

THE RAMAN STUDY OF AMPHIBOLES

ANDREI IONUȚ APOPEI¹, NICOLAE BUZGAR¹

¹ “Al. I. Cuza” University of Iași, Department of Geology, 20A Carol I Blv., 700505 Iași, Romania

Abstract

Raman spectroscopy is a simple, powerful and fast method to identify and distinguish between different minerals from the amphibole group of the inosilicate class. We analyzed samples of grunerite, actinolite, nephrite, Cr – actinolite (smaragdite), uralite (var. of actinolite), tremolite, pargasite, glaucophane and riebeckite in order to determine their Raman spectra and their fingerprint. The structure of these amphiboles belongs to the space group $C2/m$. Also, through this work we intend to show types of linkages between Si and bridging O (O_b) or non-bridging O (O_{nb}), and complex vibrations that occur in all amphibole spectra, corresponding to the symmetric stretching modes (v_s) of the Si- O_b -Si bridges or O-Si-O linkages and to the asymmetric stretching modes (v_{as}) of the Si- O_b -Si bridges and O-Si-O linkages. The most distinct Raman peak detected in this Raman study of amphiboles is around $660\text{-}675\text{ cm}^{-1}$, which is assigned to the v_1/v_s (symmetric stretching vibrations) of the Si- O_b -Si bridges. Some spectra present two very weak peaks at $\sim 2330\text{ cm}^{-1}$ and $\sim 2437\text{ cm}^{-1}$, respectively, due to the substitution of K or Na with H_3O^+ ($K, Na \leftrightarrow H_3O^+$) and NH_4^+ ($K, Na \leftrightarrow NH_4^+$); these spectral bands were identified at potassium micas.

Keywords: amphiboles, Raman spectra, double chain silicates, Si_4O_{11} vibrations, smaragdite, uralite.

Raman modes in amphiboles

For double chain silicates (amphiboles), the assignment process is very complicated, because of the major differences regarding the assignment of the peaks/vibrations encountered in the works of various authors; this is due to the very complex structure of the amphibole minerals.

¹ e-mail: andrei.apopei@geology.uaic.ro

In general, the Raman bands in amphibole spectra are classified into three main types, as follows:

- vibrations modes from the interactions between the cation and oxygen (M-O);
- vibrations of $\text{Si}_4\text{O}_{11}^\infty$ ribbons, also called internal vibrations;
- vibrations of the hydroxyl molecule (OH)

A correct assignment of the spectral bands is very difficult in the 210-625 cm^{-1} spectral region, where the vibrational modes of the cations are active; also, Fornero et al. (2008) have tentative assignments of the bending (deformation) modes of the SiO_4 tetrahedra in this spectral region. According to Nakamoto (2009), ν_2 (SiO_4) and ν_4 (SiO_4) are bending modes and they exhibit at the following values: $\nu_2 - 340 \text{ cm}^{-1}$ and $\nu_4 - 527 \text{ cm}^{-1}$. This tentative assignment is uncertain for several reasons, one of them being the large number of vibrational units and interlinking of the SiO_4 tetrahedra. The possibility that some bands may be mixed and appear as a result of overlapping modes is taken into account.

According to Bard et al. (1997), Klopogge et al. (2001), Shurvell et al. (2001), Rinaudo et al. (2004) and Petry et al. (2006), the bands situated below 625 cm^{-1} may be ascribed to the bending (deformation) modes of the double chain silicate and vibrations involving cations in the various *M* sites.

Klopogge et al. (2001) assign some spectral bands in this region (below 625 cm^{-1} ; more precisely around 302, 534, 587 and 612 cm^{-1}) to the OH⁻ group (OH⁻ libration/rotation and OH⁻ translation); Rinaudo et al. (2004) ascribe the bands between 200-300 cm^{-1} to the O-H-O group (where O are the apical oxygen of the SiO_4 tetrahedra and H is the hydrogen of the OH group). This assignment is based on the fact that in the Raman spectra of minerals containing OH⁻ in the tetrahedral rings (phyllosilicates, in particular) the vibrations mentioned above are present (Rinaudo et al., 2004). Shurvell et al. (2001) and Huang (2003) ascribe the bands between 200 and 300 cm^{-1} to lattice vibration. Makreski et al. (2006) are more specific and assign the bands between 300-420 cm^{-1} to T(M-OH) – where T represents the translational mode; M = Mg or Fe, and the 420-610 cm^{-1} spectral region to the deformation (bending) mode of the Si-O-Si or δ (Si-O-Si).

The 625-1130 cm^{-1} spectral region (internal vibrations) is easy to understand. The types of bonds that are involved in the internal vibration of the $\text{Si}_4\text{O}_{11}^\infty$ ribbons are illustrated in figure 1. In this figure, the double chains of silica tetrahedrons (SiO_4 ; T1 in the center and T2 on the side) are aligned along the *c*-axis, and the *a*-axis is perpendicular to the $\text{Si}_4\text{O}_{11}^\infty$ layer.

We took into account the state of bridging oxygen (O_b) or non-bridging oxygen (O_{nb}) if it is basal or apical. However, without taking into account the spatial orientation of each identity unit ($\text{Si}_4\text{O}_{11}^\infty$), there are four tetrahedra which have two Si- O_b -Si, four O-Si-O ($\text{O}_{\text{basal/nb}}\text{-Si-O}_b$, $\text{O}_{\text{basal/nb}}\text{-Si-O}_{\text{apical/nb}}$, $\text{O}_b\text{-Si-O}_{\text{apical/nb}}$ and $\text{O}_b\text{-Si-O}_b$) and two Si-O ($\text{Si-O}_{\text{basal/nb}}$ and $\text{Si-O}_{\text{apical/nb}}$) types of bonds. There are two bridges of Si- O_b -Si, because one of them is between T1-T2 and the other between T1-T1; these bridges are highlighted in green in figure 1. The $\text{O}_{\text{basal/nb}}\text{-Si-O}_b$ linkage is highlighted in purple, $\text{O}_{\text{basal/nb}}\text{-Si-O}_{\text{apical/nb}}$ in orange, $\text{O}_b\text{-Si-O}_{\text{apical/nb}}$ in cyan and $\text{O}_b\text{-Si-O}_b$ in yellow. The last two groups: Si- $\text{O}_{\text{basal/nb}}$ is highlighted in black and Si- $\text{O}_{\text{apical/nb}}$ in blue.

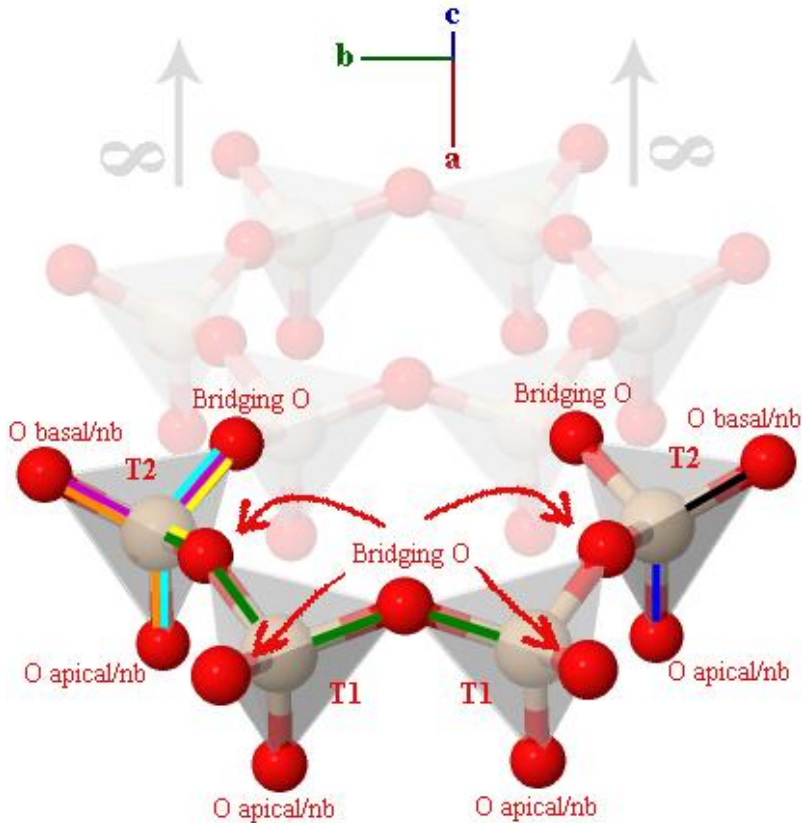


Fig. 1 Graphical representation of the types of bonds (represented by different colors) that are involved in the internal vibration of the amphiboles

This kind of interpretation assumes that bond types (a total of eight) can vibrate both symmetrically and asymmetrically (ν_s and ν_{as}). Therefore, theoretically, from the $Si_4O_{11}^{\infty}$ group 16 bands are expected to appear in the Raman spectra. These 16 bands are in good agreement with the number suggested by Kieffer (1980) and Andrut et al. (2000); however, these authors offer other assignments of these 16 bands (depending on the type of the bands/bridges/links between Si and $O_{b/nb}$).

