

COMPARATIVE INFRARED SPECTROSCOPIC STUDY OF NATURAL CA-AMPHIBOLES

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Abstract

Powder IR spectra of natural Ca-amphiboles were studied in the spectral range 4000 to 400 cm^{-1} . The examined samples are: actinolite, tremolite, Mg-hornblende and pargasite. According to their spectra all the minerals of the four species present common features at 3658-3660, 919, 683-687, 661-668, 505-513, 457-464 and 419 cm^{-1} . Additionally to these bands, the spectra of the actinolites, tremolites and Mg-hornblendes present common characteristics at 3673, 1094-1098, 989-998, 951, 752-758 and 441-449 cm^{-1} . Moreover, six absorption bands are shown in the spectra of the pargasites at 3690, 981-984, 931, 805-811, 734 and 696-698 cm^{-1} , in addition to the common bands appeared in all Ca-amphiboles, which do not appear in the spectra of the actinolites, tremolites and Mg-hornblendes. The spectra of pargasites are remarkably different from the spectra of the other three mineral species. These discrepancies could be attributed to differences in the structure of pargasites relative to the other three species as well as to the occupancy of the A site especially with Na^+ .

Key words: FTIR, actinolite, tremolite, Mg-hornblende, pargasite.

Περίληψη

Μελετήθηκαν φυσικές ασβεσταμφίβολοι με τη μέθοδο της φασματοσκοπίας υπερόθρου με μετασχηματισμούς Fourier (FTIR), στην περιοχή 4000-400 cm^{-1} του μεσαίου υπερόθρου (MIR). Τα δείγματα που αναλύθηκαν είναι ακτινόλιθοι, τρεμολίτες, Mg-κεροσιτίλβες και παρασιτίτες. Από τη μελέτη των φασμάτων τους προέκυψε ότι και τα τέσσερα είδη ασβεσταμφιβόλων παρουσιάζουν παρόμοια φάσματα. Συγκεκριμένα, και στα τέσσερα είδη εμφανίζονται κοινές κορυφές στα 3658-3660, 919, 683-687, 661-668, 505-513, 457-464, και 419 cm^{-1} . Τα φάσματα των ακτινόλιθων, των τρεμολιτών και των Mg-κεροσιτίλβων εμφανίζουν επιπλέον κοινές κορυφές στα 3673, 1094-1098, 989-998, 951, 752-758 και 441-449 cm^{-1} και δεν μπορεί να γίνει περαιτέρω διάκριση των ειδών μεταξύ τους. Στα φάσματα των παρασιτιτών εμφανίζονται επιπλέον των κοινών κορυφών και κορυφές στα 3690, 981-984, 931, 805-811, 734 και 696-698 cm^{-1} που δεν εμφανίζονται στους ακτινόλιθους, στους τρεμολίτες και στις Mg-

κεροσίλβες και τα διαφοροποιούν αρκετά από τα φάσματα των τριών άλλων. Η εμφάνιση των διαφορών αυτών οφείλεται πιθανότατα στην αρκετά διαφοροποιημένη δομή του πλέγματος των παρασιτών σε σχέση με τα άλλα τρία είδη και στην κατάληψη της θέσης Α κυρίως από Na^+ .

Λέξεις κλειδιά: FTIR, ακτινολίθος, τρεμολίτης, Mg-κεροσίλβη, παρασίτης.

1. Introduction

Among the common methods usually used for the identification of minerals are the X-ray diffraction (XRD) method and the electron microprobe analysis (EMPA). FTIR analysis is, also, a useful method and FTIR spectra of synthetic and natural minerals have been obtained. However, although there are many FTIR studies, there is interest on the comparative examination of natural minerals, especially of minerals with complicated structures and formula units as the group of amphiboles, towards the identification of common characteristics. In this paper, natural Ca-amphiboles identified and classified by chemical microanalysis and X-ray diffraction techniques are investigated and characterized by FTIR spectra. The aim of the paper is the comparative study of natural Ca-amphiboles through their FTIR spectra as well as the attribution of characteristic bands to specific atomic groups and bond vibrations. The possibility to discriminate the species of the Ca-amphiboles on the basis of characteristic bands of their FTIR spectra is also examined.

2. Materials and Methods

2.1. Samples

The Ca-amphibole samples (Table 1) were collected mainly from the collections of the Mineralogy and Petrology Museum of the Aristotle University of Thessaloniki (A.U.Th.), while two samples (H2 and H3) from Xanthi plutonite were given by G. C. and correspond to the samples 250 and 117 respectively, of his Ph.D. thesis (Christofides, 1977).

