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CHARACTERIZATION OF OH–F SHORT-RANGE ORDER IN POTASSIUM-FLUOR-RICHTERITE BY INFRARED SPECTROSCOPY IN THE OH-STRETCHING REGION

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ABSTRACT

The infrared spectrum of a sample of potassium-fluor-richterite (PFR) is compared with that of a synthetic "potassium-richterite" having a similar OH–F content. The PFR spectrum shows an additional absorption band with respect to the synthetic sample, and this is assigned to a configuration involving $^{[T1]}$Al. The spectra show that there is strong short-range order of OH in the structure of PFR, that involves coupling between H and (Si,Al) rings of tetrahedra in response to the bond-valence requirements on the bridging atoms of oxygen in Al–O–Si dimers of tetrahedra.

Keywords: potassium-fluor-richterite, FTIR spectroscopy, O–H-stretching region, OH–F short-range order.

SOMMAIRE

Nous comparons le spectre infra-rouge d'un échantillon de potassium-fluor-richtérite (PFR) avec celui d'un échantillon synthétique de "potassium-richtérite" ayant une proportion semblable de OH et de F. Le spectre de PFR contient une absorption additionnelle par rapport à l'échantillon synthétique, que nous attribuons à un agencement impliquant $^{[T1]}$Al. Le spectre montre qu'il y a mise en ordre à courte échelle des groupes OH dans la structure de PFR, impliquant un couplage entre H et les anneaux de tétraèdres (Si,Al) suite aux exigeances des valences de liaison des atomes d'oxygène assurant le pont dans les dimères de tétraèdres Al–O–Si.

(Traduit par la Rédaction)

Mots-clés: potassium-fluor-richtérite, spectroscopie dans l'infra-rouge, région de l'étirement O–H, mise en ordre OH–F à courte échelle.

INTRODUCTION

In the last few years, there has been much crystal-structure work on amphiboles, and we now have a good understanding of long-range order (LRO) in the amphibole structure. However, our understanding of short-range order (SRO) is still incomplete. Infrared spectroscopy in the OH-stretching region is sensitive to both LRO and SRO. It has a great potential to characterize SRO in OH-bearing minerals (Della Ventura 1992, Della Ventura *et al.* 1996a, Hawthorne *et al.* 1996a). For amphiboles, infrared (IR) spectroscopy was used extensively in the late 1960s. However, the method soon fell into disuse because of the many problems involved in the interpretation of the spectra (*e.g.*, Hawthorne *et al.* 1996a). Recent systematic work on synthetic amphiboles has provided us with a good understanding of band assignments correlated to unique solutions of the cation arrangements around the O–H dipole (Della Ventura 1992). Furthermore, we now know how to fit single components to the experimental envelopes involving overlapping bands (Della Ventura *et al.* 1996a, b). The latter method has been applied to derive SRO information for Na, K and Al in tremolite

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(Hawthorne *et al.* 1996b). Here we discuss the results obtained on potassium-fluor-richterite (PFR), and show that careful examination of the OH-stretching spectrum of amphiboles provides detailed information on local structure.

Experimental details

The synthetic amphibole examined here was obtained at 750°C and a P(H_2O) of 1 kbar by Robert *et al.* (1989). Powder infrared spectra were recorded at room temperature on a Perkin–Elmer 1760 spectrophotometer equipped with a KBr beam splitter and a DTGS detector. Both samples were prepared as KBr pellets. Details of sample preparation and run conditions may be found in Robert *et al.* (1989). Digitized spectra were fitted by interactive optimization followed by least-squares refinement, using the PEAKFIT system of programs provided by the Jandel Corporation. The background was modeled to be linear, and all peaks were modeled as being Gaussian (Strens 1974), following the method and the spectrum-fitting philosophy described in Della Ventura *et al.* (1996a). In short, the spectra were fitted with the smallest number of peaks needed for an accurate description of the spectral profile. For each component peak, the spectral parameters were fixed at values derived from previous studies on synthetic amphiboles. The final R^2 is equal to 0.99 for both samples.

RESULTS

Figure 1 shows the FTIR spectrum of PFR in the OH-stretching region compared with the spectrum of a synthetic (OH–F) equivalent of PFR, here called "potassium-richterite", from Robert *et al.* (1989). The spectrum of PFR (Fig. 1a) shows a very broad band centered at 3710 cm^{-1}, a weaker band at 3670 cm^{-1}, and a very weak component at 3730 cm^{-1} on the high-frequency tail of the main broad band. The spectrum of synthetic (OH–F) "potassium-richterite" (Fig. 1b) consists of a well-defined doublet at 3735–3714 cm^{-1} plus a weaker band at 3670 cm^{-1}.

