

Infra-Red Absorption Spectra Study of Some Amphibole Minerals

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ABSTRACT

Infrared spectra of some amphibole minerals show that the absorptivity of the fundamental vibrational OH band is strongly wave number dependent. The investigated have been done on sample include amphibole of termolite, actinolite, anthophyllite, grunerite, riebeckite and amphibole asbestos. Spectra obtained from Ca and Fe-Mg amphiboles consist of sharp, well resolved bands. The emphasis on the hydroxyl stretching region, but the vibrational spectra of the silicate anions also discussed.

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INTRODUCTION

Spectroscopic methods have been widely used in the quantitative analysis of amphibole. infrared spetoscopy provides a sensitive tool for the detection of H₂O molecules or hydroxyl (OH) groups in minerals (Reece et al., 2002). Calibrations for OH contents in amphiboles are difficult for two reasons: (1) Minor and Trace amounts of OH are not easily determined by other analytical methods. (2) Even though hydrous amphiboles contain large quantities of H₂O and OH, which are easily analized by other methods such as, IR absorption bands are commonly so used, that samples must be extremely thin sample, which is a difficult task.

Nevertheless, several investigations have now been produced. (Palin E.J. et al., 2003), proposed an investigation of IR absorption bands for the determination of H₂O and OH in hydroxyl amphiboles. For amphiboles well- established correlation exist

between OH stretching frequency and the chemical formula of the different M-cation's bonded to hydroxyl (Kasir and Abada, 1989). For example, for each Fe^{2+} substituting for Mg at M(1) and M(3) sites, there is a decrease in OH wave number of 15 cm^{-1} . Similarly, for each Al substituting for Mg, there is a reduction of 20 to 30 cm^{-1} . The value of OH stretching wave number is also affected by the contents of Na. Infrared spectra of three glaucophane-nyboite amphiboles were analyzed (Palin et al., 2003) and the OH-stretching wave number used to infer the state of Al-Mg ordering. The spectra of all three amphiboles comprise only two peaks at 3662 cm^{-1} and 3720 cm^{-1} . Amphiboles of termolite –fluorotermolite series were analyzed and IR spectra were recorded in the principal OH-stretching region and a mathematical model is developed to describe local (OH,F) ordering in amphiboles (Robert et al., 1999). The Fourier transform infrared spectra were recorded and analyzed (Hawthorne et al., 2000), on a series of synthetic amphiboles. The fitted spectra showed two arrangements that give rise to five distinct bands in the IR spectra that indicate there are two conclusions: (1) infrared spectra in the OH-stretching region can be affected by the next nearest neighbor O_3 anions interactions; (2) the small number of bands due to next –nearest-neighbor interactions indicate that amphiboles show strong short-range order.

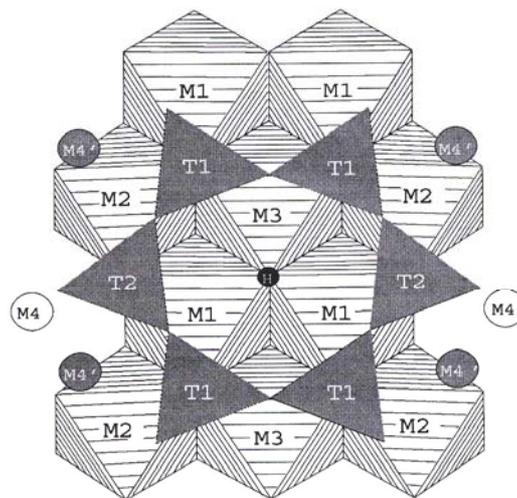


Figure 1. Local environment of the proton in the tremolite structure. The M(4) sites (white) are on a level with the octahedral strip. The M(4) sites (grey) belong to adjacent upper left and right neighbor I-beams (after Hawthorne 1983).

Figure (1), illustrated the cation sites in the vicinity of proton (Hawthorne, 1983). This figure shows the sites within the amphibole I-beam, the tetrahedra belonging to the upper $(\text{Si,Al})_4 \text{O}_{11}$ chain, the M(4)-sites belonging to this I-beam and the upper left and right neighbour I-beam M(4). The tetrahedral of the lower double chain are not shown because the effect of any vibration in charge distribution in this chain which could

influence the vibration of the upper proton is, as a first approximation, shielded by the octahedral chain.

