case study of Khankuie ultramafic complex, southeast of Iran

BAHRAMBEGI BAHRAM¹, MOEINZADEH HESAM^{1,*}, PRAKASH DIVYA²
and WEBER IRIS³

¹Department of Geology, Faculty of Science, Shahid Bahonar University of Kerman, Kerman, Iran.

²Centre of Advanced Study in Geology, Institute of Science, Banaras Hindu University, Varanasi 221 005, India.

³Institut für Planetologie, Wilhelm-Klemm-Street 10, 48149 Münster, Germany.

*Corresponding author. e-mail: hmoeinzadeh@uk.ac.ir

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Chrysotile, antigorite, and lizardite were analyzed to determine their chemical and structural properties as a function of Raman spectral patterns. Serpentine polymorph discrimination is a challenging issue as each polymorph represents different crystal structure and different thermodynamic phase situation of formation. Microtextural investigation, SEM (Scanning Electron Microscope), XRD (X-Ray Diffraction), and EMPA (Electron Microprobe Analysis) illustrate that there are some chemical and structural variations between our studied serpentine polymorphs. In the case of the three strongest Raman peaks at around 230, 390 and 690 cm^{-1} , we obtained that antigorite tends to lower Raman Stoke lines, lizardite to moderate wavenumbers and the highest Raman Stoke lines belong to chrysotile. These main bands with principal peaks were used to find special spectral peak patterns of each polymorph, along with some other ‘weak’ peaks (around 350, 520, and 620 cm^{-1}) with different behaviours. When Raman Stoke line shifts were plotted against each other, we reached to 25 scatter plots with different classified validation. The best 2d scatter discrimination diagrams are those of 230–390 cm^{-1} and 350–390 cm^{-1} with the overall accuracy rate of 94% and 98%, respectively. Also, there are proportional relations between chemical band vibrations of SiO_4 , MgO , and H_2O , and Raman Stoke lines of 390, 620 and 230 cm^{-1} , respectively. This information increases our ability to predict polymorph types and geochemical trends of serpentine group minerals just using the Raman spectra.

Keywords. Serpentine polymorphs; Raman spectroscopy; Raman Stoke line shifts; chemical band vibrations; discrimination diagrams.

1. Introduction

Mg-rich serpentine minerals are trioctahedral phyllosilicates. They present a structural complexity because of the lattice mismatch between octahedral (O) and tetrahedral (T) layers. The compensation of this mismatch is made by

chemical changes or by a curvature of the layers (Wicks and O’Hanley 1988; Rinaudo *et al.* 2003).

Raman spectroscopy is an experimental technique that permits the identification of mineral species without long and costly preparation of the sample. It is a simple and rapid technique that necessitates no sample preparation but allows

conclusions significant for the application on bodies even in our Solar System (Weber *et al.* 2014). It has been used by a number of investigators for general polymorph identifications (Alavipanah 2004) and chrysotile identification e.g., Lewis and Griffiths (1996), Bard *et al.* (1997) and Kloprogge and Frost (1999). In addition, Pasteris and Wopenka (1987) tried to identify lizardite by Raman spectroscopy. However, Guillot and Hattori (2013) and some other authors (e.g., Auzende *et al.* 2004; Petriglieri *et al.* 2015) studied lizardite and antigorite structure via Raman peak identification.

Serpentine minerals usually occur in altered ultramafic complexes. Ophiolites are the most important lithologies that hosted serpentinites and meta-peridotites, which contain mainly serpentine minerals. The history of collisional orogenic belts involved multiple collision steps that often are along with the formation of ophiolitic lithology (Dilek *et al.* 2008). One of the most important collisional orogenic belts is the Mesozoic Alpine–Himalayan belt with which this paper deals. Ophiolite preserved in a collisional orogeny could form at different stages of a Wilson cycle.

Khankuie area is located in the central position of the Alpine–Himalayan orogenic belt. Area covered with mantle-derived serpentinized ultramafic rocks that are common as fragments in the ophiolitic mélanges. Studying meta-peridotite and serpentinites from varying parts of the target area illustrate the presence of all main serpentine polymorphs in mélanges of Khankuie area.

The aim of our investigation is to represent new ranges of Raman Stoke line for each Alpine–Himalayan serpentine polymorph in comparison to expensive chemical-structural classification studies and to represent a new quantity approach of diagram fields in 2d scatter plot formats for fast serpentine polymorph identification and discrimination via Raman peak positions.