Table 1 – Classification of the samples

Sample	Origin	Identification based on	
		XRPD	Chemical composition
A1	Vermont, France	Actinolite	Actinolite
A2	Unknown, DeLaSalle College Collection, Thessaloniki, Greece	Actinolite	Actinolite - Tremolite
H1	Skarn, Xanthi, Greece	Mg-hornblende	Mg-hornblende
H2	Granodiorite, Xanthi, Greece	Mg-hornblende	Mg-hornblende
H3	Monzogranite, Xanthi, Greece	Mg-hornblende	Mg-hornblende
P1	Marbles, Pargas, Finland	Pargasite	Pargasite
p2	Marbles, Pargas, Finland	Pargasite	Pargasite
p3	Marbles, Pargas, Finland	Pargasite	Pargasite
T1	Greiuer, Tirol, Anstria	Tremolite (+Chlorite)	Tremolite
T2	Chester, Vermont, U.S.A.	Tremolite (+Chlorite)	Tremolite
T3	Fahlun, Finland	Tremolite	Tremolite

2.2. X-Ray Powder Diffraction (XRPD)

Powder XRD patterns were obtained on a PHILIPS PW1820/00 X-ray diffractometer of the Department of Mineralogy – Petrology – Economic Geology, School of Geology, A.U.Th., carrying a

PW1710 microprocessor and using the PC-APD software. Operating conditions for all samples were 35 kV and 25 mA using Ni-filtered $\text{CuK}_{\alpha\text{ave}}$ radiation. The 2θ (2θ) scanning range was between 3° and 63° and the scanning speed was $1.2^\circ/\text{min}$. Silicon was used as external standard. The identification of the samples was made with the JCPDS-ICDD 2003 database.

2.3. Electron Microprobe Analysis (EMPA)

Electron Microprobe Analysis was carried out in the Scanning Microscope Laboratory, A.U.Th., using a JEOL JSM-840A Scanning Electron Microscope (SEM) equipped with an Energy Dispersive Spectrometer (EDS) with 20 kV accelerating voltage and 0.4 mA probe current. Pure Co was used as an optimization element. Line analyses from the center of the crystal towards the rim were performed. The chemical composition of each sample represents mean values of five to eight spots.

2.4. Fourier Transform Infrared Spectroscopy (FTIR)

Powdered samples were prepared by grinding about 10 mg of sample in an agate mortar with acetone, to avoid oxidizing the Fe^{2+} , until the grain size was generally less than $20\ \mu\text{m}$. After drying to evaporate the acetone, 2.5 mg of Ca-amphibole was homogenized with 250 mg of KBr by grinding in an agate mortar. The mixture was pressed at 7 tn for 5 min using a hydraulic hand press in an evacuated die into a 13 mm pellet. The pellets were dried at $110\ ^\circ\text{C}$ for 2 hours before the collection of the spectra.

The infrared spectra of the samples were recorded in the region of mid IR (MIR, 4000 to $400\ \text{cm}^{-1}$) with mean average of 32 scans and resolution $4\ \text{cm}^{-1}$ on a PERKIN-ELMER FTIR Spectrum 1000 Spectrometer of the Solid State Physics Section, Physics Department, A.U.Th. A pure KBr pellet was used as reference.

3. Results

3.1. General

The XRPD patterns of four representative samples are presented in Figure 1 while the identification of all samples based on the patterns is presented in Table 1. According to the patterns, the samples are divided in four species: actinolites (A1 and A2), tremolites (T1, T2 and T3), Mg-hornblendes (H1, H2 and H3) and pargasites (P1, P2 and P3). It must be noted that in the T1 and T2 sample patterns a quite large amount of chlorite is observed.

The results of microanalysis of the samples are presented in Table 2. The calculation of the chemical formulae and the $\text{Fe}^{3+}/\text{Fe}^{2+}$ estimation were based on the method proposed by Leake *et al.* (1997, appendix 2). The Ca cations in B site are ≥ 1.5 atoms per formula unit (apfu) in all samples, and according to Leake *et al.* (1997, 2003) they belong to the Ca-amphibole group. The samples with Na and K in A site ≤ 0.5 apfu are plotted on Figure 2a (Leake *et al.* 1997, 2003) in the fields of actinolite (A1 and A2), Mg-hornblende (H1, H2 and H3) and tremolite (T1, T2 and T3). The samples with Na and K in A site ≥ 0.5 apfu are plotted on Figure 2b (Leake *et al.* 1997, 2003) in the field of pargasite (P1, P2 and P3), (Table 1). The nomenclature of the samples, based on the chemical analyses, is in agreement with their identification by the XRPD method. The $\text{Mg}/(\text{Mg}+\text{Fe}^{2+})$ ratio is relatively high in all samples and ranges between 0.78 and 1.00 (except H2 sample where it is 0.72). Concerning the concentrations of Si and Al, they are quite different among the samples. Specifically, in actinolites, tremolites and Mg-hornblendes the concentration of Si ranges between 7.17 and 7.93 apfu and the concentration of Al ranges from 0.14 to 0.99 apfu.

In pargasites the concentration of Si is lower than that of the other three species, ranging between 6.22 and 6.49 apfu while the concentration of Al is higher and ranges from 1.97 to 2.34 apfu.