The lattice parameters of the end members tremolite, cummingtonite and richterite correlate linearly with the cation occupancies on the A-site and M(4)-site, two systems of OH-stretching bands are observed (Melzer et al., 2002), the first band system between 3669 and 3678 cm^{-1} is due to a vacant A-site and the second between 3721 and 3737 cm^{-1} due to a filled A-site.

(Kiyoyake et al., 2000), examined the fine structure in the principal of infrared OH-stretching bands in natural amphiboles of the tremolite-ferro actinolite series and analyze the fine structure in the infrared OH-stretching bands in anthophyllites that indicated the occurrence of two symmetrically distinct OH groups in the crystal structure. On the other hand, infrared spectra in the OH-stretching region on riebeckite (Gianluca et al., 2002), show a single sharp band centered at 3618 cm^{-1} . Mossbauer spectra collected for the riebeckite composition (Kasir and Abada., 1989), show Fe^{2+} distributed between M(1) and M3-sites and Fe^{3+} ordered at M(2)-site. These evidences confirm that the riebeckite is close to the nominal composition.

This paper presents investigations based on the infrared absorption spectra of six natural amphiboles that extend over a wide energy range of OH-stretching fundamentals and that appears applicable to the analysis of minor and trace amounts of hydrous species in minerals.

EXPERIMENTAL METHODS

Six natural amphiboles minerals, (tremolite actinolite, anthophyllite, grunerite, riebeckite and amphibole asbestos) were examined in this study. The infrared spectra were recorded using the Thermo-Mattson IR300 spectrometer operating in the wavenumber region starting from 3800 cm^{-1} to 330 cm^{-1} with a resolution of 4 cm^{-1} . This measurements have done in Physics Department Science College, Salahaldeen University-Erbil-Iraq.

The geological locations of the six natural amphiboles are shown in Table1, which are obtained from Ward's National Scientific Establishment (Kasirand and Abada, 1989).

The fine-dispersed amphibole samples were milled in an a gate vial then sieved to a grain-size of 85 micrometer. Then 0.022 gm of sample were dispersed on 0.22 gm of dry KBr.

Band intensities (peak heights) were easily obtained for minerals with strong hydrogen bonds but the grunerite sample provided additional difficulties because of the very broad OH stretching band at low energies, the accuracy of the peak position is limited to $\pm 50 \text{ cm}^{-1}$. In addition, superposition of this broad band with other overtones introduces an uncertainty of $\pm 10 \%$ in the intensity measurements.

Table 1: Geological location and chemical Formula of amphibole samples.

Sample Index	Location	Chemical formula
Tremolite TR1	Malagasay Republic	$\text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$
Actinolite AC1	Chester vermont	$\text{Ca}_2\text{Mg}_2\text{Fe}_3^{+2}\text{Si}_8\text{O}_{22}(\text{OH})_2$
Anthophyllite AN1	Colorado	$\text{Mg}_2\text{Fe}_5^{+2}\text{Si}_8\text{O}_{22}(\text{OH})_2$
Grunerite GU1	Michiqanne	$\text{Fe}_7^{+2}\text{Si}_8\text{O}_{22}(\text{OH})_2$
Riebeckite RB1	Colorado	$\text{Na}_2\text{Fe}_2^{+2}\text{Fe}_2^{+3}\text{Si}_8\text{O}_{22}(\text{OH})_2$
Amphibole asbestos AS1	Canada	$\text{A}_{0-1}\text{X}_2\text{Y}_5\text{Z}_8\text{O}_{22}(\text{OH},\text{F})_2$

RESULTS AND DISCUSSION

Infrared absorption spectra were recorded for the six natural amphibole minerals. The emphasis was on the hydroxyl stretching region, but, the vibrational spectra of the silicate anions are also discussed. The spectra of the six minerals all contain absorption bands between 3700 and 3400 cm^{-1} due to stretching vibrations of the OH groups. There are also a very strong broad absorption bands between 1150 and 400 cm^{-1} . These bands in all the six amphiboles have several shoulders and peaks in the range 1100 to 950 cm^{-1} . These absorption bands were attributed to silicon–oxygen stretches and silicon-oxygen-silicon stretching as in the reference (Skogby and Rossman, 1991).

