LETTERS

Short-range order of (Na,K) and Al in tremolite: An infrared study

FRANK C. HAWTHORNE,[1] GIANCARLO DELLA VENTURA,[2] AND JEAN-LOUIS ROBERT[3]

[1]Department of Geological Sciences, University of Manitoba, Winnipeg, Manitoba R3T 2N2, Canada
[2]Dipartimento di Scienze Geologiche, Terza Università di Roma, via Ostiense 169, I-00154 Rome, Italy
[3]CRSC-CNRS, 1A Rue de la Ferollerie, F-45071 Orléans Cedex 2, France

ABSTRACT

Assignment of the component bands in the infrared spectrum of tremolite containing ^{A}(Na,K) and ^{T}Al shows that the nontremolite components in the crystal are not randomly distributed throughout the structure but show extreme short-range order. Na and K at the A site are locally associated with Al at an adjacent T1 site.

INTRODUCTION

There has been much crystal-structure work on amphiboles, focusing in particular on the ordering of cations over nonequivalent sites. We now have a reasonably comprehensive knowledge of long-range ordering (LRO) in amphiboles. The same cannot be said for short-range ordering (SRO). Crystal-structure refinement provides us with only a long-range average view of the structure and cannot directly give us information on SRO. However, SRO is very important in (1) understanding some crystal-chemical couplings within the amphibole structure, (2) developing accurate expressions for configurational entropy, and (3) developing realistic activity models for amphiboles. This is true particularly for SRO connected with polyvalent-cation substitutions in amphiboles, and infrared spectroscopy in the principal OH-stretching region is a particularly sensitive probe of such local configurations.

EXPERIMENTAL METHODS

All synthetic amphiboles examined here were crystallized at 750 °C, 1 kbar P_{H_2O}, as described by Della Ventura et al. (1993). The tremolite was characterized in detail by Hawthorne and Grundy (1976) and designated tremolite 56 by Hawthorne (1983). Infrared spectra of synthetic tremolite, synthetic richterite, and a synthetic tremolite-potassium-richterite solid solution of composition $TR_{80}KR_{20}$ were recorded on a Perkin-Elmer model 1760 spectrometer equipped with a DTGS detector and a KBr beamsplitter operating at a nominal resolution of 1 cm^{-1}. The spectrum of tremolite was recorded on a microscope equipped with a nitrogen-cooled MCT detector operating at a nominal resolution of 2 cm^{-1}.

RESULTS

Infrared spectra for the amphiboles are shown in Figure 1. The spectrum of synthetic tremolite (Fig. 1a) consists of a sharp, slightly asymmetric band at 3674 cm^{-1}. The spectrum of synthetic richterite (Fig. 1c) consists of a broad fairly symmetric band at 3730 cm^{-1} and a weak band at 3674 cm^{-1}. The spectrum of synthetic $TR_{80}KR_{20}$ (Fig. 1d) consists of two broad bands at 3735 and 3672 cm^{-1}. The spectrum of tremolite 56 consists of a broad, slightly asymmetric band at 3670 cm^{-1}, a broad band at 3705 cm^{-1}, a weak shoulder at 3730 cm^{-1}, and a weak band at ~3640 cm^{-1}. To determine the positions of the higher frequency bands more precisely, this part of the spectrum was fitted to two Gaussian curves by least-squares refinement; the fit is shown by the dotted curves in Figure 1b.

DISCUSSION

The band assignments of the spectra (Fig. 1) are summarized in Table 1. All the amphiboles examined here have M1 = M2 = M3 = Mg (except possibly for a very small amount of Al in tremolite 56), and all bands in the principal OH-stretching region may be assigned to the local configuration MgMgMg-OH. Thus, the different bands in the spectra shown in Figure 1 must be assigned to local configurations adjacent to the MgMgMg-OH arrangement. There is one band in synthetic tremolite, occurring at 3674 cm^{-1} (Fig. 1a), and this band must be assigned to the local configuration MgMgMg-OH-$^A\square$-^{T1}Si (i.e., the configuration MgMgMg-OH associated with a vacancy at the adjacent A site and Si at the adjacent T1 sites). This band is also present in synthetic nominal end-member richterite (Fig. 1c); previous studies (Della Ventura 1992; Robert et al. 1989) have assigned this band to the MgMgMg-OH-$^A\square$-^{T1}Si configuration and have used the presence of this band as evidence that synthetic nominal end-member richterite departs significantly from its ideal composition. A similar band is also observed in synthetic nominal end-member potassium-richterite and has been assigned to the same local configuration (Table 1). This assignment is further supported by the higher intensity of the 3674 cm^{-1} band in synthetic tremolite-

potassium-richterite solid solutions (Fig. 1d). The strong band at 3674 cm^{-1} in tremolite 56 may be assigned in the same fashion to the local configuration MgMgMg-OH-$^A\square$-^{T1}Si.