In the FTIR spectra of the investigated samples (Fig. 3) two regions can be distinguished:

1. The region between 400 and 1600 cm^{-1} (Fig. 4) where bands are attributed to the vibrations of Si and Al bonds with O in the structure of the minerals (Si-O, Si-O-Si, Si-O-Al, etc.).
2. The region between 3200 and 4000 cm^{-1} (Fig. 5) where bands are attributed to the stretching vibrations of OH^- groups coordinated by M1 and M3 cations (Farmer 1974).

In the region between 2300 and 2400 cm^{-1} the weak bands are attributed to the atmospheric CO_2 in the sample chamber.

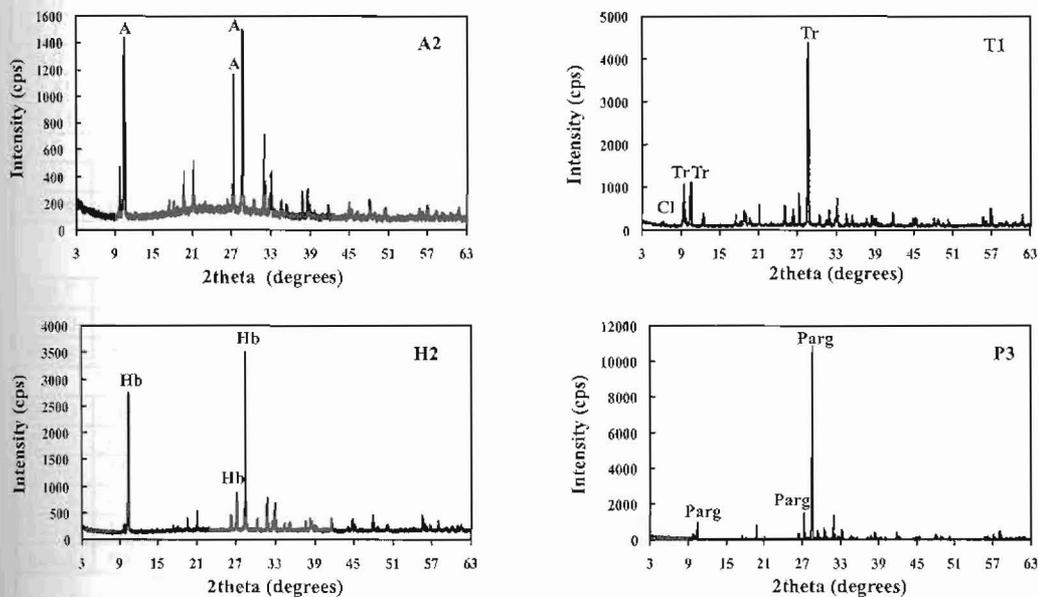


Figure 1 – XRPD pattern of representative samples (A: actinolite, Parg: pargasite, Hb: Mg-hornblende, Tr: tremolite, Cl: chlorite)

3.2. Actinolites, Tremolites, Mg-Hornblendes

3.2.1. Low frequency region: 400-1600 cm^{-1}

The spectra of these minerals are presented in Figures 3a to c and 4a to c. Generally, in all mineral spectra it can be seen that around 1000 cm^{-1} appear absorption bands, which are ascribed to stretching vibrations of the T-O bonds, while below 600 cm^{-1} , absorption bands appear, due to the bending vibrations of T-O-T bonds. The sharp band at 459 cm^{-1} is attributed to Si-O bending (Gopal *et al.* 2004) while the band at 668 cm^{-1} to small amounts of Fe^{2+} in the amphibole structure (Hawthorne 1981, Carmichael 1982, Prasad *et al.* 2000). According to Gopal *et al.* (2004) the bands at 685 and 757 cm^{-1} are attributed to symmetrical stretching of Si-O-Si bonding. Lucania *et al.* (2002) supported that the bands at 919 and 951 cm^{-1} are characteristic in natural actinolites, while Prasad *et al.* (2000) reported that these absorption bands are characteristic in the spectra of natural tremolites. All the above mentioned absorption bands are common in all the investigated samples of actinolites, tremolites and Mg-hornblendes. Although the samples are classified in three different species of Ca-amphiboles, they have small differences in their chemical composition (Table 2, Figs 2a, b). The band at about 951 cm^{-1} , corresponding to the 955 cm^{-1} of Gopal *et al.* (2004), can be attributed to the symmetric in-plane stretching vibration of the Si-O bond. This bond existing in all amphiboles is observed in the spectra of all samples. The band at 1094-1098 cm^{-1} is reported by Prasad *et al.* (2000) and according to Gopal *et al.* (2004) this band is ascribed to antisymmetrical stretching vibration of Si-O-Si bond. Furthermore, there are four more absorption bands at 989-998, 505-513, 441-449 and 419 cm^{-1} in the spectra of the actinolites, tremolites and Mg-hornblendes which can not be related with specific bond vibrations according to

the existing literature. All the above mentioned absorption bands are common in all the investigated samples of actinolites, tremolites and Mg-hornblendes.