Interpretation of the spectra

The band assignment for synthetic samples of (OH,F)-richterite is well known from the work of Robert *et al.* (1989, 1995a). End-member richterite shows a main band at 3735–3730 cm^{-1} due to the vibration of an O–H dipole directly bonded to three octahedrally coordinated Mg cations facing a ring of tetrahedra of composition Si_6 and directed toward K or Na at the *A* site. In intermediate (OH–F) samples, a new band appears in the spectrum of synthetic richterite, centered at 3714 or 3710 cm^{-1}, respectively, for K and Na at *A*. The position of this band is constant for varying amounts of F in the amphibole, whereas its intensity is directly correlated to the amount of F present. This band is assigned to a local OH–$^{[A]}$(K,Na)–F configuration (Robert *et al.* 1989). Finally, the weak band at 3670 cm^{-1} is assigned to local OH–$^{[A]}\square$–OH configurations ($\square$: vacancy), *i.e.*, to tremolite-like configurations, and indicates that richterite departs from its ideal composition (Robert *et al.* 1989, Hawthorne *et al.* 1996b). These band assignments are summarized in Table 1.

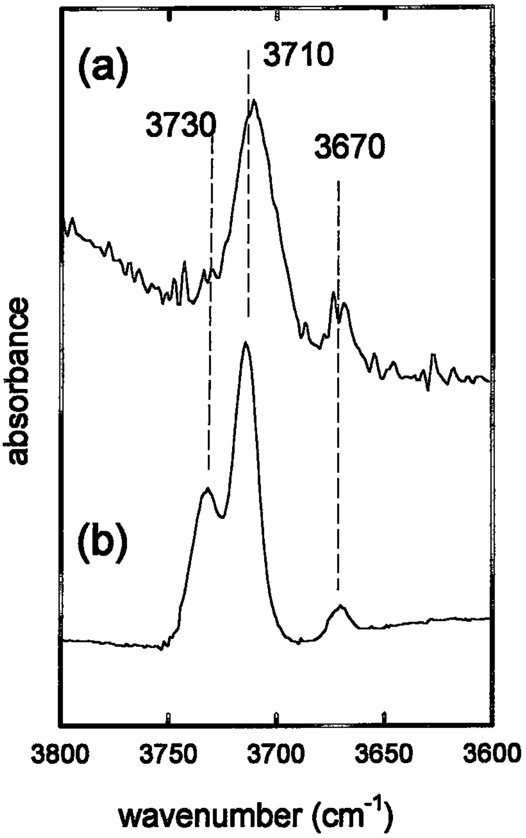

FIG. 1. FTIR spectra in the OH-stretching region of (a) potassium-fluor-richterite and (b) synthetic "potassium-richterite" with an anion composition ($F_{1.2}OH_{0.8}$).

The PFR sample examined here is well characterized from chemical and structural points of view (Della Ventura *et al.* 1992, Oberti *et al.* 1992, sample R3). Its anionic composition is $F_{1.26}OH_{0.74}$, and it contains virtually only Mg at the octahedral sites, so that the bands present in its IR spectrum *must* be assigned to configurations adjacent to MgMgMg–OH arrangements. Thus the main band at 3710 cm^{-1} is assigned to the OH–$^{[A]}$(K,Na)–F configuration, and the weak bands

TABLE 1. SUMMARY OF BAND POSITIONS AND ASSIGNMENTS FOR SYNTHETIC AMPHIBOLES AND PFR

	A	O3	*T*1	λ, cm^{-1}	ref.
MgMgMg–OH	Na,K	OH	Si	3730	(1)
MgMgMg–OH	Na,K	F	Si	3710	(1)
MgMgMg–OH	Na,K	OH	Al	3705	(2)
MgMgMg–OH	Na,K	F	Al	3694	(3)
MgMgMg–OH	□	OH	Si	3670	(1)

(1) Robert *et al.* (1989), (2) Semet (1973), (3) Robert *et al.* (1995b).
PFR: potassium-fluor-richterite.

at 3730 and 3670 cm^{-1}, to the OH–$^{[A]}$(K,Na)–OH and OH–$^{[A]}$□–OH configurations, respectively. Note that although the microprobe-derived crystal-chemical formula given below shows the *A* site to be fully occupied in PFR, the single-crystal X-ray structural refinement indicates that the amphibole in fact contains a small amount of empty *A*-sites (Oberti *et al.* 1992), and these show up in the IR spectrum, since IR spectroscopy is very sensitive to such local features (Hawthorne *et al.* 1996b).