In the spectrum of synthetic richterite (Fig. 1c), the most intense band is at 3730 cm^{-1} and is assigned to the configuration MgMgMg-OH-^{A}Na-^{T1}Si. In the spectrum of synthetic potassium-richterite, the most intense band is at 3735 cm^{-1} (cf. Fig. 1d) and is assigned to the configuration MgMgMg-OH-^{A}K-^{T1}Si. In natural amphiboles, in which disorder causes significant band broadening in the infrared spectra, resolution of bands for configurations involving ^{A}Na and ^{A}K is usually not observed. Thus, we assign the weak 3730 cm^{-1} band in the spectrum of tremolite 56 (Fig. 1b) to the local configuration MgMgMg-OH-^{A}(Na,K)-^{T1}Si.

The prominent band at 3705 cm^{-1} in the spectrum of tremolite 56 (Fig. 1b) does not correspond to any band observed in synthetic richterite or synthetic tremolite and must therefore correspond to another local configuration. The unit formula of tremolite 56 is $(K_{0.12}Na_{0.23})(Ca_{1.81}Na_{0.15}Fe_{0.01}Mg_{0.03})(Mg_{4.98}Al_{0.02})(Si_{7.79}Al_{0.21})O_{22}(OH)_{1.33}F_{0.67}$ (Hawthorne and Grundy 1976). The principal departures from an ideal tremolite formula involve Na and K at the A site, Al at the T sites, and F at the O3 site. Possible local configurations in tremolite 56 are listed in Table 2. First, let us consider the effect of F at an adjacent O3 site (Configuration 2, Table 2). As shown by Robert et al. (1989), this configuration results in an additional band at 3714 cm^{-1} in both richterite and potassium-richterite. In tremolite, substitution of F for OH does not result in an additional band (Della Ventura et al., in preparation) but causes a reduction in the intensity of the main tremolite band at 3674 cm^{-1}. Substitution of Al for Si in micas reduces the frequency of the principal band by ~25 cm^{-1}. Because the local arrangement around OH in richterite and potassium-richterite is similar to that in Si-rich micas, substitution of Al for Si in a local richterite configuration would reduce the frequency of the principal OH-stretching band by ~25 cm^{-1}: 3730 − 25 = 3705 cm^{-1}. Substitution of Al for Si in a local tremolite-like configuration would reduce the frequency of the principal OH-stretching band by >25 cm^{-1} because there is no A cation to compensate for the local reduction in bond valence around the bridging anions, and hence the increase in hydrogen bond interaction would be greater than the corresponding change in a richterite-like configuration. Thus, the corresponding band would occur at 3674 − (>25) = <3649

$\longrightarrow$
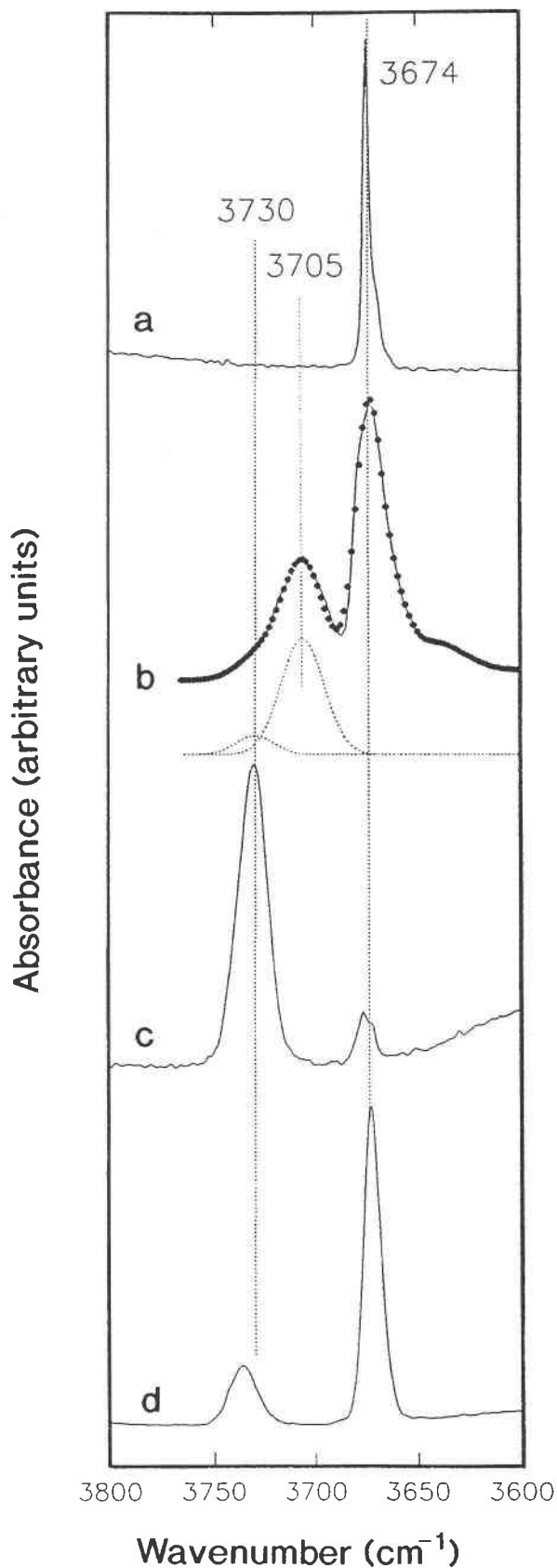
FIGURE 1. Infrared absorption spectra in the principal OH-stretching region for (a) synthetic tremolite; (b) tremolite 56 of Hawthorne and Grundy (1976); (c) synthetic richterite with minor tremolite component; (d) synthetic tremolite–potassium-richterite of composition TR$_{80}$KR$_{20}$. The dotted curves in b denote the two component bands of the higher energy peak in the spectrum, and the vertical dotted lines show the position of the component bands in b relative to the peaks in the other spectra.