According to Klopogge et al. (2001) and Rinaudo et al. (2004), four $Si-O_b-Si$ and four $O-Si-O$ antisymmetric (or asymmetric) stretching vibrations (ν_{as}) can be observed in amphiboles within the $950-1130\text{ cm}^{-1}$ range. Moreover, the vibrations between $1000-1130\text{ cm}^{-1}$ are ascribed to the asymmetric stretching vibrations (ν_{as}) of the $Si-O_b-Si$ bridges. Then, vibrations between $950-1000\text{ cm}^{-1}$ are assigned to the ν_{as} of $O-Si-O$ linkages. According to

the same authors, the bands in the 750-950 cm^{-1} region may be ascribed to the symmetric stretching modes (ν_s) of the O-Si-O linkages. The Raman bands in the 650-750 cm^{-1} spectral region are assigned to the symmetrical stretching vibration (ν_s) of the Si-O_b-Si bridges. We respect these assignments ($\nu_s < \nu_{as}$ - in terms of frequency), given that in many papers dealing with the Raman study of amphiboles (Kieffer, 1980; Klopogge et al., 2001; Rinaudo et al., 2004; Rinaudo et al., 2005; Makreski et al., 2006; Petry et al., 2006; Fornero et al., 2008) this is a basic rule. Apart from this, Nakamoto (2009) confirms this assignment of the asymmetric vibrations in the upper spectral region and of the symmetric vibrations below the asymmetric ones, $\nu_3 > \nu_1$ and $\nu_4 > \nu_2$ (MO_4^{2-} type compounds) where ν_1 and ν_2 are symmetric and ν_3 and ν_4 are asymmetric.

For our samples of amphiboles, the Raman spectra show one peak (in most cases, this band is very sharp) with a very high intensity; according to Klopogge et al. (2001); Rinaudo et al. (2004) and Fornero et al. (2008), this peak is assigned to the ν_1 (A_{1g}) – symmetrical stretching vibration of the Si-O_b-Si bridges (between 650-750 cm^{-1}).

Finally, the vibrational assignment of the OH⁻ group is an exception regarding the difficulty of the assignment of spectral bands.

According to some authors, the peaks of the spectral region ranging from 200-625 cm^{-1} may be assigned to the OH⁻ libration and translation. After other authors, the hydroxyl stretching region is between 3600-3700 cm^{-1} (Huang, 2003; Klopogge et al., 2001 and Su et al., 2009). Unfortunately, this region is not found in our spectral domain (210-3400 cm^{-1}). This is a disadvantage, as bands from the OH⁻ stretching region indicate a correlation between chemical and cation compositions (Su et al., 2009) or help us investigate the spectra obtained on two or more samples from the same series of amphiboles; for example, in the case of tremolite samples, Huang (2003) makes a correlation between Fe²⁺ and the number of bands in the region of the OH⁻ stretching modes – if the Fe²⁺ content increases, the Raman vibration mode shifts from one to three. Also, Jovanovski et al. (2009) make a similar correlation: depending on the presence and/or absence of Fe²⁺ in *M1* and *M3* sites, the number of bands (OH⁻ region) could range from one in tremolite up to four in ferro-actinolite samples. The existence of a center of inversion in all monoclinic amphiboles (the *C2/m* space group) precludes the coincidence of the OH⁻ stretching vibrations in the IR and Raman spectra of amphiboles.

According to Klopogge et al. (2001), the exact band positions (for Raman and IR spectra of holmquistite) are at slightly different frequencies (~2-3 cm^{-1}), and this is important because, thus, correlations between Raman and IR spectra can be made.

In order to render what is written above easier to understand, we suggest a schematic representation for all vibration assignment in all the Raman spectra of amphiboles (figs. 2 and 3).

As can be seen from figure 3, one band appears at 2325-2330 cm^{-1} (this band appears in a few samples of amphibole in the present paper, namely actinolite [2-1], pargasite [3-1; 3-2] and riebeckite [4-2]), and one band at ~2437 cm^{-1} (in the [4-2] riebeckite sample). The appearance of these bands is due to the substitution of K or Na with H₃O⁺ (K, Na ↔ H₃O⁺) and K or Na with NH₄⁺ (K, Na ↔ NH₄⁺); these spectral bands were also identified at potassium micas. Petry et al. (2006) assign the band at 2330 cm^{-1} to N₂. Koltashev et al.

(2009) also assign this band ($\sim 2330 \text{ cm}^{-1}$) to the fundamental vibration of molecular nitrogen N_2 .

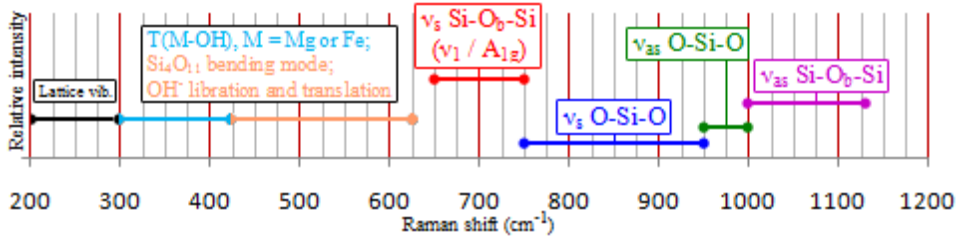


Fig. 2 Schematic representation for characteristic frequencies of amphibole minerals between 200-1200 cm^{-1} wavenumbers

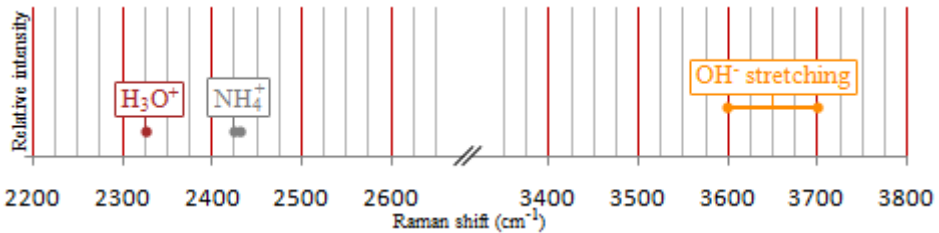


Fig. 3 Schematic representation for characteristic frequencies of amphibole minerals between 2200-3800 cm^{-1} wavenumbers

Analytical procedure and samples

The Raman spectra were obtained at room temperature with a Horiba Jobin-Yvon RPA-HE 532 Raman Spectrograph with multichannel air cooled (-70°C) CCD detector, using a wavenumber doubled frequency Nd-Yag laser (532 nm and 100 mW nominal power).

The spectral resolution was 3 cm^{-1} , and the spectral range – between 210 and 3400 cm^{-1} . The Raman system includes a “Superhead” optic fibre Raman probe for non-contact measurements, with an Olympus 50X LWD visible objective, $\text{NA} = 0.50$; $\text{WD} = 10.6 \text{ mm}$.

The data acquisition was performed in 1 - 100 s (in most cases, an acquisition time interval of 30-40 seconds was sufficient for identification), 20 – 100 aq, at a laser magnification of 90 – 100% pw, in order to improve the signal-to-noise ratio. Spectra manipulation consists in a basic data treatment, such as baseline adjustment and peak fitting (Lorentz function); however, in order to ensure a better interpretation, some spectra are raw.

Tab. 1 Classification, sample no., origin and ideal chemical formula of the samples used in the present study

No. ^a	Mineral	Sample no. ^b	Origin	Ideal chemistry
Mg-Fe-Mn-Li Amphiboles				
A. Cummingtonite – Grunerite series				
1-1	Grunerite	5848	Schneeberg, Tirol, Austria	$\square\text{Fe}^{2+}_7\text{Si}_8\text{O}_{22}(\text{OH})_2$
Calcic Amphiboles				
B. Tremolite – Ferro-actinolite series				
2-1	Actinolite	5834	St. Gothard, Switzerland	
2-2	Actinolite	5835	Tirol, Austria	
2-3	Actinolite	5836	Zemmtal, Tirol, Austria	
2-4	Nephrite	2098	Jordanów, Poland	$\text{Ca}_2(\text{Mg},\text{Fe}^{2+})_5\text{Si}_8\text{O}_{22}(\text{OH})_2$
2-5	Nephrite	5844	China	
2-6	Smaragdite	5852	Răsinari, Romania	
2-7	Uralite	5841	Brosso, Piedmont, Italy	
2-8	Tremolite	5825	Campolongo, Switzerland	$\square\text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$
2-9	Tremolite	5865	Voşlobeni, Romania	
C. Pargasite – Hastingsite series				
3-1	Pargasite	5851	Edenville, New York, USA	$\text{NaCa}_2(\text{Mg}_4\text{Al})(\text{Si}_6\text{Al}_2)\text{O}_{22}(\text{OH})_2$
3-2	Pargasite	3985	Czech Republic	
Sodic Amphiboles				
D. Glaucofane – Riebeckite series				
4-1	Glaucofane	1623	Sesia, West Alps, Italy	$\square\text{Na}_2(\text{Mg}_3\text{Al}_2)\text{Si}_8\text{O}_{22}(\text{OH})_2$
4-2	Riebeckite	5807	Iacobdeal, Dobrogea	$\square\text{Na}_2(\text{Fe}^{2+}_3\text{Fe}^{3+}_2)\text{Si}_8\text{O}_{22}(\text{OH})_2$

^aNumber of the sample used in the present study (figures); ^bSample number from the „Grigore Cobălcescu” Mineralogy and Petrography Museum.

The samples used in the study are listed in table 1. In most cases, qualitative identification of the amphibole species can be done easily on the basis of their characteristic Raman modes. In recent years, however, most papers on the Raman study of amphiboles contain chemical analyses. These additional analyses are very important for the Raman spectroscopic study of solid solution series of the amphibole classification. Nevertheless, Raman spectroscopy is a powerful tool for mineral characterization. The structure of these amphiboles belongs to the $C2/m$ space group. In the present paper, we describe the Raman

spectra obtained from 14 amphibole samples and prove that Raman spectroscopy can be used for the identification of the amphibole minerals without chemical analysis being performed prior to Raman study. These samples belong to the collection of the “Grigore Cobălcescu” Mineralogy and Petrography Museum of the “Alexandru Ioan Cuza” University of Iasi.