Table 2 – Chemical analyses of the samples

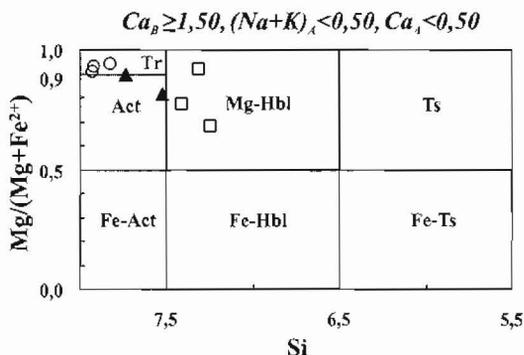
	P1	P2	P3	H1	H2	H3	A1	A2	T1	T2	T3
SiO ₂	44.82	43.88	46.78	52.34	49,36	51.94	53.59	56.24	57.24	56.19	57.49
TiO ₂	0.06	0.57	0.00	0.20	0,76	0.67	0.22	0.11	0.06	0.00	0.06
Al ₂ O ₃	14.07	13.66	12.07	5.98	4,87	4.20	4.78	2.80	1.19	1.05	0.87
FeO _t	3.04	4.73	1.30	6.19	13,68	11.22	8.67	5.81	3.48	4.18	3.38
MnO	0.03	0.09	0.06	0.26	0,56	0.83	0.14	0.17	0.19	0.36	0.45
MgO	19.49	18.95	21.82	19.76	15,05	16.44	17.64	21.13	24.10	22.10	23.17
CaO	12.01	11.20	11,97	10.88	12,35	11.03	11.68	10.86	11.06	10.91	11.54
Na ₂ O	3.27	3.42	3.34	1.23	0,84	1.03	0.88	0.86	0.48	0.26	0.16
K ₂ O	0.68	0.79	1.08	0.10	0,31	0.30	0.14	0.10	0.00	0.00	0.00
Total	97,47	97,29	98,42	96,94	97,78	97,66	97,74	98,08	97,80	95,05	97,12
Structural formula based on 23 O											
Si	6.312	6.224	6.488	7.313	7,169	7.417	7.527	7.737	7.823	7.928	7.918
Al ^{IV}	1.688	1.776	1.512	0.687	0,831	0.583	0.473	0.263	0.177	0.072	0.082
T	8.000										
Al ^{VI}	0.648	0.507	0.462	0.298	0,002	0.124	0.319	0.191	0.015	0.103	0.060
Ti	0.006	0.061	0.000	0.021	0,083	0.072	0.023	0.011	0.006	0.000	0.006
Fe ³⁺	0.178	0.365	0.144	0.359	0,378	0.328	0.194	0.158	0.085	0.024	0.031
Mg	4.090	4.007	4.394	4.116	3,258	3.499	3.692	4.333	4.894	4.649	4.758
Fe ²⁺	0.078	0.060	0.000	0.206	1,279	0.977	0.772	0.307	0.000	0.224	0.145
C	5.000										
Mg	0.000	0.000	0.117	0.000	0,000	0.000	0.000	0.000	0.016	0.000	0.000
Fe ²⁺	0.102	0.136	0.006	0.159	0,005	0.036	0.052	0.203	0.312	0.245	0.214
Mn	0.004	0.011	0.006	0.031	0,069	0.101	0.016	0.020	0.022	0.043	0.052
Ca	1.812	1.703	1.779	1.629	1,922	1.687	1.757	1.600	1.619	1.649	1.702
Na	0.082	0.150	0.092	0.181	0,004	0.176	0.175	0.177	0.031	0.063	0.032
B	2.000										
Na	0.811	0.790	0.807	0.152	0,232	0.109	0.064	0.052	0.095	0.008	0.010
K	0.122	0.143	0.191	0.018	0,057	0.055	0.025	0.018	0.000	0.000	0.001
A	0.933	0.933	0.998	0.170	0.289	0.164	0.089	0.070	0.095	0.008	0.011