TABLE 1. Band positions and assignments for the synthetic amphiboles of Figure 1

Spectrum	Figure	Band (cm^{-1})	Assignment
Tremolite	1a	3674	MgMgMg-OH-^{A}□-^{T1}Si
Richterite	1c	3730	MgMgMg-OH-^{A}Na-^{T1}Si
		3678	MgMgMg-OH-^{A}□-^{T1}Si
Potassium-richterite	1d	3734	MgMgMg-OH-^{A}K-^{T1}Si
Tremolite 56	1b	3674	MgMgMg-OH-^{A}□-^{T1}Si

TABLE 2. Possible local configurations and predicted band frequencies for tremolite 56

MgMgMg-OH configuration	A	O3	T1	Frequency (cm^{-1})
1	(Na,K)	OH	Si	3730
2	(Na,K)	F	Si	3714
3	(Na,K)	OH	Al	3705
4	(Na,K)	F	Al	3689
5	□	OH	Si	3674
6	□	F	Si	3674
7	□	(OH,F)	Al	<3649

cm^{-1}. The remaining possible configuration involves Na and K at the A site, F at the adjacent O3 site, and Al at an adjacent T1 site. As Al → Si and F → OH substitutions reduce the frequency of the principal OH-stretching band by 25 and 16 cm^{-1}, respectively, Configuration 4 would result in a band at $3730 - 25 - 16 = 3689$ cm^{-1}.

We may now compare the band positions and local configurations of Table 2 with the observed bands (Fig. 1, Table 1) and the crystal composition. The weak intensity of the band at 3730 cm^{-1} is not in accord with all the A cations in tremolite 56 being involved in Configuration 1, even allowing for differences in molar absorptivity as a function of absorption energy (Skogby and Rossman 1991). Configuration 2 would result in a band at 3714 cm^{-1}, significantly displaced from the nearest absorption maximum at 3705 cm^{-1}. Configuration 2 is possibly present in a minor amount, but the spectrum is certainly not compatible with most of the F being involved in Configuration 2. Configuration 3 would result in a band at 3705 cm^{-1}, corresponding exactly with the second most intense absorption band in the spectrum of tremolite 56 (Fig. 1). This correspondence indicates that Configuration 3 is an important local-ordering pattern in tremolite 56. Configuration 4 has no corresponding band in the spectrum and hence is not present. Configurations 5 and 6 result in the band at 3674 cm^{-1}. Configuration 7 would result in a band below 3649 cm^{-1}, presumably corresponding to the very weak absorption band at ~3640 cm^{-1} (Fig. 1).

The relative band intensities cannot be quantitatively related to the relative concentrations of local configurations because the absorptivity is related to band frequency (Skogby and Rossman 1991) in a complex manner that is not currently well characterized (unpublished data).

Moreover, there is the potential for the occurrence of local configurations that involve F at adjacent O3 sites, and these are invisible to infrared spectroscopy. Despite these problems, it is apparent from the spectra of Figure 1 and the band assignments of Table 2 that the nontremolite components ^{A}(Na,K) and ^{T}Al in this crystal are not randomly distributed throughout the structure but show extreme short-range order.

REFERENCES CITED

Della Ventura, G. (1992) Recent developments in the synthesis and characterization of amphiboles: Synthesis and crystal chemistry of richterites. Trends in Mineralogy, 1, 153–192.

Della Ventura, G., Robert, J.-L., Bény, J.-M., Raudsepp, M., and Hawthorne, F.C. (1993) The OH-F substitution in Ti-rich potassium richterite: Rietveld structure refinement and FTIR and micro-Raman spectroscopic studies of synthetic amphiboles in the system K$_2$O-Na$_2$O-CaO-MgO-SiO$_2$-TiO$_2$-H$_2$O-HF. American Mineralogist, 78, 980–987.

Hawthorne, F.C. (1983) The crystal chemistry of the amphiboles. Canadian Mineralogist, 21, 173–480.

Hawthorne, F.C., and Grundy, H.D. (1976) The crystal chemistry of the amphiboles: IV. X-ray and neutron refinements of the crystal structure of tremolite. Canadian Mineralogist, 14, 334–345.

Robert, J.L., Della Ventura, G., and Thauvin, J.-L. (1989) The infrared OH-stretching region of synthetic richterites in the system Na$_2$O-K$_2$O-CaO-MgO-SiO$_2$-H$_2$O-HF. European Journal of Mineralogy, 1, 203–211.

Skogby, H., and Rossman, G.R. (1991) The intensity of amphibole OH bands in the infrared absorption spectrum. Physics and Chemistry of Minerals, 18, 64–68.