Results and discussion

Given the fact that the samples were analyzed without having their chemical analysis, some spectra of this work are compared with reference Raman spectra (from the RRUFF website project; Downs, 2006), performed on the samples that were confirmed by X-ray diffraction and chemical analysis.

All spectra are between 210 and 1200 cm^{-1} , given the fact that, with some exceptions, there are no spectral lines beyond this limit (1200 cm^{-1}). These exceptions are included above principal spectral lines (see figs. 5, 7, 8 and 10b). Also, some spectral intervals/regions are enlarged/compressed (⤴ sign/⤵ sign) over these spectral lines (at the top of figures – not all, however) for a better understanding/investigation of the low/high-intensity peaks.

A. Cumingtonite – Grunerite series

1.1 Grunerite

Prior to any discussions about the Raman spectra of the grunerite samples, it should be noted that in some papers the term grunerite is replaced with amosite (the commercial name for grunerite).

A comparison between the Raman spectra of the grunerite sample (1-1) and two reference samples of grunerite from the RRUFF project (R070186 and R060062) is illustrated in figure 4.

For each grunerite spectrum, the peaks are listed in table 2 with all assignments. These spectra are very similar – the ν_1 (A_{1g}) symmetric stretching (ν_s) of the Si-O_b-Si bridge is shown in all spectra (fig. 4) around 660 cm^{-1} , more exactly at 665 cm^{-1} for the grunerite samples of this work and at 663 cm^{-1} and 661 cm^{-1} , respectively, for reference spectra (R070186 and R060062). In the 745-790 cm^{-1} spectral region, three bands are shown in the grunerite sample, with the main band at 761 cm^{-1} (the other two peaks are located at 747 cm^{-1} and 785 cm^{-1} , respectively). These bands are assigned to the symmetric stretching (ν_s) of the O-Si-O linkage. Also, the 909 cm^{-1} spectral band is assigned to the ν_s of the O-Si-O linkage (all of these bands assigned to the ν_s of the O-Si-O linkage have a low intensity).

The bands situated in the upper region of the 950 cm^{-1} wavenumber (950-1200 cm^{-1}) are assigned to antisymmetric (or asymmetric) stretching vibration (ν_{as}). More specifically, the band at 971 cm^{-1} may be assigned to the ν_{as} of the O-Si-O linkage. We consider that the peak at 999 cm^{-1} is part of the 1027 cm^{-1} vibration (due to the fact that, in the reference spectra of Bard et al. (1997) and Rinaudo et al. (2004), this peak is slightly overlapped), which, together with the peak at 1098 cm^{-1} , is assigned to ν_{as} Si-O_b-Si bridges. The overlapping of the 999 cm^{-1} peak can be seen even in figure 4 (in the case of R060062).

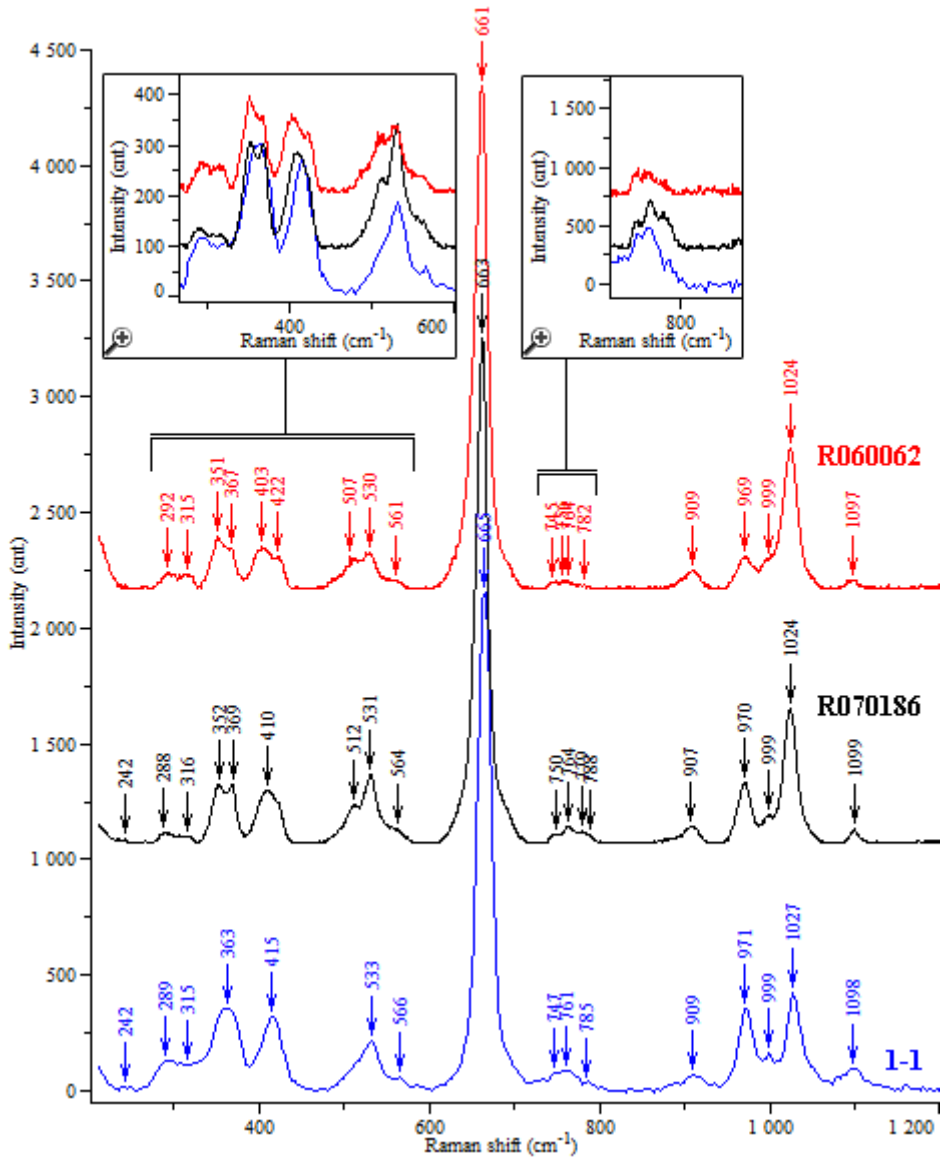


Fig. 4 Raman spectra of the grunerite sample (1-1), in comparison with grunerite reference (R070186 and R060062) spectra from RRUFF project

Tab. 2 Wavenumbers and assignments for the Raman spectra of the grunerite sample (1-1) in the 210-1200 cm^{-1} spectral region

Present study (cm^{-1})		Reference (cm^{-1})		Tentative assignment
Sample no.	Downs (2006)	Rinaudo et al. (2004)		
5848 (1-1)	R070186	amosite fibres		
-	-	155, 182	?	
242, 289	242, 288, 316	252, 289, 307		lattice mode
315				? Fe^{2+} -O
363	352, 369	348, 368		Fe^{2+} -O
415	410	400, 423		
533, 566	512, 531, 564	507, 528		deformation modes of Si_4O_{11}
665	663	659		ν_s of the Si-O_b-Si (ν_1)
747, 761,	750, 764,			ν_s of the O-Si-O
785	779, 788	-		
909	907	904		
971	970	968		ν_{as} of the O-Si-O
999, 1027	999, 1024	1020		ν_{as} of the Si-O _b -Si
1098	1099	1093		

? – questionable interpretation; ν_s – symmetric stretching; ν_{as} – asymmetric stretching.

Below 625 cm^{-1} , the wavenumber exhibits three main bands and other bands that can be considered part of the main bands. As we have discussed in the *Raman modes of amphiboles* part and according to Rinaudo et al. (2004), the bands between $210\text{-}300 \text{ cm}^{-1}$ are assigned to the O-H-O groups or, if we respect the assignments of Shurvell et al. (2001) and Huang (2003), this region may be ascribed to lattice vibration – both are questionable, but the second assignment is more plausible. Therefore, the peaks at 242 cm^{-1} and 289 cm^{-1} belong to the O-H-O group or the lattice mode. Not the same thing can be said about the peak at 315 cm^{-1} (despite the first impression), because it is more of a part of M-O vibrations. However, this assignment (of the 315 cm^{-1} peak) remains controversial if we look at the spectra compared with the 1-1 grunerite sample; another reason is the very low intensity.

If we take a look at the ideal chemical formula of grunerite ($\square\text{Fe}^{2+}_7\text{Si}_8\text{O}_{22}(\text{OH})_2$), just Fe^{2+} is involved in the external vibrations (M^{2+} -O); consequently, the bands situated at 363 cm^{-1} and 415 cm^{-1} may be ascribed to the Fe^{2+} -O vibration mode.

The spectrum of grunerite also presents two bands at 533 cm^{-1} and 566 cm^{-1} , respectively, which may be assigned to the deformation mode of the silicate chain. According to Klopogge et al. (2001), the libration and translation modes of OH^- lie in the same spectral region, are probably overlapped or the very low intensity peak at 566 cm^{-1} may be assigned to the librational or translational mode of the OH^- group – this assignment is, however, uncertain.

B. Tremolite – Ferro-actinolite series

2.1 Actinolite

Actinolite is a solid solution composition between the endmembers of the following series: tremolite and ferro-actinolite. According to Jovanovski et al. (2009), solutions with more than 90 Mg are called tremolite, between 90-50% - actinolite, and less than 50% - ferro-actinolite. We will discuss the Raman spectra of these minerals separately.