Figures (2), compare the infrared spectra of termolite (TR1), actinolite (AC1), anthophyllite (AN1), grunerite (GU1), riebeckile (RB1) and amphibole asbestos (AS1) minerals in the range 3700 to 400 cm^{-1} .

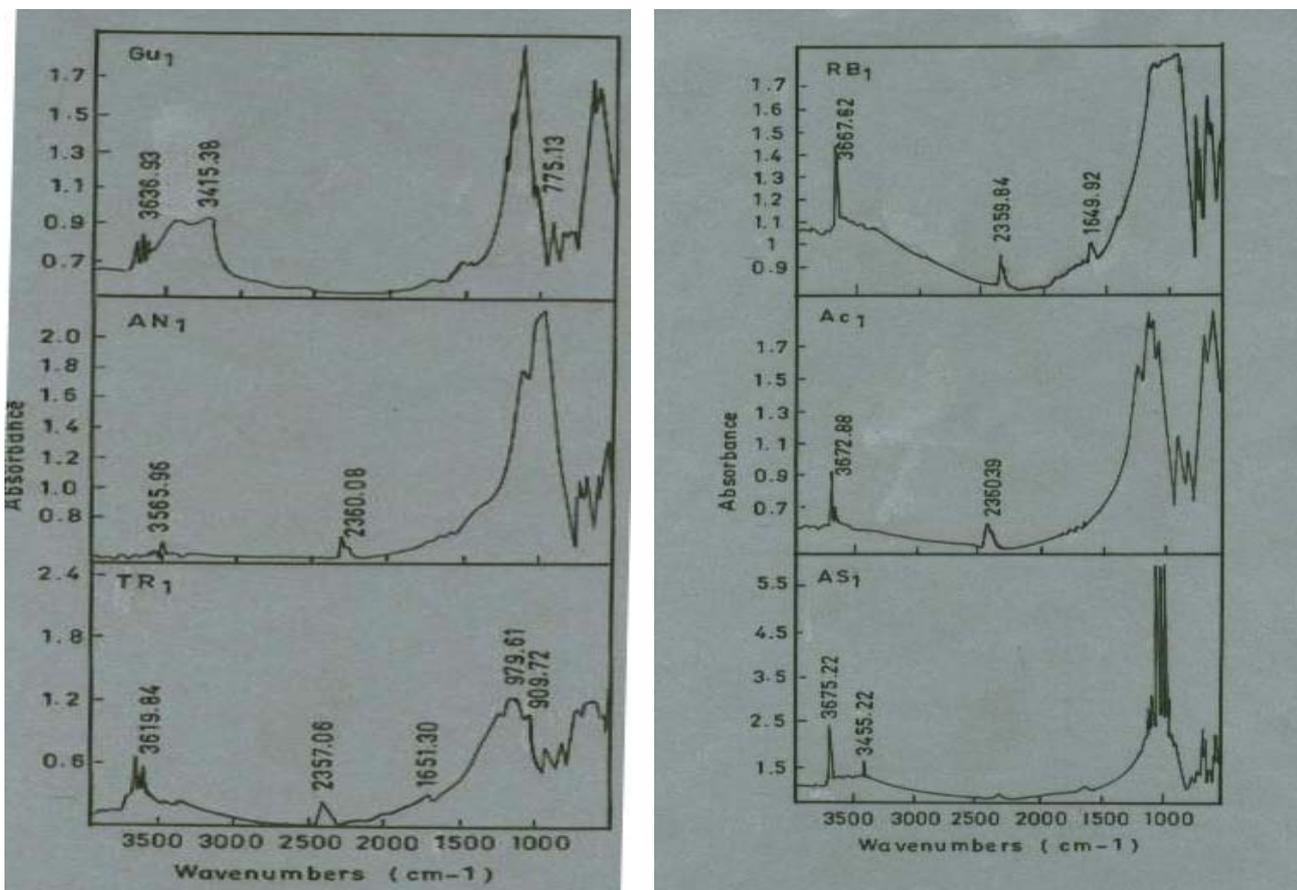


Figure 2: Infrared spectra of (GU1), (AN1),(TR1), (RB1),(AC1) and (AS1).