1.1 Raman characteristics of serpentine polymorphs

Low-wavenumber Raman spectra obtained for lizardite, antigorite, and chrysotile ranges are in close agreement to the presentation of Rinaudo *et al.* (2003) and, furthermore, studied by Auzende *et al.* (2004), which have investigated high-pressure behaviour of serpentine minerals, as well as by Groppo *et al.* (2006), which studied serpentine minerals with Raman Spectroscopy. Based on

Rinaudo *et al.* (2003), Raman Stoke lines at 230, 390, 620, and 690 cm^{-1} are similar in lizardite and chrysotile, but shifted to lower wavenumbers in antigorite. In all serpentine polymorphs, the strong peak at 230 cm^{-1} is related to O–H–O vibrations, where O is the non-bridging oxygen of a SiO_4 tetrahedron and H is the hydrogen of the outer OH group of the adjacent layer (Griffith and Lesniak 1969). The peak at 530 cm^{-1} , which is not present in chrysotile and associated with the deformation of SiO_4 – AlO_4 tetrahedra, is shifted to higher wavenumbers with respect to the 510 cm^{-1} value as reported by Lazarev (1962) and Rinaudo *et al.* (2003). On the contrary, our observed peak at 621 cm^{-1} corresponds to that reported at 630 cm^{-1} (Kloprogge and Frost 1999). No Raman peak around 520 cm^{-1} for antigorite, associated with deformation vibrations of the silicon–Oxygen layer, was reported in the literature (Lazarev 1962). On the other hand, the presence of a peak at 1044 cm^{-1} , caused by anti-symmetric stretching mode (ν_{as}) of $\text{Si-O}_b\text{-Si}$ groups (Oxygen Bridge), has proven to be decisive for the discrimination of antigorite to the other polymorphs.

1.2 Geological setting of the sampling study area

The Khankuie ultramafic complex is an important ophiolitic unit located in the inner Zagros zone of the central Iranian part in the Alpine–Himalayan ophiolite belt. The Khankuie area as a southern part of the inner zone of central Iranian ophiolites can be considered as a part of the inner ophiolites, which show the age and tectono-magmatic situation similar to Nain-Baft and Dehshir ophiolites (Shafii Moghadam *et al.* 2010). The area displays a multiphase situation of the formation over the early and late metasomatism processes that formed all serpentine polymorph types in ultramafic complexes. The present study focuses on serpentine minerals of serpentinite and meta-peridotite rocks of Khankuie mélanges, as an Alpine–Himalayan ophiolite complex containing all serpentine polymorphs (figure 1).

2. Methodology

In order to identify the Raman vibrations that are specific to each serpentine phase, more than 100 samples containing different serpentine polymorph types were examined. Since it was so difficult or

Figure 1. Local geological map of Khankuie area.

even impossible to reach a high confident serpentine polymorph classification in separated mineral grains, we designed an exact three-step procedure.

- (1) At first, 100 rock samples containing a high abundance of serpentine minerals from the study area were selected and their whole rock powders were prepared and examined via XRD. Based on the relative abundance of each polymorph, 30 samples were selected for all the three polymorph types. Therefore, for each polymorph type, 10 samples with a dominant abundance of one polymorph type were discriminated.
- (2) In this step, the slices of selected samples were chipped to 30 μm thicknesses and polished. Thin rock samples with a high abundance of one polymorph type (based on our XRD investigations) were studied optically under polarized microscope. So in a rock sample with dominant polymorph-x, minerals with high correlated optical characteristics (with polymorph-x) were tagged. Finally, ideal serpentine polymorph types were separated as one polymorph class in this step.
- (3) Optically classified points on the thin chips were analyzed under EMPA. Chemical

differences among serpentine polymorphs are not absolute, but generally accepted issue (from Whittaker and Wicks 1970 to Schwarzenbach *et al.* 2016), i.e., variable based on regional historical phenomena that formed a lithology province (Iyer 2007). Using chemical discrimination factors on selected minerals that passed two purification last steps, we lead to the most reliable polymorph classification.

Then, pure classified spot point minerals were put under Raman laser incident with a radius of 50 μm . Interestingly, our collected Raman analysis results (from the last steps classified points) were found to be in correlation with spectral peak positions presented by previous researchers in other ultramafic complexes in the world (Rinaudo *et al.* 2003, 2004; Auzende *et al.* 2004; Groppo *et al.* 2006; Petriglieri *et al.* 2015). But we presented high precision spectral peak positions for each serpentine polymorph in an area over Alpine–Himalayan ophiolitic belt.

Raman spectra were recorded by a Horiba Jobin Yvon LabRAM-HR 800 spectrometer, a confocal micro-Raman system with 532 nm laser excitation, equipped with z-focus and a software-controlled x–y sample stage for line scanning and mapping.

The spectral resolution was 2 cm^{-1} at 532 nm . The spectrometer was calibrated using the 520.6 cm^{-1} Raman peak of silicon before each experimental measurement. In addition to Raman spectroscopy characterization, the micro-textural, crystallographic and chemical properties of samples were established using scanning electron microscopy (SEM), electron microprobe analysis (EMPA) and in some cases X-ray powder diffraction (XRD). EMPA spot analyses of minerals were done at an electron X-ray microanalyzer (Cameca SX50) working at accelerating voltages up to 30 kV and beam currents up to 200 nA for the electron beam and in the range 1 pA to 65 nA for the ion-beam current. The standards were a set of natural oxides, with the exception of synthetic nickel metal for Ni. The obtained data were normalized using oxygen and cation NORM programs. SEM analysis was done using an FEI Inspect S SEM. The microscopic investigation and the analytical work were done at the Department of Geology of the University of Bahonar–Kerman (Iran) and at the Department of Lithospheric Sciences of the University of Vienna (Austria). Whole-rock compositions were analysed using the XRF (X-Ray Fluorescence) technique using a Philips PW2400 spectrometer for major and selected trace element analysis at the Department of Lithospheric Sciences of the University of Vienna. The XRD runs were done using a Bruker D8-Advance powder X-ray diffractometer of the theta–theta type with a scintillation counter, energy-dispersive Sol-X or position sensitive Lynx Eye detector, attached with a Paar XRK900 reaction chamber ($298\text{--}1173\text{ K}$), at the Department of Mineralogy and Crystallography of the University of Vienna.