The Raman spectra of these samples are shown in figure 5. All of these spectra are very similar, with small differences in the case of very low intensity peaks. In the 650-1200 cm^{-1} spectral region (the region of internal vibrations), five intense bands appear significantly at 670, 745, 928, 1027 and 1056 cm^{-1} for the 2-1 sample; 670, 744, 929, 1027 and 1059 cm^{-1} for 2-2, and 670, 744, 928, 1027, 1059 cm^{-1} for the 2-3 actinolite sample. In the case of the 928 cm^{-1} peak (for 2-2 samples this peak exhibits at 929 cm^{-1}), one or two overlapped bands with a very low intensity appear. These peaks (891, 956 cm^{-1} ; 892, 949 cm^{-1} and 946 cm^{-1} , respectively – see fig. 5) are part of O-Si-O symmetric stretching vibrations (ν_s). As discussed in the case of grunerite, the bands at 1027, 1056 cm^{-1} (2-1); 1027, 1059 cm^{-1} (2-2) and 1027, 1059 cm^{-1} (2-3), respectively, may be ascribed to the antisymmetric stretching vibrations (ν_{as}) of the Si-O_b-Si bridges; the bands at 744-745 cm^{-1} are debatable, given the fact that 750 cm^{-1} is the limit of ν_s O-Si-O and ν_s Si-O_b-Si vibrations. The most intense bands, which appear at 670 cm^{-1} (in all samples), are ascribed to the ν_1 (Ag) symmetric stretching modes (ν_s) of the Si-O_b-Si bridges.

In the 210-650 cm^{-1} region, the assignments of the M-O vibrations is problematic; three bands appear in the 300-450 cm^{-1} spectral region (for 2-1: 369, 389 and 413 cm^{-1} ; 2-2: 369, 392 and 415 cm^{-1} , and 369, 392 and 415 cm^{-1} for 2-3), where we would expect to see vibrations produced by Ca, Mg and/or Fe²⁺ cations [$\text{Ca}_2(\text{Mg,Fe}^{2+})_5\text{Si}_8\text{O}_{22}(\text{OH})_2$ – ideal chemistry for actinolite]. Nevertheless, the bands between 210-300 cm^{-1} are assigned to lattice modes (for 2-1: 221, 247 and 292 cm^{-1} , for 2-2: 226, 247, 294 cm^{-1} , and 222 and 292 cm^{-1} for 2-3).

The following bands: 479, 523 and 573 cm^{-1} (for 2-1); 482, 522 and 577 cm^{-1} (2-2), and 484, 522 and 581 cm^{-1} (2-3) correspond to the deformation modes of Si₄O₁₁, with the observation that in this region there should be a librational and translational vibration of the OH⁻ group (probably 573, 577 and 581 cm^{-1} bands; see fig. 5).

The Raman spectrum of the sample of actinolite (2-1) shows one peak at 2327 cm^{-1} ; this band may be assigned to the H₃O⁺ vibration. This is due to a substitution between H₃O⁺ and a cation from the M sites.

2.2 Nephrite, Cr – actinolite (smaragdite) and uralite (var. of actinolite)

Figure 6 shows the Raman spectra of two samples of nephrite minerals, one sample of smaragdite and, finally, one of uralite (with a spectrum of quartz, see further discussion). All these samples are varieties of actinolite; in general, discussions regarding the vibrations and assignments of samples of these varieties are the same with discussions regarding actinolite.

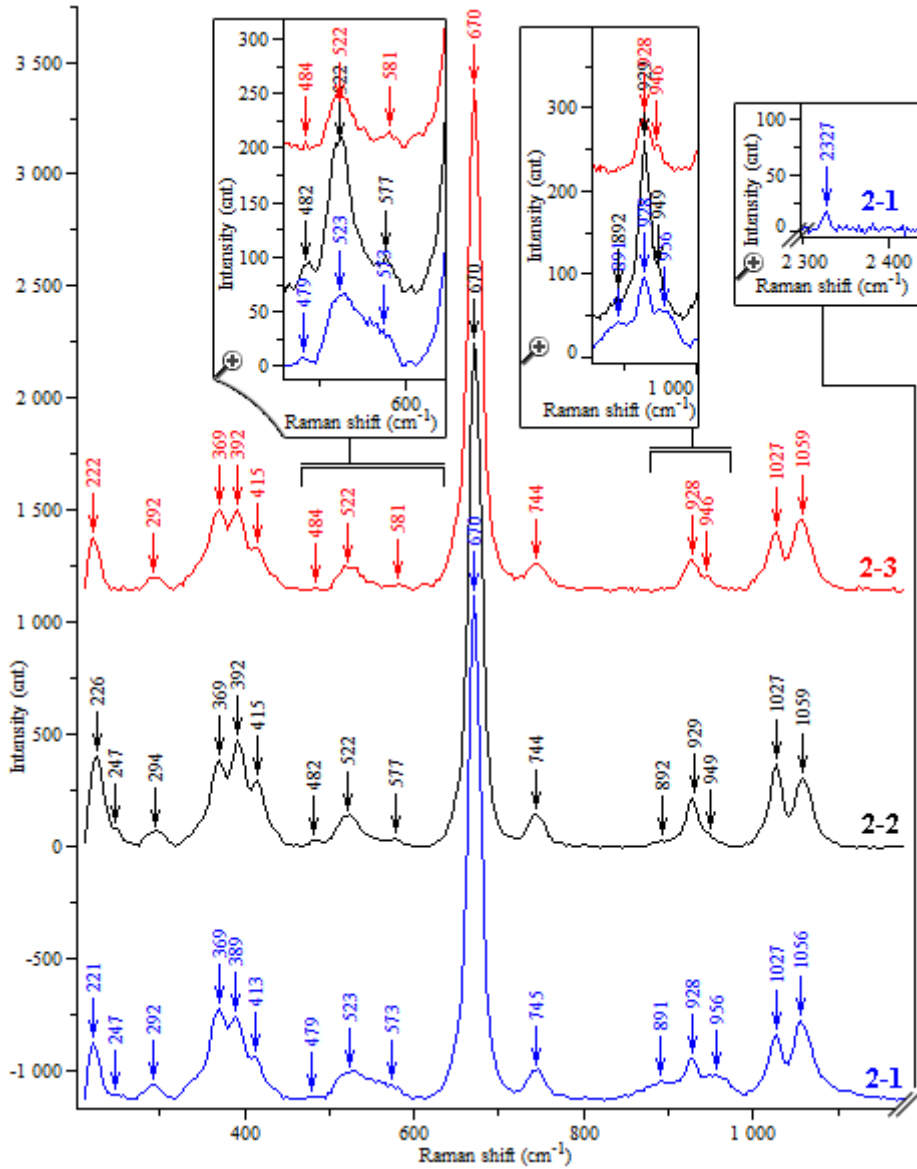


Fig. 5 Raman spectra of three samples of actinolite 2-1, 2-2, 2-3

Tab. 3 Wavenumbers and assignments for the Raman spectra of actinolite samples (2-1, 2-2 and 2-3) in the 210-1200 cm^{-1} spectral region

Present study (cm^{-1})			Reference (cm^{-1})		Tentative assignment
Sample no.			Shurvell et al. (2001)	Huang (2003)	
5834 (2-1)	5835 (2-2)	5836 (2-3)		#Mg 89.9	
221, 247, 292	226, 247, 294	222, 292	-	222, 231, 249, 263, 303	lattice mode
369	369	369	350, 369	348, 371	
389	392	392	392	393	M-O, where M = Ca and Mg, Fe^{2+}
413	415	415	415, 436	415, 434	
479, 523, 573	482, 522, 577	484, 522, 581	513, 532	529	deformation modes of Si_4O_{11}
670	670	670	673	673	ν_s of the Si-O_b-Si (ν_1)
745	744	744	740	-	? ν_s of the Si-O _b -Si
891, 928,	892, 929, 949	928, 946	749, 930, 947	749, 929, 947	ν_s of the O-Si-O
956					? ν_s of the O-Si-O
1027	1027	1027	1029	1027	
1056	1059	1059	1058	1057	ν_{as} of the Si-O _b -Si
2327	-	-	-	-	$\nu\text{H}_3\text{O}^+$

? – questionable interpretation; ν_s – symmetric stretching; ν_{as} – asymmetric stretching; Mg#=(Mg/Mg+ Fe^{2+}).

The wavenumbers of 2-4 and 2-5 (nephrite samples) are found in column 1 and 2 of table 4. The third and fourth columns of table 4 contain the wavenumbers reported in the literature (Shurvell et al., 2001; Huang, 2003). The Raman spectra of nephrite samples, like those of actinolite, are dominated by a very strong sharp band at 674 cm^{-1} ; these bands are assigned to the symmetric stretching (ν_s) of Si-O_b-Si bridges. The bands between 745-747 cm^{-1} are difficult to assign (see discussion of actinolite). Nevertheless, we consider these bands tentative assignments of Si-O_b-Si bridges (also, this assignment is valid for samples of smaragdite and uralite). The main peak of this region – 928 cm^{-1} (around 920-950 cm^{-1}) and one overlapped – 946 cm^{-1} (these values are identical in both spectra) may be ascribed to the ν_s (symmetric stretching) of the O-Si-O linkage. The asymmetric stretching region of the O-Si-O linkage (950-1000 cm^{-1}) shows (at least for sample 2-4) a peak with a very low intensity. In the case of the 1027 cm^{-1} peak and 1059 cm^{-1} highest peak (in comparison with the 1027 cm^{-1} one; in both spectra of nephrite samples), they may be ascribed to the ν_{as} (asymmetric stretching) of the Si-O_b-Si bridges.