Regarding the region with wave number ranged from 1150 to 400 cm^{-1} , there is a superficial similarity between the infrared spectra of all six amphibols, as might be expected since all mineral's are silicates. In addition all spectra show very strong broad absorption bands in the 1000 cm^{-1} region due to various silicon-oxygen stretching modes, in similar with (Skogby and Rossman) reference. The spectra of amphibole asbestos and actinolite have a large number of resolved peaks compared to those of other amphiboles. All the spectra have strong peak intensity near 1100 cm^{-1} , there is a second strong peak near 1000 cm^{-1} and a peak of medium intensity near 925 cm^{-1} . These features are assigned to various silicon-oxygen stretching modes.

Two other prominent bands are observed near 600 and 460 cm^{-1} . These are attributed to oxygen-silicon-oxygen angle deformation modes (Beran et al., 1989). Other features in the IR spectra of the six amphibole minerals are the weak absorptions near 855 cm^{-1} and 660 cm^{-1} . There are small differences between the spectra of actinolite, riebeckite and anthophyllite and the other three spectra of asbestos, grunerite and termolite. The position of the maximum of the very strong band near 1050 cm^{-1} are shifted toward higher wave number.

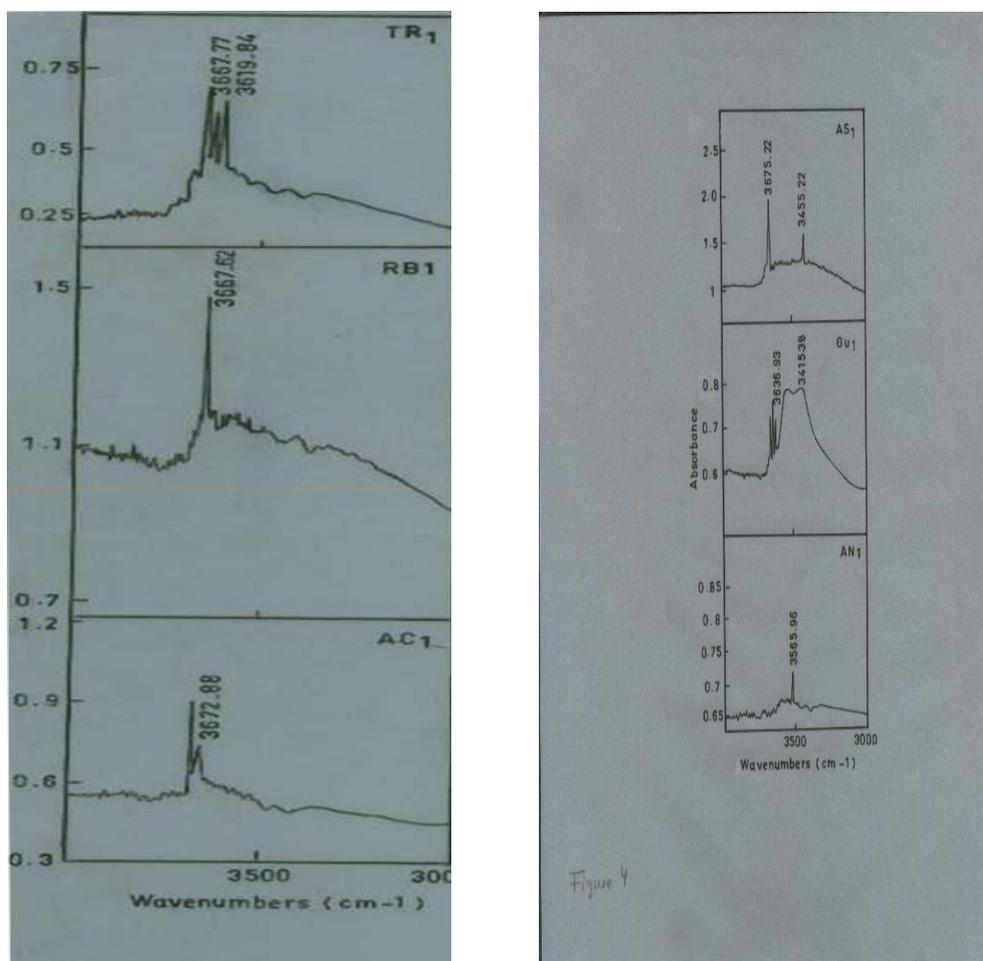


Figure 3: Infrared spectra of (TR1), (RB1), (AC1), (AS1), (G1) and (AN1) from 3700 to 3000 cm^{-1} .