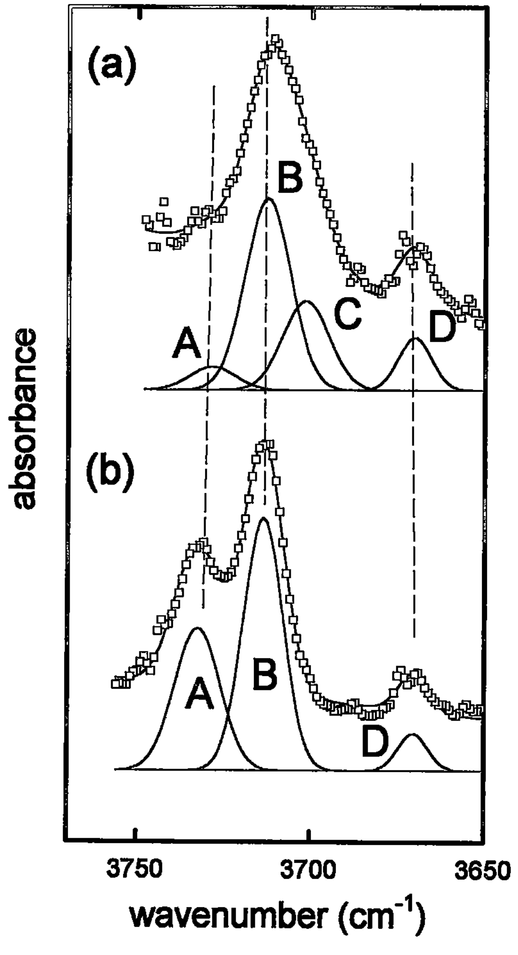

FIG. 2. Same spectra as in Figure 1, decomposed into single Gaussian peaks.

The studies of Robert *et al.* (1989, 1995a) and Robert *et al.* (1998) on synthetic fluorine-substituted richterite and "potassium-richterite" show that the absorbance of the 3730(3710) cm^{-1} band *versus* total absorbance is linearly correlated to the OH(F) content of the amphibole. It is clear from Figure 1 that the intensities of the 3730 and 3710 cm^{-1} bands are not compatible with the OH,F composition of PFR. Note that the synthetic sample has an anionic composition very close to that of PFR. The most striking difference between the spectra of Figure 1 is the width of the main band at 3710 cm^{-1} of the natural PFR sample, which is significantly larger than that of the corresponding peak of the synthetic sample. This suggests the presence of other components that partly overlap with the 3710 cm^{-1} band in PFR.

Both spectra of Figure 1 were decomposed into single bands. The results are shown in Figure 2, whereas Table 2 gives the refined spectral parameters. From Figure 2a, it is apparent that the broad envelope centered at 3710 cm^{-1} in the spectrum of PFR is the result of three overlapping components (A, B and C), whereas the spectrum of synthetic (OH,F)-richterite has only two bands in the same spectral range. Note that the spectral parameters (shape and width) used in the decomposition of the PFR spectrum have been fixed at values derived from the spectrum of the synthetic sample, whereas the peak positions and intensity were not constrained during refinement. From Figure 2a, it is apparent that bands A, B and D correspond to the configurations already described for the synthetic sample (Table 1), whereas band C, which is responsible for the broadening and asymmetry of the 3710 cm^{-1} band, corresponds to none of the configurations

TABLE 2. POSITIONS (cm^{-1}), WIDTHS (cm^{-1}) AND RELATIVE INTENSITIES (PEAK AREAS NORMALIZED TO ONE) FOR THE A–D BANDS IN THE INFRARED OH–STRETCHING SPECTRA OF THE AMPHIBOLES STUDIED

	Parameter	PFR	Synthetic
A	Position	3729.1	3732.8
	Width	16.2	15.9
	Intensity	0.10	0.37
B	Position	3712.4	3714.3
	Width	15.8	13.2
	Intensity	0.56	0.59
C	Position	3701.0	—
	Width	15.8	—
	Intensity	0.24	—
D	Position	3670.4	3670.4
	Width	11.3	9.7
	Intensity	0.10	0.04

PFR: potassium-fluor-richterite.

considered previously. The unit formula of PFR is (neglecting components present in very low amounts): $(K_{0.67}Na_{0.34})(Ca_{1.09}Na_{0.91})(Mg_{4.98}Fe_{0.02})(Si_{7.94}Al_{0.04})O_{22}(OH_{0.74}F_{1.26})$ (Della Ventura *et al.* 1992). The principal departures of PFR from an ideal (OH–F) richterite involve the presence of (i) small amounts of $^{[T1]}$Al, and (ii) very small amounts of (Fe^{2+} + Mn) at the octahedral sites.