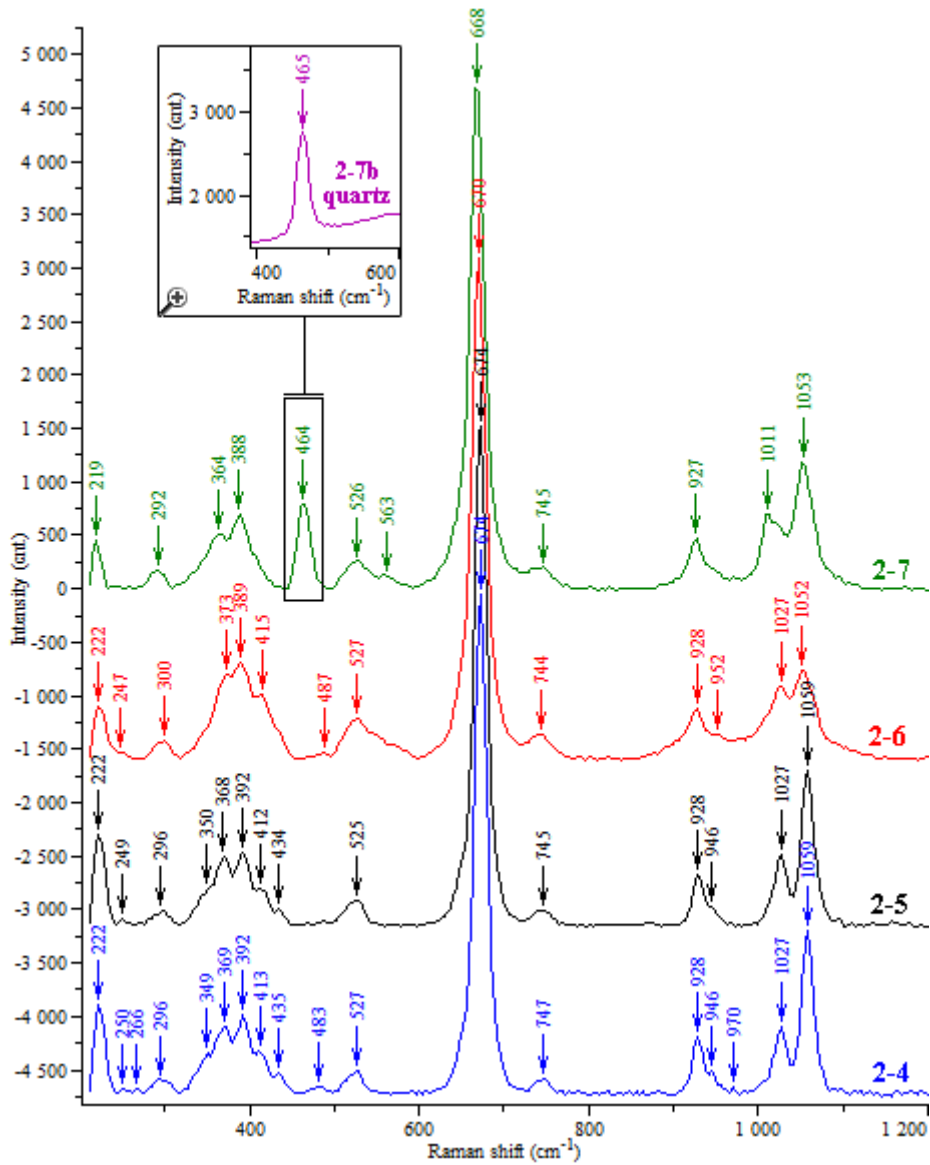


Fig. 6 Raman spectra of two samples of nephrite (2-4 and 2-5), one of smaragdite (2-6) and one of uraltite (2-7); at the top of this figure there is a spectrum of quartz (2-7b) enlarged in the 400-600 cm^{-1} spectral region

Tab. 4 Wavenumbers and assignments for the Raman spectra of nephrite samples (2-4 and 2-5) in the 210-1200 cm^{-1} spectral region

Present study (cm^{-1})		Reference (cm^{-1})		Tentative assignment
Sample no.		Shurvell et al. (2001)	Huang (2003)	
2098 (2-4)	5844 (2-5)		#Mg 90	
222, 250, 266,	222, 249,	225, 232,	222, 230, 248,	lattice mode
296	296	249, 301	286, 301	
349	350	351	350	
369	368	370	368	
392	392	393	392	M-O, where M = Ca and Mg, Fe^{2+}
413	412	415	414	
435	434	436	435	
483, 527	525	516, 529	528	deformation modes of Si_4O_{11}
674	674	673	653, 673	ν_s of the Si-O _b -Si (ν_t)
747	745	747	738, 748	? ν_s of the Si-O _b -Si
928, 946	928, 946	868, 931, 947	929, 946	ν_s of the O-Si-O
970	-	-	-	? ν_{as} of the O-Si-O
1027, 1059	1027, 1059	1029, 1059	1028, 1057	ν_{as} of the Si-O _b -Si
-	-	1114	-	
-	-	1140	-	

? – questionable interpretation; ν_s – symmetric stretching; ν_{as} – asymmetric stretching; $\text{Mg}\#=(\text{Mg}/\text{Mg}+\text{Fe}^{2+})$.

In the external vibration region, a group of five peaks (for 2-4: 349, 369, 392, 413, 435 cm^{-1} and for 2-5: 350, 368, 392, 412, 434 cm^{-1}) centred on a band at 392 cm^{-1} (in both spectra of nephrite samples) are shown in the spectral domain assigned to M-O vibration. Shurvell et al. (2001) state that these Raman bands are characteristic for nephrite, in comparison with the jadeite mineral. The peaks between 210-300 cm^{-1} may be ascribed to lattice modes. For 2-4, two bands, namely at 483 cm^{-1} (low intensity) and 527 cm^{-1} , respectively, may be assigned to the deformation mode of the Si_4O_{11} group. In another sample of nephrite (2-5), only one peak appears, at 525 cm^{-1} , which is assigned to the same deformation mode of the Si_4O_{11} group.

The Raman spectrum of smaragdite (2-6) is slightly different from those recorded on samples of actinolite (the same thing may be said about the Raman spectrum of the uralite sample, but this will be discussed separately). The wavenumbers and assignments of smaragdite and uralite samples (quartz included) are found in table 5 in comparison with (2-2) actinolite, in order to emphasize small differences between them.

The intense band (ν_1) of the smaragdite spectrum corresponds to the symmetric stretching of Si-O_b-Si bridges at 670 cm⁻¹. The differences mentioned above consist in two regions with slightly moved peaks, as follows: in the region of asymmetric stretching of Si-O_b-Si (1000-1130 cm⁻¹), two peaks appear (1027 cm⁻¹ and 1052 cm⁻¹), the second peak being slightly shifted to the left in comparison with 2-2 (see figs. 5 and 6); the second difference lies in the region of M-O vibrations, where the highest intensity peak is located at 389 cm⁻¹. The other peaks are very similar to peaks observed in actinolite samples (see table 5 for the assignments of all peaks).

The Raman spectrum of uralite is a special case, as one band at 464 cm⁻¹ is from quartz. It should be noted that the sample of uralite contains some crystals of quartz, this being the reason of the presence of the 464 cm⁻¹ band. The spectrum of the quartz sample is labelled with 2-7b. As smaragdite spectrum, small differences appear in two regions, namely around 1010 cm⁻¹ and in M-O region (see table 5). It should be pointed out that no Raman data have been found in the literature for these minerals species (smaragdite and uralite).

In the case of nephrite samples, in Shurvell et al. (2001) there are two bands in the spectrum of nephrite, at 1114 cm⁻¹ and 1140 cm⁻¹, respectively, which are assigned to OH⁻ bending modes. In our samples (2-4 and 2-5), however, these bands do not appear (see fig. 6).

Tab. 5 Wavenumbers and assignments for the Raman spectra of smaragdite (2-6) and uralite (2-7) samples, compared with an actinolite sample (2-2) in the 210-1200 cm⁻¹ spectral region

Present study (cm ⁻¹)			Tentative assignment
Sample no.			
5852 (2-6)	5841 (2-7)	5835 (2-2)	
222, 247, 300	219, 292	226, 247, 294	lattice mode
373	364	369	
389	388	392	M-O, where M = Ca and Mg, Fe ²⁺
415	-	415	
-	464	-	from quartz
487, 527	526	482, 522, 577	deformation modes of Si ₄ O ₁₁
670	668	670	ν_s of the Si-O_b-Si (ν_1)
744	745	744	? ν_s of the Si-O _b -Si
928, 952	927	892, 929, 949	ν_s of the O-Si-O
1027	1011	1027	
1052	1053	1059	ν_{as} of the Si-O _b -Si

? – questionable interpretation; ν_s – symmetric stretching; ν_{as} – asymmetric stretching.

2.3 Tremolite

The vibrational assignments of the peaks are given in table 6, while the Raman spectra for the tremolite samples are shown in figure 7. Above the tremolite spectra there is the calcite spectrum (2-8b) obtained from the 2-8 sample. Both spectra of tremolite show the ν_1

symmetric stretching of the CO₃ group at 1083 cm⁻¹; also, the 711 cm⁻¹ peak is assigned to the v₄ bending mode of the CO₃ group (Buzgar and Apopei, 2009). The v₄ bending mode of the CO₃ group is present only in the 2-9 spectrum of the tremolite sample (with a very low intensity). According to Buzgar et al. (2009), the 285 cm⁻¹ band may be ascribed to the vibration (translational vibration) between cation and oxygen (M-O) of the CO₃ group [T(Ca, CO₃)]; this peak (285 cm⁻¹) is present in the same spectrum of tremolite (2-9) with the v₄ bending mode of the CO₃ group. These characteristic bands of calcite (CaCO₃) are normal because our tremolite is associated with calcite (in carbonate rocks).