3. Textural and geochemical polymorph discrimination in comparison to Raman characteristics

3.1 Textural serpentine polymorph discrimination

The textural investigation illustrated that the pseudomorphic olivine as well as the mesh-textured serpentines, which developed after olivine (figure 2A and B), represent lizardite polymorphs and occasionally the resultant chrysotile with shear fractures. Non-pseudomorphic textures are only displayed by fibrous, interlocking and massive textures that are antigorite in these several forms.

Generally, the pseudomorphic textures are represented by mesh-textured and bastite serpentines. Mesh-textured serpentines that developed after olivine are lizardite. Non-pseudomorphic textures are only displayed as antigorite in several forms such as fibrous, interlocking and massive texture. The transition between the mentioned textures is also common. In some cases, antigorite is replaced by lizardite texture represented by brucite, identified optically (figure 2E). Occasionally, there are some retrograde products of both relatively old pseudomorphic and non-pseudomorphic serpentines that are dominant during the late stages of serpentinization (Wicks and O'Hanley 1988). In the Khankuie area, in thermal stages, the fibrous antigorites were deformed and the size increases (figure 2E) as it replaces finer regional antigorite (figure 2F). Pseudomorphic bastites are common in samples, which are made of fibrous replaced antigorites of different sizes (figure 2F). Rarely, there are minor values of Tremolite in some altered samples. Additionally, minerals are relict magmatic Cr-spinels no matter whether the rock is regionally or thermally metamorphosed. On the other hand, magnetite is irregular and maybe a product of the breakdown of ferromagnesian minerals during serpentinization. A summary of the mineralogy that characterizes the Khankuie serpentinites is given in table 1. Figure 3 displays the chemical relation of serpentine polymorph textures represented by different colours.

3.2 Chemical polymorph discrimination

EMPA analyses of distinguished serpentine polymorphs (classified structurally and texturally via microscopic studies and SEM analysis) provide distinguishable chemical mineral characteristics. Based on Evans (2010), Deer *et al.* (2009), Evans *et al.* (2013), Klein *et al.* (2015), McCollom and Bach (2009), O'Hanley and Wicks (1995), and Surour (2017), there are chemical dissimilarities between serpentine polymorphs that is variable based on deferent phase situations that performed on deferent regional lithology province (Iyer 2007). Based on previous researches, geochemical factors of ΣOct (total octahedral cations per formula unit), MgO , and calculated H_2O *vs.* SiO_2 and Al_2O_3 *vs.* MgO could provide the distinguishing factors for serpentine polymorph discrimination in several ultramafic complexes in other world places than Alpine–Himalayan ophiolitic belt. Data processing

Figure 2. Petrographic characteristics of the studied Khankuie serpentinites. All microphotographs except B were taken with crossed-Nicols. Abbreviations are after Whitney and Evans (2010). (A and B) Mesh textured serpentinite made up of Lizardite with Olivine and Spinel relict minerals and replaced Magnetite as metasomatism results. (C) Dense aggregates of chrysotile with spinel relicts and some replaced Magnetite. (D) Chrysotile originated in cracks in the mass Antigorite background with spinel relict minerals. (E) Recrystallized Antigorite along with Brucite and Spinel. (F) Fibrous antigorites replaced on orthopyroxene pseudomorphs as Bastite and Growth of thermal antigorite at the background with the expense of finer-grained regional antigorite. Abbreviations: Ol: Olivine, Bast: Bastite, Atg: Antigorite, Ter: Tremolite, Brc: Brucite, MAG: Magnetite, Ctl: Chrysotile, Lz: Lizardite.

of obtained EMPA results of the studied serpentine polymorphs discover some coincident and also some different chemical characteristics. For instance, antigorite has the highest SiO_2 and MgO , and the lowest value of ΣOct , Al_2O_3 and calc. H_2O . In contrast, lizardite has the lowest SiO_2 and MgO , and the highest value of ΣOct , Al_2O_3 and calculated H_2O . Chrysotile has a moderate chemical composition (between antigorite and lizardite). Consequently, in the first step, we tried to select the most ideal separated polymorphs (structurally, texturally and chemically) and removed a few minerals with transitional characteristics between

ideal polymorphs. Concerning all mentioned chemical relations among elemental 2d scatter matrix plots, the diagram of SiO_2 vs. calc. H_2O turned out as the best feature for discrimination ideal polymorphs (figure 3).

4. Raman results

4.1 Raman peak investigation

In our Raman investigation, based on previous studies (Rinaudo *et al.* 2003; Auzende *et al.* 2004; Groppo *et al.* 2006; Petriglieri *et al.* 2015) and more

Table 1. Mineralogy of the studied serpentinites from Khankuie Melanges based on petrography, Raman spectroscopy and XRD data.