3.2.2. OH absorption region

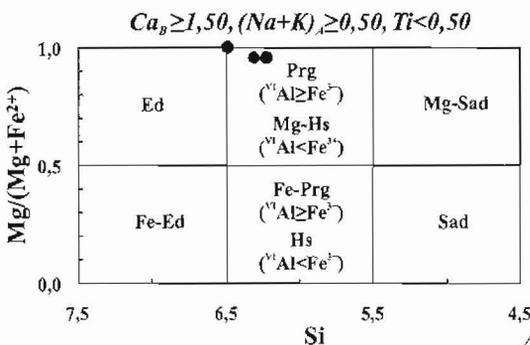
In the region with wavenumber between 3200 and 4000 cm⁻¹, the OH area (Figs 5a-c), the OH-metal ion bonds are present. In the amphibole structure, the OH group is bonded to two M1 and one M3 cations and the H atom projects into the A site cavity, which can be vacant or occupied (Della Ventura *et al.* 1999, Hawthorne *et al.* 2000, Della Ventura *et al.* 2003). The small band at 3658-3660 cm⁻¹ is attributed to the presence of Mg in the M1 sites and Fe²⁺ in the M3 site (Burns and Strens 1966, Burns and Greaves 1971). The sharp band at 3673 cm⁻¹ is attributed to the presence of Mg in the M1 and M3 sites (Burns and Strens 1966, Burns and Greaves 1971, Hawthorne *et al.* 2000, Jenkins *et al.* 2003). A weak band at 3641 cm⁻¹ observed only in the spectra of H2 and H3 samples is attributed to the presence of MgFe²⁺Fe²⁺ in the M1M1M3 sites (Burns and Strens 1966, Burns and Greaves 1971). This observation is also confirmed from the chemical analysis where the amount of FeO_t is higher than the amount of the rest samples.

It must be noticed here that the co-existence of chlorite in the samples T1 and T2 (Fig. 1), identified by XRPD, is also confirmed from their FTIR spectra. Although in the low frequency region

the absorption bands of chlorite (at 991, 824, 756, 664 and 446 cm^{-1}) are overlapped by the absorption bands of tremolite, in the OH absorption region its presence is recognized from a broad double absorption band at 3420-3430 and 3571 cm^{-1} (Oinuma and Hayashi 1968, Farmer 1974). Furthermore, a sharp band at about 3673 cm^{-1} is also common in the spectra of the two minerals and overlapped by the tremolite's band.



(a)



(b)

Figure 2 – Nomenclature diagrams. \circ – T1, T2, T3, \blacktriangle – A1, A2, \square – H1, H2, H3, \bullet – P1, P2, P3. (Tr: tremolite, Act: actinolite, Fe-Act: Fe-actinolite, Mg-Hbl: Mg-hornblende, Fe-Hbl: Fe-hornblende, Ts: tschermakite, Fe-Ts: Fe-tschermakite, Ed: edenite, Fe-Ed: Fe-edenite, Prg: pargasite, Fe-Prg: Fe-pargasite, Mg-Hs: Mg-hastingsite, Hs: hastingsite, Mg-Sad: Mg-sadanagaite, Sad: sadanagaite)

3.3. Pargasites

3.3.1. Low frequency region: 400-1600 cm^{-1}

The spectra of pargasites (Figs 3d, 4d) present the common characteristics of Ca-amphiboles at about 1000 cm^{-1} and below 600 cm^{-1} that were mentioned above. In the investigated samples, the presence of a band at 457-464 cm^{-1} is characteristic of the spectra of natural actinolites (Gopal *et al.* 2004) and is attributed to Si-O bending vibration. Since this bond is common characteristic in all Ca-amphiboles, potentially it can be also related to the Si-O bending vibration in pargasites. Prasad *et al.* (2000) mentioned that the absorption band at 661-668 cm^{-1} is related with the presence of Fe^{2+} in the structure of the mineral. The band at 683-687 cm^{-1} is attributed to symmetrical stretching vibration of Si-O-Si bond (Gopal *et al.* 2004). Eight more absorption bands (at 981-984, 931, 919, 805-811, 734, 696-698, 507-513 and 419 cm^{-1}) are observed in the spectra of the pargasites, but there are no references relating them to specific bond vibrations.