Tab. 6 Wavenumbers and assignments for the Raman spectra of tremolite samples (2-8 and 2-9) in the 210-1200 cm⁻¹ spectral region and values of the calcite spectrum (2-8b) obtained from the 2-8 sample

Present study (cm ⁻¹)		Reference (cm ⁻¹)		Tentative assignment
Sample no.		Huang (2003)	Shurvell et al. (2001)	
5825 (2-8)	5865 (2-9)	#Mg 93.8		
225, 252, 290	226, 250	221, 230, 250, 288	304	lattice mode
-	285	-	-	T(Ca, CO ₃) (<i>calcite inclusions</i>)
351	349	332, 343	352	
372	369	368	374	
394	394	393	395	M-O, where M = Ca and Mg
415	415	415	417	
438	438	434	437	
483, 528	484, 525	523	516, 530	deformation modes of Si ₄ O ₁₁
-	583	-	-	? HO ⁻ libration/translation
674	674	653, 672	656, 675	v_s of the Si-O_b-Si (v₁)
-	711	-	-	v ₄ bending mode of the CO ₃ group (<i>calcite inclusions</i>)
746	747	739, 749	747	? v _s of the Si-O _b -Si
928, 949	928, 945	929, 945	932, 947	v _s of the O-Si-O
1028, 1060	1027, 1059	1027, 1057	1031, 1061	v _{as} of the Si-O _b -Si
1087	1083	-	-	v ₁ symmetric stretching of the CO ₃ group (<i>calcite inclusions</i>)
-	-	-	1112	

? – questionable interpretation; v_s – symmetric stretching; v_{as} – asymmetric stretching; Mg#=(Mg/Mg+Fe²⁺).

The discussion regarding the 1112 cm⁻¹ peak, which appears in the reference spectrum of tremolite samples (Shurvell et al., 2001), is similar to that of nephrite samples. In the spectrum of Shurvell et al. (2001), however, this peak (extremely weak intensity) appears and is assigned to the OH⁻ bending modes.

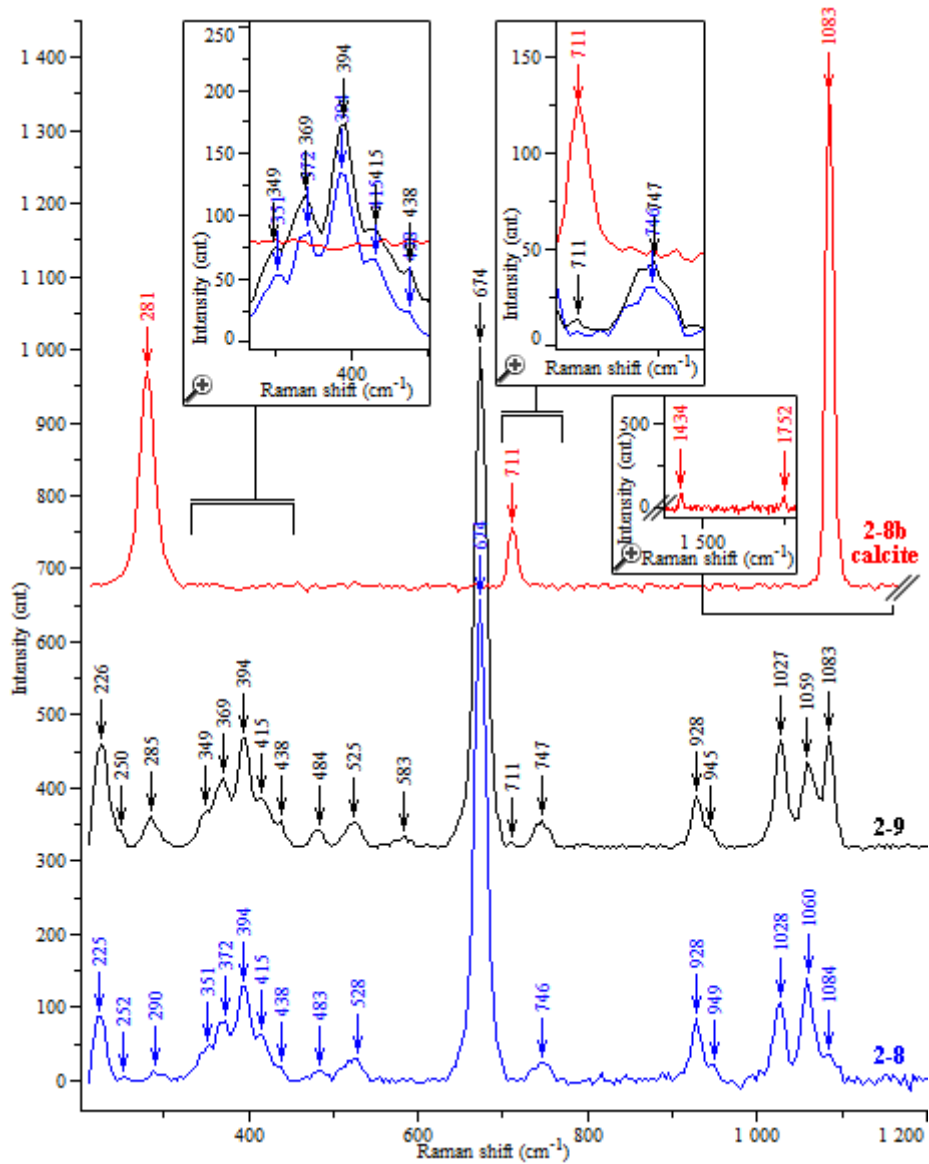


Fig. 7 Raman spectra of two samples of tremolite (2-8 and 2-9) and calcite (2-8b)

Both spectra of tremolite samples contain a very strong band at 674 cm^{-1} , which lies in the same spectral region as the symmetric stretching (ν_s) of the Si-O_b-Si bridges. The 746 cm^{-1} (2-8) and 747 cm^{-1} (2-9) bands are debatable (see previous discussions); nevertheless, we assign these bands to the ν_s of the Si-O_b-Si bridges. In the region between 900 and 1100 cm^{-1} , two symmetric stretching modes of the O-Si-O linkage and two asymmetric stretching vibration modes of the Si-O_b-Si bridges are exhibited.

The lower wavenumber region ($<600\text{ cm}^{-1}$) is characteristic for the deformation mode of the silicate network with OH⁻ libration/translation (in most cases - overlapped) modes (in the case of the 2-9 sample of tremolite, the 583 cm^{-1} band is probably a vibration of the OH⁻ libration/translation mode), metal-oxygen modes ($300\text{-}450\text{ cm}^{-1}$) and lattice modes ($210\text{-}300\text{ cm}^{-1}$).

Bearing in mind the Raman spectra of actinolite samples (fig. 5) and the Raman spectra of tremolite, it is very important to note the differences between these members of this series. Without chemical analysis, the OH⁻ spectral region and/or IR spectra of these minerals, it is very difficult to differentiate between members of a series. Nevertheless, some differences between tremolite and actinolite spectra could be observed. As has been discussed above, the presence of CaCO₃ in tremolite spectra may be one reason for the difference between actinolite and tremolite spectra. Another explanation for the similarity between the spectra of actinolite and tremolite lies in the fact that the #Mg content of both minerals is somewhere up to of 90%.

C. Pargasite – Hastingsite series

3.1 Pargasite

A comparison between the Raman spectra of the pargasite samples (3-1, 3-2 and 3-2) and one reference sample of pargasite from the RRUFF project (R060632) is illustrated in figure 8. As has been discussed in the *Analytical procedure* section, some spectra are raw for a better interpretation, and these particular spectra are some of them. Also, the Raman spectra of these samples were very difficult to obtain. Table 7 summarizes the entire discussion about the assignments of the peaks.

The ν_s (ν_1) of the Si-O_b-Si lies at 663 , 667 , 663 and 665 cm^{-1} (for 3-1; 3-2; 3-2 and R060632, respectively). In our spectra, a very broad band exhibits at $758\text{-}766\text{ cm}^{-1}$, while in the case of R060632 two bands appear at 750 and 801 cm^{-1} . If we look carefully at the highest peak (assigned to ν_1), on the right it exhibits a one shoulder band (around $692\text{-}695\text{ cm}^{-1}$), which appears in all spectra of pargasite and may be due to 2Al in the *T* site. The high intensity of the band at $\sim 760\text{ cm}^{-1}$ can also be explained by 2Al in the *T* site or the orientation of the laser beam on the pargasite samples.

The interpretation of the spectra in the $850\text{-}1200\text{ cm}^{-1}$ is generally based on the bands dominantly arising from the vibrations of symmetric stretching and asymmetric stretching (Si₄O₁₁), as follows: the bands between 885 and 928 cm^{-1} may be ascribed to the symmetric stretching (ν_s) of the O-Si-O linkage; the peaks observed in the $950\text{-}1000\text{ cm}^{-1}$ region are attributed to the asymmetric stretching (ν_{as}) of the O-Si-O linkage. The highest-frequency bands, observed in $1000\text{-}1100\text{ cm}^{-1}$ spectral region, may be ascribed to the asymmetric stretching vibration of the Si-O_b-Si bridges.

All three spectra of pargasite samples (3-1 and 3-2; 3-2) present one peak at ~ 2330 cm^{-1} , which may be assigned to H_3O^+ vibrations; the appearance of this band is due to the substitution of K or Na with H_3O^+ ($\text{K, Na} \leftrightarrow \text{H}_3\text{O}^+$).