No. sample	Kh-1	Kh-2	Kh-3	Kh-4	Kh-5	Kh-6	Kh-7	Kh-8
Bastite pseudomorph	R	R	R	VC	C	C	R	R
Mesh texture	C	R	R	A	C	A	R	R
Antigorite	R	C	VC	C	VC	VC	VC	VC
Lizardite	C	R	R	C	C	R	C	A
Chrysotile	R	C	C	R	R	C	R	C
Olivine pseudomorph	VC	R	R	R	VC	C	R	R
Spinel	R	C	C	R	C	R	R	C
Magnetite	R	R	R	C	C	VR	R	R
Tremolite	R	A	R	A	A	A	A	R
Brucite	A	R	A	A	R	A	R	R
Rock type	Dunite	Peridotite	Peridotite	Harz	Dunite	Harz	Lherz	Lherz

Note. R: rare; VR: very rare; C: common; VC: very common; A: absence.

Figure 3. Discrimination diagrams of serpentine polymorphs (shape classified) with texturally colour classification from regionally and thermally metamorphosed serpentinites and metaperidotites of Khankuie and surrounding area (diagram modified from Bahrambeygi *et al.* 2019).

than 80 separated polymorph samples, we obtained five best peaks for wavenumbers under 1000 cm^{-1} (table 2, where they are compared with former studies). Based on a large number of samples examined, we presented the peak positions in a particular range, so we found some diversity peak positions in some minerals with same structural, textural and chemical characteristics that belong to a clearly perfect polymorph type. Therefore, all peak positions of each polymorph were grouped. Finally, we tried to present the range of diversity peak positions in each wavenumber. Table 3 displays some statistic indices of the five main peaks. Figure 4 exhibits Raman spectra of each polymorph and range of variations for each peak position in every polymorph. Figure 5 displays a

waterfall diagram of all studied Raman spectrum of separated serpentine polymorphs. Based on our results with agreement by former investigations, in Raman spectral patterns of serpentine minerals, there are three most intense peaks at wavenumbers around 230 , 390 and 690 cm^{-1} (table 2). But, there are some important weak peaks (at about 350 , 520 and 620 cm^{-1}) that have been debated in the literature (table 2).

4.1.1 Peaks in wavenumber position around 230 cm^{-1}

The band of around 230 cm^{-1} is a low number intense peak of serpentine minerals related to O–H–O vibrations, where O is the non-bridging

Table 2. *Best distinguishable wavenumber Raman peaks (fewer than 1000 cm⁻¹) in comparison to other former studies.*

		Petriglieri <i>et al.</i> (2014)	Grosso <i>et al.</i> (2006)	Auzende <i>et al.</i> (2004)	Rinaudo and Gastaldi (2003)	Current study
230	Liz-230	230	233	241	233	229.15–231.30
230	Ant-230	229	230	235	230	224.52–230.70
230	Ctl-230	232	231	235	231	230.70–234.82
350	Liz-350	349	350	351	350	–
350	Ant-350					–
350	Ctl-350	345	345	346	345	345.53–347.55
380	Liz-380	386	388	393	388	382.86–385.88
380	Ant-380	377	375	377	375	376.82–382.36
380	Ctl-380	388	389	391	389	382.86–390.90
532	Liz-532	532	510	527	510	–
532	Ant-532		520	528	520	–
532	Ctl-532					–
621	Liz-621	621	630		630	619.52–650.33
621	Ant-621	631	635		635	635.68–650.33
621	Ctl-621	622	620		620	619.03–623.93
690	Liz-690	689	690	695	690	685.84–690.69
690	Ant-690	687	683	685	683	681.48–687.78
690	Ctl-690	691	692	694	692	689.24–691.17

Table 3. *Statistic indexes of Raman peak wavenumbers of the main five serpentine polymorph peak positions contain: Standard division (STD); Maximum peak position wavenumber of every band (Max); Minimum peak position wavenumber of every band (Min) and average peak position wavenumber of bands for every polymorph.*

	Peak-230	Peak-350	Peak-380	Peak-650	Peak-690	Type
STD	1.33	–	1.46	4.63	1.61	Ant
Max	230.71	–	382.36	650.33	687.78	Ant
Min	224.52	–	376.82	635.67	681.47	Ant
Average	227.70	–	380.18	646.24	685.16	Ant
STD	1.62	0.76	2.78	1.45	0.67	Chrt
Max	234.82	347.55	390.90	623.93	691.17	Chrt
Min	230.71	345.53	382.86	619.03	689.24	Chrt
Average	232.79	346.70	386.62	621.42	690.35	Chrt
STD	0.64	–	0.86	11.91	1.45	Liz
Max	231.32	–	385.88	650.33	690.69	Liz
Min	229.15	–	382.86	619.51	685.84	Liz
Average	230.33	–	384.33	630.19	688.45	Liz

oxygen atom of the tetrahedron SiO₄, and H is the hydrogen atom of the OH group tilted towards an octahedral cation vacancy (Griffith and Lesniak 1969). In this wavenumber position, the Raman bands that tend to be of the lowest value generally reflected antigorite (224–230), moderate wavenumbers (229–231) fit with lizardite and highest wavenumbers in a reasonable range belong to

chrysotile (231–235). The experimentally obtained ranges from the lowest to the highest wavenumbers for each band (in each polymorph) are represented in table 2 and figure 4. The colour classified histogram in the scatter plot matrix (figure 6) display peak wavenumber distribution around 230 cm⁻¹, which has a relatively normal distribution with a little negative skewness related to antigorite distribution