Figures (3), demonstrate the IR spectra of the six amphibole minerals in the wave number region ranged from 3700 to 3000 cm^{-1} . There were many differences appeared between the six spectra in the OH stretching regions, where the spectrum of tremolite has three bands at 3667, 3643 and 3619 cm^{-1} , of actinolite has two bands at 3672 and 3650 cm^{-1} , the spectrum of anthophyllite has one band at 3565 cm^{-1} the spectrum of grunerite has three bands at 3636, 3530 and 3415 cm^{-1} , and riebeckite has one band at 3667 cm^{-1} and amphibole asbestos has two bands at 3675 and 3455 cm^{-1} .

The broad bands observed in tremolite at 3667-3619 cm^{-1} and in actinolite at 3672-3649 cm^{-1} are assigned to mainly two types of stretching configurations (Gosttschalk et al., 1999), resulted from different ion occupations to the different sites.

Tables (2 and 3), contain the observed wave numbers in the infrared spectra, line intensities (absorbances) in arbitrary units of the six amphibole minerals.

Table 2 : Infrared spectra (wave number, cm^{-1}) and intensities of Amphibole asbestos, tremolite and actinolite.

Amphibole asbestos (AS1)		Tremolite (TR1)		Actinolite (AC1)		Assignment and Comments reference (Skogby and Rossman, 1991)
Wave. No. cm^{-1}	Intensity (a.u.)	Wave. No. cm^{-1}	Intensity (a.u.)	Wave. No. cm^{-1}	Intensity (a.u.)	
3675	1.974	3667.8	0.7045	3672	0.9	OH stretching
		3643	0.62	3649	0.75	
		3619	0.66			
3455	1.6053					
2359	0.917	2357	0.24	2360	0.62	CO ₂
1144	2.5					Si-O Stretching
1125	2.7					
1106	2.95			1099	1.6	
1068	3.15					Si-O-Si Stretching
1050	3.25					O-Si-O Stretching
1013	6.0					
992	6.0			989	1.87	
973	6.0	979.6	1.2			
956	3.1					Modes Si-O-and Si-O-Si stretching modes
937	2.5					
916	2.15	909	1.1	918		
898	2.05	778	0.93	758	1.75	
686	1.9	684	0.95	685	1.13	
668	2.3				1.05	
552	2.65			505	1.925	Modes Si-O and Si-O-Si Bending modes
		434	1.175			
		384	1.19	397	1.48	

Table 3: Infrared spectra (wave number, cm^{-1}) and intensities of Riebeckite, grunerite and anthophyllite

Riebeckite (RB1)		Grunerite (GUI)		Anthophyllite (AN1)		Assignments and comments reference (Skogby and Rossman ,1991)
Wave. No. cm^{-1}	Intensity (a.u.)	Wave. No. cm^{-1}	Intensity (a.u.)	Wave. No. cm^{-1}	Intensity (a.u.)	
3667	1.476					OH stretching mode
		3636	0.77			
		3530	0.793	3566	0.175	
		3415	079			
2359	0.942			2360	0.6571	CO₂
1650	1.00					H₂O bending
		1128	0.875			Si-O-stretching
		1082	1.125			Si-O-Si stretching
				1005	2.23	O-Si-O stretching
961	1.84	995	1.43			
782	1.59	775	0.63			Si-O-Si stretching
755	1.41			762	1.05	
711	1.64			724	1.075	
690	1.65					Si-O-Si stretching
661	1.56	667	0.59	647	1.13	
				587	1.35	Si-Ostretching
		483	1.25			Si-O-Si bending mode
		450	1.15			
		429	1.2			

CONCLUSION

Most of the stretching vibrations of trace OH in amphibole minerals are observed in the high-energy region between 3700 and 3200 cm^{-1} . The present investigations for OH in amphibole minerals seem applicable to a wide spectrum of oxide and silicate minerals. Because large groups of hydrous minerals like acid phosphates, arsenates, sulfates, a recommendation for these minerals to be investigated. Rather, the different structure's drive the hydrogen bonding, and because most of the O-H vibration (stretching or bending, modes) is in the strength (correlated with the wave number of the bond) determines the absorbance (intensity) instead of the remaining structure.

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