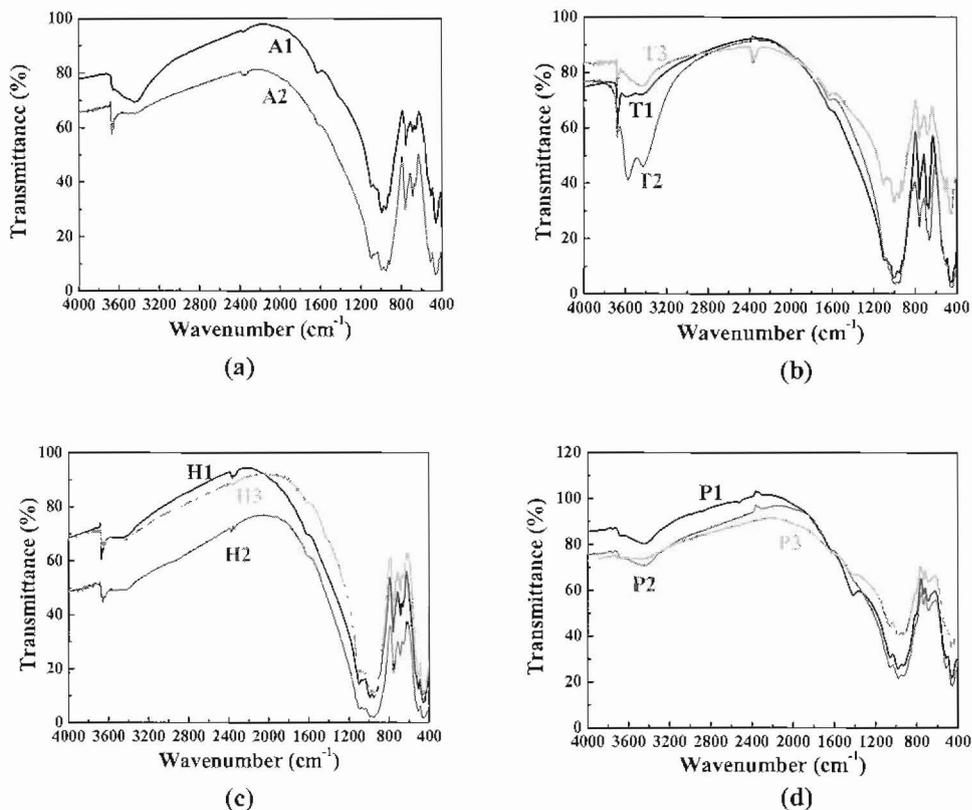


Figure 3 – FTIR spectra in the region 4000-400 cm^{-1} . Samples as in Table 1

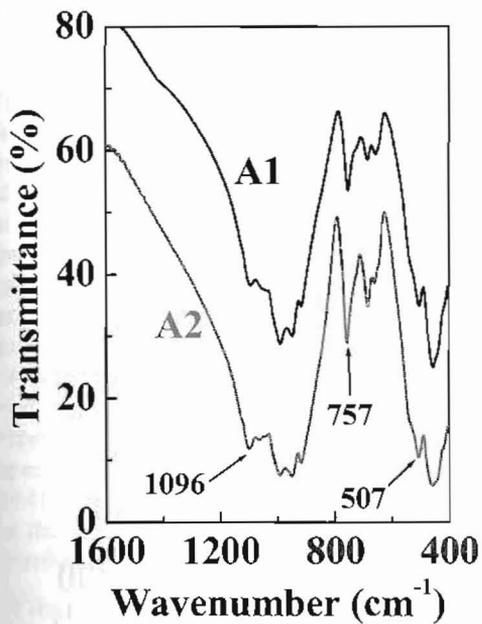
3.3.2. OH absorption region

Della Ventura *et al.* (2003) reported that the absorption band at about 3690 cm^{-1} is observed when in the structure of pargasites the M3 and T1 sites are occupied by Al, the M1, M2 and M3 sites by Mg and the A site by Na. Burns and Strens (1966) and Burns and Greaves (1971) reported a band at 3658 cm^{-1} attributed to the presence of Mg in the M1 sites and Fe^{2+} in the M3 site in the tremolite-actinolite series. This band is also observed in the spectra of pargasites and it can potentially be attributed to the presence of Mg in M1 sites and Fe^{2+} in M3 site.

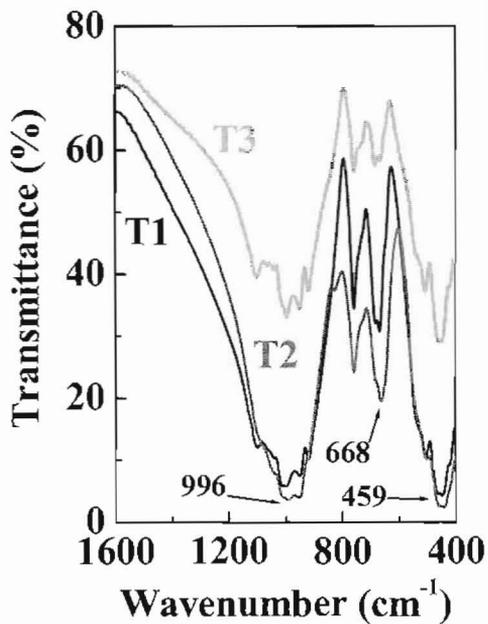
4. Discussion

Several key observations have come from the investigation and comparison of the FTIR spectra of the four species of natural Ca-amphiboles.