Figure 4. Spectrum samples of Raman spectral pattern of each polymorph and range of variations for each peak position in every polymorph. Ctl: Chrysotile; Ant: Antigorite; Liz: Lizardite.

in low wavenumber peaks. Chrysotile and lizardite have closer distribution in comparison to antigorite. As it is observable in the graph in figure 4 and in the compared scatter diagrams in figure 6, this distinguishable band distribution could be helpful to separate serpentine polymorphs especially when the band position used as an axis *vs.* other bands.

Figure 5. Waterfall diagram of all studied Raman spectrums of separated serpentine polymorphs. Ctl: Chrysotile; Ant: Antigorite; Liz: Lizardite.

4.1.2 Peaks in wavenumber position around 350 cm^{-1}

The Raman Stoke line around 350 cm^{-1} , which is investigated prominently in this study, is one of the important peaks related to vibrations of the SiO_4 tetrahedra, already introduced by Klopogge and Frost (1999). The obtained results display absences of Stoke line around 350 cm^{-1} in antigorite and irregular presence in lizardite and a fine distinguishable presence in chrysotile (figure 4). In figure 6, histogram of the band of 350 cm^{-1} demonstrates a bimodal feature distribution. In this band, there were some samples with no clear peak, there are very weak peaks with the highest wavenumber than other samples with clear peaks. The second mode in the declared histogram is related to these samples. Based on Alavipanah (2004), we attributed ‘non-real peaks’ to these very weak Raman peaks, but as they all happened in the

Figure 6. 2d-scatter diagrams for all the five Raman main peaks of serpentine polymorphs (as a 5×5 matrix); experimentally obtained Raman peaks at around 230, 390, 690, 350, 520, and 620 cm^{-1} plotted against each other to get the best separator features. As it could be seen four identified (represented by star) best discrimination diagrams are: (1) band around 230 cm^{-1} vs. the band around 390 cm^{-1} , (2) band around 230 cm^{-1} vs. the band around 620 cm^{-1} , (3) band around 230 cm^{-1} vs. the band around 690 cm^{-1} , and (4) band around 350 cm^{-1} vs. the band around 390 cm^{-1} .

highest wavenumbers we used them for samples without a clear peak in this band. Consequently, overlooking the second part of the histogram (contains non-real peaks), we have a relatively negative skewness histogram exhibiting the distribution of all chrysotile polymorphs and some lizardite. The issue that antigorite has no clear peak in this band (figure 4) is an excellent topic to

polymorph discrimination as it could be seen in two compared matrix scatter diagrams in figure 6.

4.1.3 Peaks in wavenumber position around 390 cm^{-1}

The strong Raman Stoke line at around 390 cm^{-1} is an important peak ascribed to bending modes of

Figure 7. (A) Discrimination diagram of peak position around 230 cm⁻¹ vs. the band around 390 cm⁻¹; with calculated confusion matrix; (B) Discrimination diagram of peak position around 230 cm⁻¹ vs. the band around 620 cm⁻¹; with the calculated confusion matrix.

SiO₄ tetrahedra (Kloprogge and Frost 1999). In this position, similar to the band around 230 cm⁻¹, the Raman bands tend to the lowest value according to antigorite (377–382), moderate bands can be reflected lizardite (382–385) and the highest values in reasonable range belongs to chrysotile (383–391). The colour classified histogram in the scatter plot matrix (figure 7) displays band distribution around 390 cm⁻¹. As it is apparent in figure 6, this distinguishable band distribution could be useful, to separate serpentine polymorphs especially when it is used as an axis vs. band around 230 or 350 cm⁻¹.

4.1.4 Peaks in wavenumber position around 520 and 620 cm⁻¹

The weak peak at the wavenumber position around 520 cm⁻¹ is an irregular band that based on Rinaudo *et al.* (2003) and Lazarev (1962) is associated to the deformation of the SiO₄–AlO₄ tetrahedra. This band was not detected as a systematic useful distinguishable band to polymorph discrimination. On the contrary, another weak peak observed around 620 cm⁻¹ corresponds to our investigation target and it could be useful to apply as a suitable variable to polymorph discrimination. This is reported as a peak produced by OH–Mg–OH translation modes (Kloprogge *et al.* 2002). The colour classified histogram at 620 cm⁻¹ displayed in the scatter plot matrix of figure 6 illustrates that chrysotile has

a tendency to low wavenumbers (619–624) and antigorite tends to higher wavenumbers in reasonable range (636–650) while lizardite has spread distribution in a range (619–650).