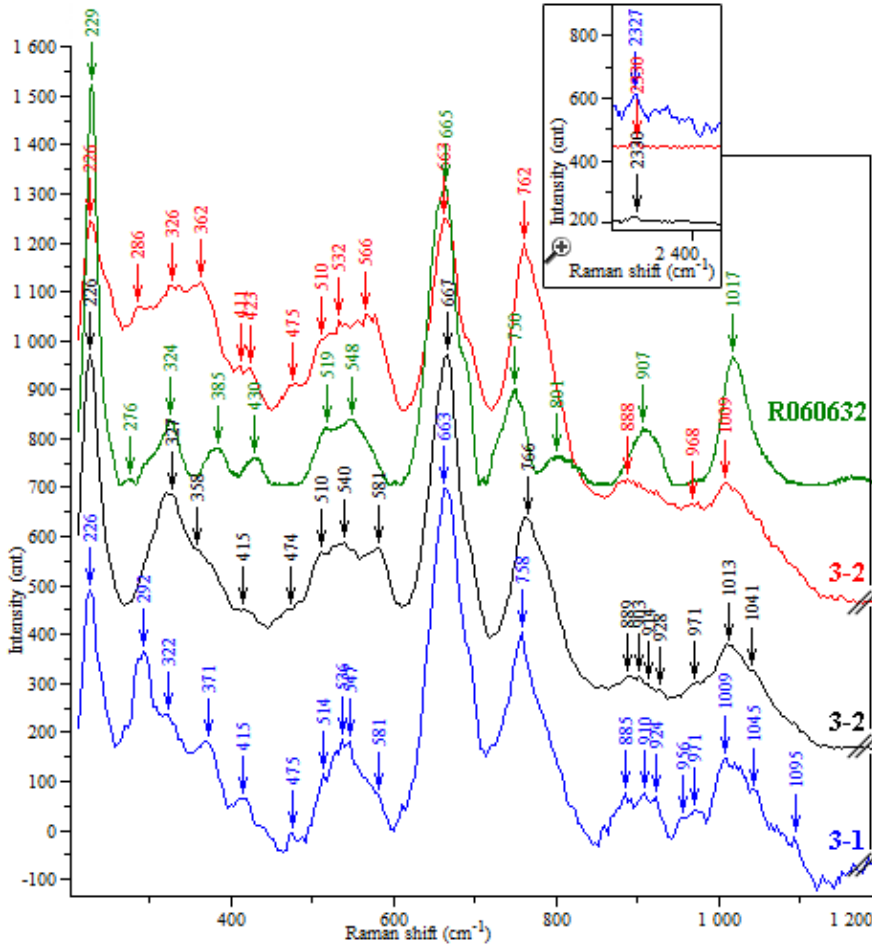


Fig. 8 Raman spectra of two samples of pargasite (3-1 and 3-2; 3-2) and reference (R060632) spectra from RRUFF project

A. Glaucophane – Riebeckite series

4.1 Glaucophane

A comparison between the Raman spectra of glaucophane samples (three recorded spectra at different parameters) and one reference spectrum from the RRUFF project is

illustrated in figure 9. The minor discrepancies concern the shifted peaks in our spectra at: 1011 cm^{-1} , 1014 cm^{-1} and 1010 cm^{-1} , respectively (for 4-1, 4-1 and 4-1), while in the glaucophane reference spectrum the band exhibits at 984 cm^{-1} . The interpretation of the spectra in the 200-650 cm^{-1} region is generally based on the bands dominantly arising from the vibrations of the M-O (cation-oxygen; between 300 and 450 cm^{-1}) and bending vibrations of the main Si_4O_{11} structural unit (between 450 and 615 cm^{-1}).

Tab. 7 Wavenumbers and assignments for the Raman spectra of pargasite samples (3-1; 3-2 and 3-2) in the 210-1200 cm^{-1} spectral region

Present study (cm^{-1})			Reference (cm^{-1})		Tentative assignment
Sample no.			Huang (2003)	Downs (2006)	
5851 (3-1)	3985 (3-2)	3985 (3-2)	#Mg 38.5	R060632	
226, 292	226	226, 286	200, 271	229, 276	lattice mode
322	327	326	-	324	
371	358	362	364	385	M-O, where M = Ca and Mg
415	415	414, 423	420	430	
475, 514, 536, 547, 581	474, 510, 540, 581	475, 510, 532, 566	549	519, 548	deformation modes of Si_4O_{11}
663	667	663	669	665	ν_s of the Si-O_b-Si (ν_1)
758	766	762	719, 772	750	? ν_s of the Si-O _b -Si
885, 910, 924	889, 903, 914, 928	888	920	907	ν_s of the O-Si-O
956, 971	971	968	995	-	ν_{as} of the O-Si-O
1009, 1045, 1095	1013, 1041	1009	1020, 1094	1017	ν_{as} of the Si-O _b -Si
2327	2330	2330	-	-	$\nu\text{H}_3\text{O}^+$

? – questionable interpretation; ν_s – symmetric stretching; ν_{as} – asymmetric stretching; Mg#=(Mg/Mg+Fe²⁺).

The dominant peak (385-388 cm^{-1}) of the lower spectral region is characteristic to glaucophane Raman spectra; if we look carefully, this band has a shoulder peak at 409-410 cm^{-1} (in our spectra and in reference R050333). The bands below 300 cm^{-1} may be assigned to the lattice mode. The highest-frequency peak, observed in the Raman spectra of glaucophane samples at 670 cm^{-1} , also present in the reference spectra at 669 cm^{-1} , is attributed to the symmetric stretching (ν_1) of the Si-O_b-Si bridges.

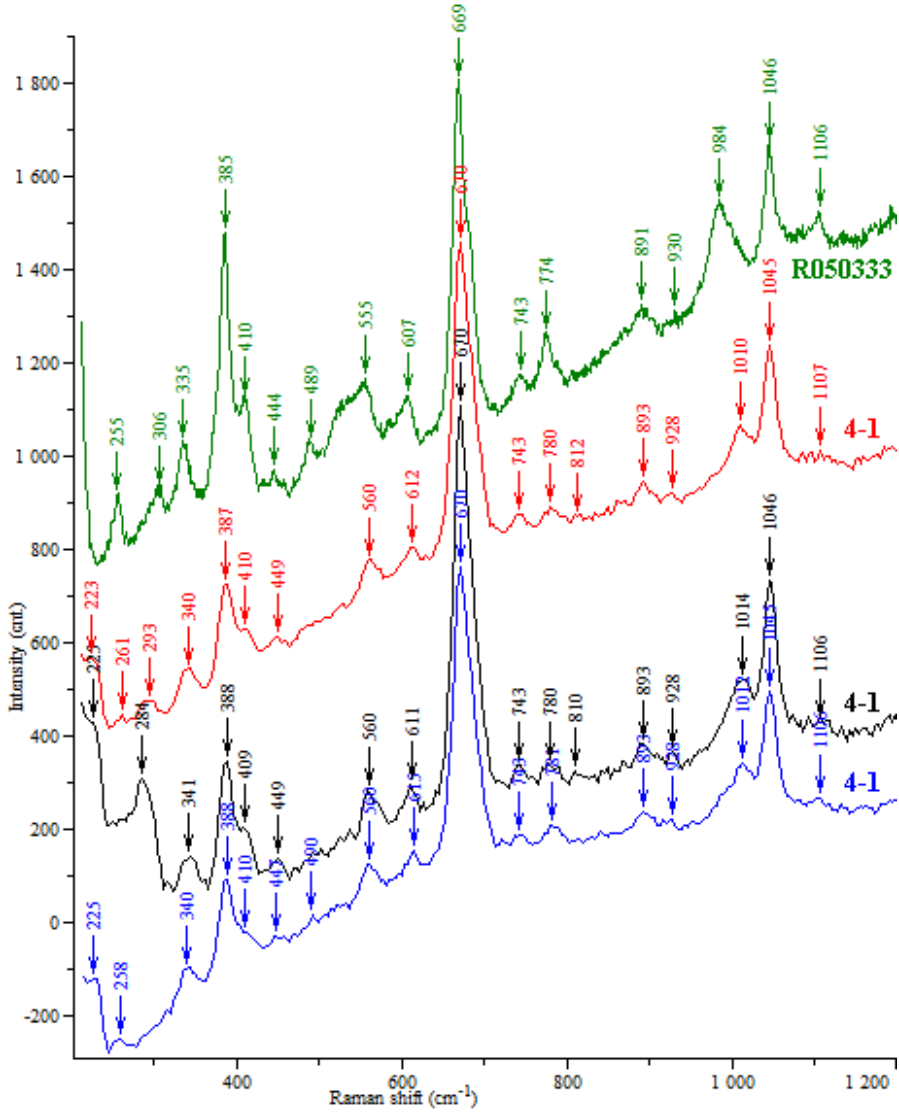


Fig. 9 Raman spectra of glaucophane samples (4-1, 4-1 and 4-1), in comparison with glaucophane reference (R050333) spectra from RRUFF project

Also, the spectral lines around $\sim 743 \text{ cm}^{-1}$ may be ascribed to the symmetric stretching vibration of the Si-O₆-Si bridges. The symmetric stretching (ν_s) of the O-Si-O linkage is

represented by the bands between 774 cm^{-1} and 895 cm^{-1} . As is visible in figure 9, one band exhibits in all spectra around $\sim 928 \text{ cm}^{-1}$, and may be assigned to the asymmetric stretching vibration of the O-Si-O group. The bands at 985 and 984 cm^{-1} are shifted with $\sim 30 \text{ cm}^{-1}$, in comparison with our spectra; the assignment of these bands remains questionable because they are probably the ν_{as} of the Si-O_b-Si, although the peak value is in the ν_{as} region of the O-Si-O linkage. The wavenumbers between 1000 and 1110 cm^{-1} are assigned to the ν_{as} (asymmetric stretching) of the Si-O_b-Si bridges. The 1100 region of the 4-1 spectra presents a very low signal-to-noise ratio.