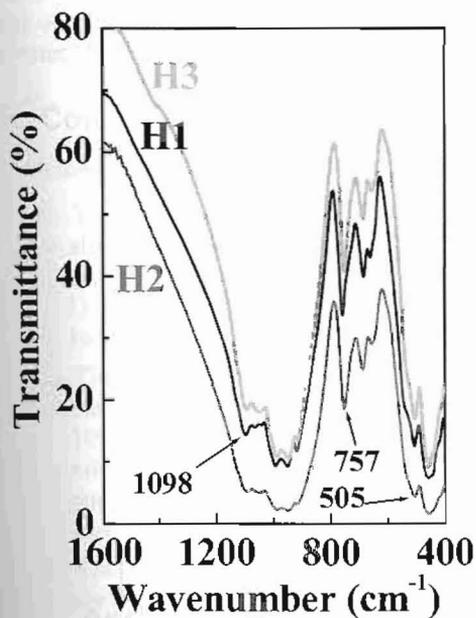
It is clear that in the spectra of all samples many similarities have been observed in specific wavenumber regions. In these regions absorption bands corresponding to bonds of common elements in the crystal structure of the Ca-amphiboles are observed. Particularly, in all samples there have been observed the same absorption bands at $3658\text{-}3660$, $983\text{-}987$, 919 , $661\text{-}668$, $505\text{-}513$, $457\text{-}464$ and 419 cm^{-1} . According to Lucania *et al.* (2002), who claim that in the spectra of natural actinolites there are characteristic bands at 919 , $683\text{-}687$, $661\text{-}668$ and $441\text{-}445 \text{ cm}^{-1}$, it is considered that the above four bands are characteristic not only for actinolites, but also for tremolites, Mg-hornblendes and pargasites. This is predictable because all samples belong to the same group, crystallize in the same system (monoclinic) and consist of the same chemical elements.



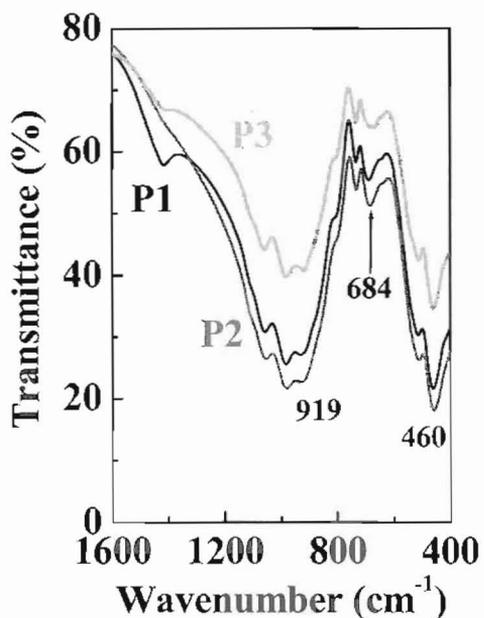
(a)



(b)

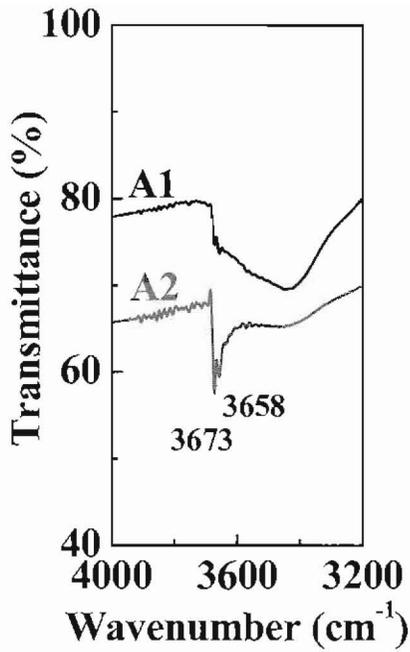


(c)

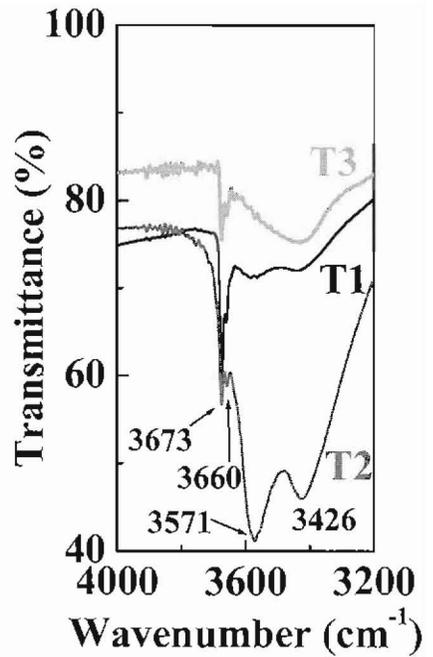


(d)

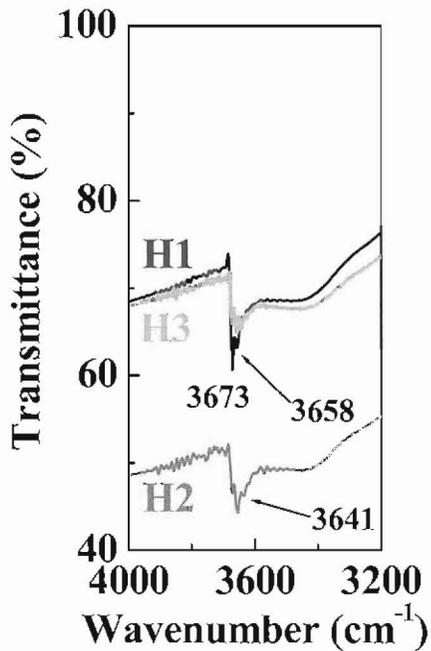
Figure 4 – FTIR spectra in the region 1600-400 cm^{-1} . Samples as in Table 1