4.1.5 Peaks in wavenumber position around 690 cm⁻¹

The peak around 690 cm⁻¹ is another important strong band attributed to the symmetric stretching mode of the Si–Ob–Si (Bridging Oxygen) groups. As is displayed in matrix scatter plot colour classified histogram of 690 cm⁻¹ (figure 6), similar to two recent strong bands (230 and 390 cm⁻¹), the Raman bands incline to lower values, reflected antigorite, moderate bands belong to lizardite and highest values in a reasonable range are belonging to chrysotile. Polymorph distribution histogram illustrated that the recent band could be an advantage for making discrimination diagrams.

4.2 Best Raman discrimination 2d scatter diagrams

To get the best separator features, experimentally obtained Raman peaks at around 230, 390, 690, 350, 520, and 620 cm⁻¹ have plotted against each other (figure 6). Investigating 2d scatter matrix of all five main peaks of serpentine polymorphs (as a

Figure 8. (A) Discrimination diagram of peak position around 230 cm^{-1} vs. the band around 690 cm^{-1} ; with calculated confusion matrix; (B) Discrimination diagram of peak position around 350 cm^{-1} vs. the band around 390 cm^{-1} ; with the calculated confusion matrix.

5×5 matrix) leads to discovering four best discrimination diagrams among 25 scatter plots (figure 6). Based on Van Genderen *et al.* (1978), Alavipanah (2004), and Bahrambeygi and Moeinzadeh (2017), confusion matrices will provide a quantitative comparison factor between a truth classified data set and results of a prediction analysis. In this approach, we will obtain conformity indices by an overall accuracy rate. In the following sections, conformity indices or overall accuracy rate of the truth classified polymorph and predicted polymorph types are presented for each discrimination diagram.

4.2.1 Discrimination diagram of peak position around 230 cm^{-1} vs. the band around 390 cm^{-1}

Discrimination diagram of peak position around 230 cm^{-1} vs. peak position around 390 cm^{-1} (figure 7A) is an excellent feature for perfect separation of antigorite polymorphs without any common area by other polymorphs. However, the peak position of the lizardite and chrysotile bands has a small common area in the middle part of the diagram; nevertheless, all samples could be classified with a total coefficient of 94.5% (figure 7A). The advantages of this diagram could be demonstrated by using very strong bands that are clear and easy to find in all serpentine polymorphs.

4.2.2 Discrimination diagram of peak position around 230 cm^{-1} vs. the band around 620 cm^{-1}

The mentioned diagram is another feature of the low common polymorphic separation associated with an end member lizardite. There is perfect discrimination between antigorite and chrysotile, but some interference with lizardite polymorphs. Nevertheless, as it is presented in the confusion matrix (figure 7A and B), this diagram has an overall accuracy coefficient of 83.2%. In this diagram, relatively strong bands were used. These two bands always have a clear presence in serpentine polymorphs and have an advantage to fast discrimination.

4.2.3 Discrimination diagram of peak position around 230 cm^{-1} vs. the band around 690 cm^{-1}

There is perfect discrimination for antigorite and chrysotile in this diagram (figure 8A) without common area sample (100% discrimination coefficient). With regard to antigorite and lizardite, we only encounter one interference sample of antigorite in the lizardite area (1/22 equal to 95.5% discrimination coefficient) and a strong interference to the lizardite samples in the antigorite area (2/27 equal to discrimination coefficient of 92.6%). There are more interference samples in the

Figure 9. Proportional relation of chemical band vibrations and Raman peak positions around main bands according to linear regression analysis. **(A)** peaks around 390 cm^{-1} and SiO_2 contents, **(B)** peaks around 690 cm^{-1} and SiO_2 contents, **(C)** peaks around 620 cm^{-1} and MgO contents, **(D)** peaks around 230 cm^{-1} and calc. H_2O contents and **(E)** peaks around 690 cm^{-1} and total octahedral contents.

common area of lizardite and chrysotile but this diagram has an overall accuracy of 88.7% for this discrimination diagram (figure 8A).

4.2.4 Discrimination diagram of peak position around 350 cm^{-1} vs. the band around 390 cm^{-1}

The best-obtained discrimination diagram is the 2d scatter feature of the bands around 350 cm^{-1} vs. $\sim 390\text{ cm}^{-1}$. It should be mentioned that an

acceptable peak range in this band is $345\text{--}355\text{ cm}^{-1}$. Samples plotted in an area out of this range have no real clear peaks in this band. Values presented out of the explained range are signs of absence peaks for this band, reflected antigorites and some lizardites. The explained absence is an advantage factor to separate the polymorphs. In the feature of bands around 350 cm^{-1} vs. the band around 390 cm^{-1} , there are perfect discrimination lines between lizardite–antigorite and chrysotile–antigorite with a discrimination coefficient of 100%. Just one lizardite sample

plotted in the chrysotile area (1/27). This leads to a discrimination coefficient of 96.3%. Consequently, this diagram is the best feature for serpentine polymorph discriminations with an excellent overall correction coefficient of 98.76% (figure 8B).

4.2.5 *MgO and 620 cm⁻¹ wavenumber peak relation*

Based on Kloprogge and Frost (1999), the Raman Stoke line at 620 cm⁻¹ can be assigned to OH–Mg–OH vibration. According to linear regression analysis in lizardites, Raman shifts at ~620 cm⁻¹ has a relatively direct proportional relationship to the MgO content of minerals. There is a relatively inverse proportion in antigorite, and in chrysotile, there is a weak relative direct proportional relationship (figure 9C).