Tab. 8 Wavenumbers and assignments for the Raman spectra of glaucophane samples (4-1; 4-1 and 4-1) in the 210-1200 cm^{-1} spectral region

Present study (cm^{-1})			Reference (cm^{-1})		Tentative assignment
Sample no.			Huang (2003)	Downs (2006)	
1623 (4-1)	1623 (4-1)	1623 (4-1)	#Mg 52	R050333	
225, 258	225, 284	223, 261, 293	209, 227, 254	255	lattice mode
340	341	340	336	306, 335	
388, 410	388, 409	387, 410	386, 405	385, 410	M-O
447	449	449	445	444	
490, 560, 615	560, 611	560, 612	520, 558, 609	489, 555, 607	deformation modes of Si ₄ O ₁₁
670	670	670	668	669	ν_s of the Si-O_b-Si (ν_1)
743	743	743	682, 740	743	ν_s of the Si-O _b -Si
781, 893	780, 810, 893	780, 812, 893	776, 789, 895	774, 891	ν_s of the O-Si-O
928	928	928		930	ν_{as} of the O-Si-O
-	-	-	985	984	?
1011, 1045, 1106	1014, 1046, 1106	1010, 1045, 1107	1008, 1045, 1104	1046, 1106	ν_{as} of the Si-O _b -Si

? – questionable interpretation; ν_s – symmetric stretching; ν_{as} – asymmetric stretching; Mg#=(Mg/Mg+Fe²⁺).

4.2 Riebeckite

Given the fact that these spectra are very complex and that their quality is not very good (low signal-to-noise ratio), we divided the spectra (figs. 10a and 10b) into two major regions: 210-480 cm^{-1} and 480-1200 cm^{-1} . Apart from this, these spectra were difficult to obtain due to high fluorescence. Riebeckite has a variety called *crocidolite* that is

appears at 329 cm^{-1} , while in our spectra (4-2, 4-2 and 4-2) this spectral line does not appear. In the $350\text{-}480\text{ cm}^{-1}$ spectral region, some peaks appear at different frequencies; however, these bands cannot be compared because the low signal-to-noise ratio influences the interpretation of these peaks.

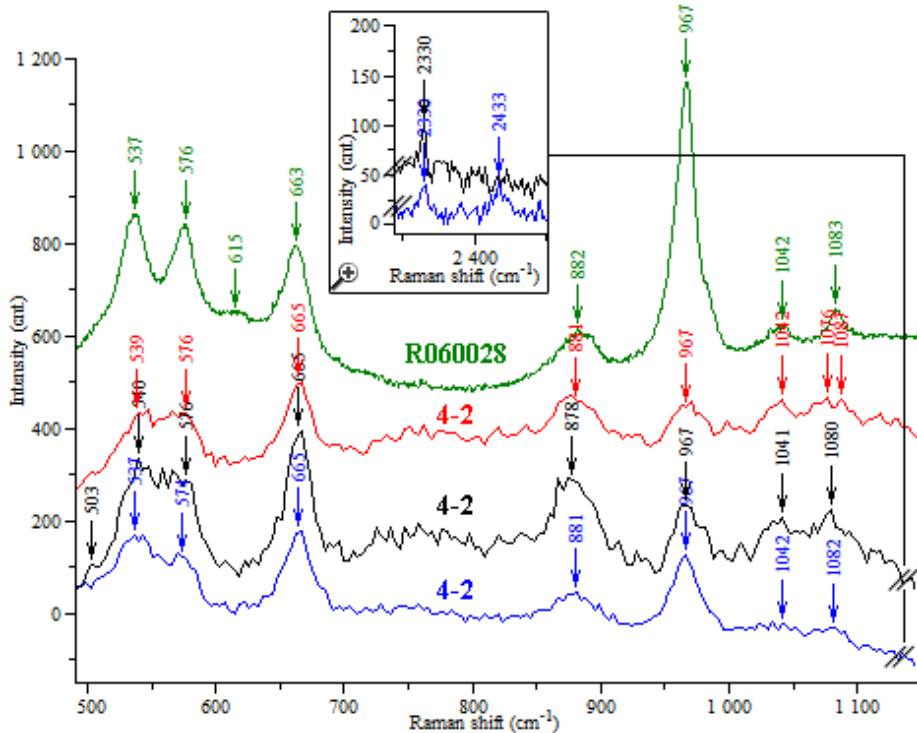


Fig. 10b Raman spectra (between $480\text{-}1200\text{ cm}^{-1}$) of riebeckite samples (4-2, 4-2 and 4-2), in comparison with riebeckite reference (R060028) spectra from RRUFF project

The assignment of the bands in the $480\text{-}1200\text{ cm}^{-1}$ region follows the previous assignment of the peaks. The assignment of the spectral lines is summarized in table 9.

The bands between 503 and 615 cm^{-1} may be ascribed to Si_4O_{11} deformation modes. These peaks (~ 537 and $\sim 576\text{ cm}^{-1}$ doublet peaks), at these values, are a factor in the discrimination between a riebeckite/crocidolite sample and other samples discussed above.

The reference spectrum presents a band at 615 cm^{-1} ; in our spectra, this peak may appear, but the low signal-to-noise ratio of this region ($605\text{-}625\text{ cm}^{-1}$) and the very low intensity of this peak prevents us from developing a discussion on this spectral band. The ν_1 symmetric stretching (ν_s) of the $\text{Si-O}_b\text{-Si}$ bridge is shown in all spectra (fig. 10b) around

665 cm⁻¹, more exactly at 665 cm⁻¹ for the riebeckite samples of this work and at 663 cm⁻¹ for the reference spectrum (R060028). As has been discussed above, the spectral bands located at 967 cm⁻¹ in all spectra (fig. 10b) may be ascribed to the symmetric stretching (ν_s) of the O-Si-O group. The ν_{as} (asymmetric stretching) vibrations of the same group (O-Si-O) lie at 967 cm⁻¹ (for all spectra).

Tab. 9 Wavenumbers and assignments for the Raman spectra of riebeckite samples (4-2; 4-2 and 4-2) in the 210-1200 cm⁻¹ spectral region

Present study (cm ⁻¹)			Reference (cm ⁻¹)	Tentative assignment
Sample no.			Downs (2006)	
5807 (4-2)	5807 (4-2)	5807 (4-2)	R060028	
246, 269, 284	245, 270, 285	219, 243, 268, 285	213, 243, 271, 287, 293, 298	lattice mode
-	-	-	329	
359	362	362	358	
404	411, 443	435	429	M-O
474	472	461, 475	472	
537, 574	503, 540, 576	539, 576	537, 576, ?615	deformation modes of Si ₄ O ₁₁
665	665	665	663	ν_s of the Si-O_b-Si (ν_1)
881	878	881	882	ν_s of the O-Si-O
967	967	967	967	ν_{as} of the O-Si-O
1042, 1082	1041, 1080	1042, 1076, 1087	1042, 1083	ν_{as} of the Si-O _b -Si
2330	2330	-	-	$\nu\text{H}_3\text{O}^+$
2433	-	-	-	νNH_4^+

? – questionable interpretation; ν_s – symmetric stretching; ν_{as} – asymmetric stretching; $Mg\#=(Mg/Mg+Fe^{2+})$.

The following bands: 1042 and 1082 cm⁻¹ (for 4-2); 1041 and 1080 cm⁻¹ (4-2); 1042, 1076 and 1087 cm⁻¹ (4-2); 1042 and 1083 cm⁻¹ (R060028) correspond to the asymmetric stretching (ν_{as}) vibration modes of the Si-O_b-Si groups.

The Raman spectrum of the riebeckite samples (4-2 and 4-2) shows one peak at 2330 cm⁻¹ and one band at 2433 cm⁻¹ (in the case of the 4-2 spectrum); the first band (2330 cm⁻¹) may be assigned to H₃O⁺ vibration, and the second (2433 cm⁻¹) – to NH₄⁺. This is due to a substitution of cations from the M sites by H₃O⁺ or NH₄⁺.

Conclusions

The comparison of our spectra and those from the literature proved that they are in good agreement.

The results discussed above illustrate the ability of Raman spectroscopy to discriminate among amphiboles without IR spectroscopy, OH⁻ spectral region or chemical analysis for amphibole samples. However, due to high fluorescence, low signal-to-noise ratio and impurities, there are some uncertainties. Further studies on minerals and their fibrous form, that are lacking in this work, are needed to make a more correct and complete discrimination between members of some amphibole series.

Some spectra display a considerable diversity of spectral bands involving substitutions of cations in the M sites by H₃O⁺ and NH₄⁺ and the presence of calcite and quartz inclusions.

Raman data for actinolite varieties – uralite and smaragdite samples, have not, to the best of our knowledge, been published yet.

It should be noted that some spectra show questionable interpretations for reasons such as: substitutions, impurities, high fluorescence, laser focus or acquisition time.

The characteristic bands for each mineral can be shifted for the same reasons listed above (especially substitutions, e.g. Si ↔ Al in T sites).

Acknowledgements

This work was supported by CNCISIS – UEFISCSU, project number PNII – IDEI code 2119/2008.

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Received: April, 2010

Revised: May, 2010

Accepted: May, 2010