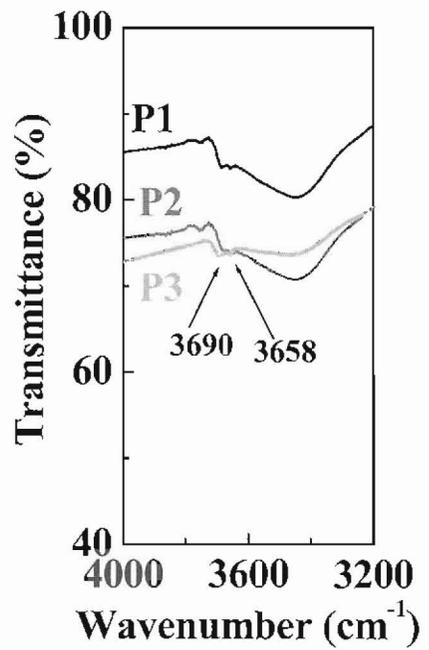
(a)



(b)



(c)



(d)

Figure 5 – FTIR spectra in the region 4000-3200 cm⁻¹. Samples as in Table 1

In the spectra of actinolites, tremolites and Mg-hornblendes six more absorption bands (at 3673, 1094-1098, 989-998, 951, 752-758 and 441-449 cm^{-1}) apart from the common ones are observed. These bands have not been detected in the spectra of pargasites (see below). This arises from the fact that the same sites of the crystal structure of the three species are occupied by the same elements. Although the samples are classified as three different species of Ca-amphiboles, they plot close to the separating lines in the nomenclature diagram (Fig. 2a) and they have only small differences in their chemical composition (Table 2). Also it must be mentioned that the investigated samples are natural crystals and consequently they have lattice defects that disturb the periodicity of the crystal. The elements which are close to a bond they slightly affect it. In the quite complicated amphibole structure, the A site, which is vacant in the ideal chemical formula of actinolites, tremolites and hornblendes (Leake *et al.* 2003), is partly occupied by Na and K in the examined samples (Table 2). The small differences in their chemical composition, the not ideally crystallized structure and the occupancy of the typically vacant sites by cations, change the lengths and the angles among the bonds and affect their vibrational frequency. All these alterations are represented as shifting of the absorption bands in the FTIR spectra and consequently the three species of natural Ca-amphiboles can not be obviously distinguished. A weak absorption band at 3641 cm^{-1} observed only in the spectra of H2 and H3 samples, is due to their higher amount of Fe in their structure than the other samples and can not be characterized as a special feature of Mg-hornblendes' spectra.

In the spectra of pargasites, six absorption bands (at 3690, 981-984, 931, 805-811, 734 and 696-698 cm^{-1}), apart from the common ones, are observed, making possible its discrimination from the other three species of Ca-amphiboles. These differences in their spectra are probably due to the A site occupancy, mostly by Na ions, and the higher concentration of Al relative to the rest three species. These differences can shift, reveal or even suppress some bands.

5. Conclusions

From the study of the FTIR spectra of natural Ca-amphiboles, it can be observed that:

1. The spectra of natural actinolites, tremolites, Mg-hornblendes and pargasites have common absorption bands at 3658-3660 cm^{-1} (MgMgFe^{2+} in M1M1M3 sites), 683-687 cm^{-1} (Si-O-Si symmetrical stretching vibration), 661-668 cm^{-1} (small amount of Fe^{2+}), 457-464 cm^{-1} (Si-O bending vibration), 919, 505-513 and 419 cm^{-1} (no literature exist concerning these bands).
2. The spectra of natural actinolites, tremolites and Mg-hornblendes have six more absorption bands in addition to the common ones, at 3673 cm^{-1} (MgMgMg in M1M1M3 sites), 1094-1098 cm^{-1} (Si-O-Si antisymmetrical stretching vibration), 951 cm^{-1} (Si-O bending vibration), 752-758 cm^{-1} (Si-O-Si symmetrical stretching vibration), 989-998 and 441-449 cm^{-1} (no literature exist concerning these bands). In samples H2 and H3 observed an extra band at 3641 cm^{-1} ($\text{MgFe}^{2+}\text{Fe}^{2+}$ in M1M1M3 sites).
3. The spectra of natural pargasites have six more absorption bands in addition to the common ones at 3690 cm^{-1} (Al in M3 and T1 sites, Mg in M1, M2 and M3 sites and Na in A site), 981-984, 931, 805-811, 734 and 696-698 cm^{-1} (no literature exist concerning these bands). These bands are not present in the spectra of the other three species, hence they can be used to discriminate them.

Therefore, it can be concluded that FTIR method seems to be capable in discriminating pargasites from the rest Ca-amphiboles.

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7. References

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