4.2.6 *H₂O and 230 cm⁻¹ wavenumber peak relation*

Based on Griffith and Lesniak (1969), and Loh (1973), one band lying at around 231 cm⁻¹ in a region of the spectrum where vibrations of the O–H–O groups are expected so that O is the non-bridging oxygen atom of the tetrahedron SiO₄, and H is the hydrogen atom of the OH group tilted towards an octahedral cation vacancy. According to linear regression analysis, it is concluded that in lizardite, Raman shifts at ~230 cm⁻¹, has a relatively inverse proportion to calculated H₂O content. In antigorite and chrysotile, there is a relatively weak direct proportional relationship (figure 9D).

4.2.7 *SiO₂ vs. 390 and 690 cm⁻¹ wavenumber peak relation*

After Kloprogge and Frost (1999), Raman Stoke lines ~690 cm⁻¹ can be ascribed to bending modes of the SiO₄ tetrahedra. In our conclusions, linear regression analysis resulted in a weak inverse proportional relationship between Raman shifts at wavenumber peak position around 390 and 690 cm⁻¹ due to the SiO₂ content of minerals. It means that the high value of silica content of metaperidotite and serpentinites shifted Raman peak positions to low wavenumbers (figure 9A and B).

4.2.8 *ΣOct and 690 cm⁻¹ wavenumber peak relation*

Rosasco and Blaha (1980) introduced an intense band around 683 cm⁻¹ produced by symmetric stretching modes of SiO₄. Stretching modes of SiO₄ are affected by octahedral occupancy cations that are calculated as ΣOct in the studied samples. It could be seen in the diagram that according to linear regression analysis, there is a strong direct proportional relationship between peak positions around 683 cm⁻¹ and ΣOct content in antigorite and a clear direct proportional relation to lizardite, while chrysotile polymorphs show a weak reverse proportional relationship (figure 9E).

5. Conclusions

A comparison of the peak wavenumber positions of the three strongest bands of serpentine polymorphs 230, 390 and 690 cm⁻¹ (classified with the advanced micro-textural investigation, XRD, SEM and EMPA studies) shows a clear distributional relationship. 2d scatter diagrams and statistical histograms of considered band positions demonstrate that antigorite tends to low wavenumber Raman peak positions. Moderate Raman peak wavenumbers in a reasonable range correspond to lizardite and the highest fits with chrysotile. These distribution relations provide clear discrimination features for simple and fast polymorph discriminations.

There are other bands with weak but important Raman peak positions around 350, 520 and 620 cm⁻¹ with different behaviours. They can be attributed to chrysotile at low wavenumbers and to lizardite and antigorite in the case of higher values.

Based on our general interpretations, we presented four Raman diagrams of serpentine polymorph discriminations using five important peak positions. Peak position ~230 *vs.* ~390 cm⁻¹; peak position around ~230 *vs.* ~620 cm⁻¹; peak position ~230 *vs.* ~690 cm⁻¹ and peak position ~350 *vs.* ~390 cm⁻¹ with overall discrimination coefficients of 94.5, 83.2, 88.7 and 98.8%, respectively.

According to calculated linear regressions, Raman Stoke lines around 390 and 690 cm⁻¹ clearly shift to lower wavenumbers, if SiO₄ contents of serpentine polymorphs shift to higher values. Similarly, at 620 cm⁻¹, the band shifts to higher wavenumbers with increasing MgO content

for lizardite and chrysotile, but to lower wavenumbers for antigorite. In the case of increasing calculated H_2O contents, Stoke lines around 230 cm^{-1} shift to high wavenumbers for antigorite and chrysotile, but to lower wavenumbers for lizardite. Increasing total concentrations, octahedral cations result in a positive shift of Stoke lines around 690 cm^{-1} for antigorite and lizardite, but negative wavenumbers for chrysotile.

Our results lead to an increase in the ability to predict serpentine polymorph types and some chemical trends by exclusive use of Raman spectra of the sample. The presented diagrams also increase our ability to predict geochemical trends of serpentine group minerals using Raman spectra.

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References

- Alavipanah S 2004 *Application of remote sensing and spectroscopy in the earth sciences (soil)*; University of Tehran Press, ISBN, 117p.
- Auzende A-L, Daniel I, Reynard B, Lemaire C and Guyot F 2004 High-pressure behaviour of serpentine minerals: A Raman spectroscopic study; *Phys. Chem. Miner.* **31** 269–277.
- Bahrambeygi B and Moeinzadeh H 2017 Comparison of support vector machine and neutral network classification method in hyperspectral mapping of ophiolite mélanges – A case study of east of Iran; *Egypt. J. Remote Sens. Space Sci.* **20** 1–10.
- Bahrambeygi B, Moeinzadeh H and Alavipanah S K 2019 Mineralogy, geochemistry and Raman Spectroscopy of multi-genesis serpentine polymorphs of Darepahn Ophiolites; *J. Sci. I. R. Iran* **30** 251–269.
- Bard D, Yarwood J and Tylee B 1997 Asbestos fibre identification by Raman microspectroscopy; *J. Raman Spectrosc.* **28** 803–809.
- Deer W A, Howie R A and Zussman J 2009 *Rock forming minerals: Layered silicates excluding micas and clay minerals*; Vol. 3B, Geological Society of London, 314p.
- Dilek Y, Furnes H and Shallo M 2008 Geochemistry of the Jurassic Mirdita Ophiolite (Albania) and the MORB to SSZ evolution of a marginal basin oceanic crust; *Lithos* **100** 174–209.
- Evans B W 2010 Lizardite versus antigorite serpentine: Magnetite, hydrogen, and life (?); *Geology* **38** 879–882.
- Evans B W, Hattori K and Baronnet A 2013 Serpentinite: What, why, where? *Elements* **9** 99–106.
- Griffith W and Lesniak P 1969 Raman studies on species in aqueous solutions; *Chem. Soc. Theor.* **46** 1066–1071.
- Groppa C, Rinaudo C, Cairo S, Gastaldi D and Compagnoni R 2006 Micro-Raman spectroscopy for a quick and reliable identification of serpentine minerals from ultramafics; *Eur. J. Mineral.* **18** 319–329.
- Guillot S and Hattori K 2013 Serpentinites: Essential roles in geodynamics, arc volcanism, sustainable development, and the origin of life; *Elements* **9** 95–98.
- Iyer K 2007 Mechanisms of serpentinization and some geochemical effects; University of Oslo, 111p.
- Klein F, Grozeva N G, Seewald J S, McCollom T M, Humphris S E, Moskowitz B, Berquó T S and Kahl W-A 2015 Experimental constraints on fluid-rock reactions during incipient serpentinization of harzburgite; *Am. Mineral.* **100** 991–1002.
- Klopprogge J and Frost R 1999 Single crystal Raman microscopic study of the asbestos mineral chrysotile; *PCCP* **1** 2559–2564.
- Klopprogge J T, Wharton D, Hickey L and Frost R L 2002 Infrared and Raman study of interlayer anions CO_3^{2-} , NO_3^- , SO_4^{2-} , and ClO_4^- in Mg/Al-hydrotalcite; *Am. Mineral.* **87** 623–629.
- Lazarev Y A 1962 Line Broadening in Rotational and Rotation – Vibrational Raman Spectra of Gases; *Opt. Spectrosc.* **13** 373.
- Lewis I R and Griffiths P R 1996 Raman spectrometry with fiber-optic sampling; *Appl. Spectrosc.* **50** 12A–30A.
- Loh E 1973 Optical vibrations in sheet silicates; *J. Phys. C: Solid State Physics* **6** 1091.
- McCollom T M and Bach W 2009 Thermodynamic constraints on hydrogen generation during serpentinization of ultramafic rocks; *Geochim. Cosmochim. Acta* **73** 856–875.
- O’Hanley D S and Wicks F J 1995 Conditions of formation of lizardite, chrysotile and antigorite, Cassiar, British Columbia; *Can. Mineral.* **33** 753–773.
- Pasteris J D and Wopenka B 1987 Use of a laser Raman microprobe to trace geological reactions; *Microbeam Analysis – Am. Mineral.*, 205p.
- Petriglieri J, Salvioli-Mariani E, Mantovani L, Tribaudino M, Lottici P, Laporte-Magoni C and Bersani D 2015 Micro-Raman mapping of the polymorphs of serpentine; *J. Raman Spectrosc.* **46** 953–958.
- Rinaudo C, Belluso E and Gastaldi D 2004 Assessment of the use of Raman spectroscopy for the determination of amphibole asbestos; *Mineral. Mag.* **68** 455–465.
- Rinaudo C, Gastaldi D and Belluso E 2003 Characterization of chrysotile, antigorite and lizardite by FT-Raman spectroscopy; *Can. Mineral.* **41** 883–890.
- Rosasco G and Blaha J 1980 Raman microprobe spectra and vibrational mode assignments of talc; *Appl. Spectrosc.* **34** 140–144.

- Shafii Moghadam H, Stern R J and Rahgoshay M 2010 The Dehshir ophiolite (central Iran): Geochemical constraints on the origin and evolution of the Inner Zagros ophiolite belt; *Geol. Soc. Am. Bull.* **122** 1516–1547.
- Surour A A 2017 Chemistry of serpentine ‘polymorphs’ in the Pan–African serpentinites from the Eastern Desert of Egypt, with an emphasis on the effect of superimposed thermal metamorphism; *Mineral. Petrol.* **111** 99–119.
- Van Genderen J, Lock B and Vass P 1978 Remote sensing: Statistical testing of thematic map accuracy; *Remote Sens. Environ.* **7** 3–14.
- Weber I, Böttger U, Pavlov S, Jessberger E and Hübers H–W 2014 Mineralogical and Raman spectroscopy studies of natural olivines exposed to different planetary environments; *Planet. Space Sci.* **104** 163–172.
- Wicks F and O’Hanley D S 1988 Serpentine minerals: Structures and petrology; In: *Hydrous Phyllosilicates* **19** 91–168.

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