The position of band C closely corresponds to a configuration involving Al in the double chain of tetrahedra, *i.e.*, to a local pargasite-like configuration (Semet 1973, Raudsepp *et al.* 1987, Della Ventura *et al.* 1997). Band C is therefore assigned to the MgMgMg–OH–$^{[A]}$Na–(Si,Al) configuration.

OH–F distribution in natural richterite

The bands present in the spectrum of Figure 2a, together with the band-assignment discussed above, lead to the following crystal-chemical considerations concerning the distribution of cations in PFR:

i) In the spectrum of PFR, band B must be correlated with the amount of F in the amphibole. The intensity of this band, after decomposition of the broad absorption at 3710 cm^{-1}, is approximately 60% of the total absorbance (Table 2) and corresponds to 1.2 atoms of F per formula unit (*apfu*) in the amphibole. This value is in excellent agreement with the crystal-chemical formula of this amphibole, and indicates that the model used here is a good one.

ii) The intensity of band A at 3730 cm^{-1} is much weaker than the intensity of the corresponding band in the spectrum of the synthetic sample with a similar anion composition, and is not in accord with all the OH groups in the natural amphibole being involved in the OH–$^{[A]}$(K,Na)–Si_6 configuration (richterite configuration, Table 1). Conversely, we note that the combined intensity of bands A + C closely corresponds to the amount of OH in the amphibole. This suggests that there is no F associated with hexagonal rings of composition $(Si,Al)_6$. In other words, there is strong SRO of F, which is preferentially associated with the richterite-like configuration, and in turn, there is strong SRO of H, which is preferentially associated with $(Si,Al)_6$ rings of tetrahedra. This conclusion is also supported by the absence of a band at 3694 cm^{-1} (Table 1) which is associated with the distribution of OH and F in pargasite (Robert *et al.* 1995b). Monoclinic amphiboles show two kinds of behavior in the OH-stretching region with respect to OH–F substitution: (1) in tremolite, the OH-band simply decreases in intensity for increasing F content at the O(3) site (one-mode behavior); (2) in richterite, there is the appearance of a second lower-frequency band, which increases in intensity with increasing F content of the amphibole (two-mode behavior). The recent work of Robert *et al.* (1998) shows that two-mode behavior of richterite must be due to coupling between NNN (next-nearest-neighbor) O(3) anions across the *A*-site cavity through the A cation. This being the case, the absence of the 3694 cm^{-1} band suggests that configurations such as (Si,Al)–OH–$^{[A]}$(K,Na)–OH–(Si,Al) must also be locally associated, and that configurations like (Si,Al)–OH–$^{[A]}$(K,Na)–F–Si_6 are avoided. Any OH group in this latter configuration, even if locally SR-ordered close to $(Si,Al)_6$ rings, will absorb at 3694 cm^{-1}.

Similar OH–F SR-ordering has recently been shown in synthetic (OH,F) Al-rich phlogopite (Papin *et al.* 1997) and is also observed in intermediate richterite – pargasite synthetic amphiboles with varying OH–F content (Robert & Della Ventura, unpubl. data).

Finally, the intensity of band C of PFR seems too high for the small amount of $^{[T1]}$Al in the amphibole. This discrepancy is readily explained considering (i) the presence of some Fe^{2+} (+Mn) at *M*(1,3), and (ii) the possible inhomogeneity of the crystals used to prepare the KBr pellet. Regarding point (i), it is well known (Della Ventura *et al.* 1966b) that where a divalent cation substitutes for Mg at *M*(1,3), the relative OH-stretching band is shifted to lower frequency (to a value near 3705 cm^{-1}). Regarding point (ii), it must be noted that the microchemical formula of PFR given above pertains to the single grain used for crystal-structure refinement, whereas the KBr pellet was prepared by crushing several small grains whose Al content could vary somewhat. Another source of discrepancy, probably the most likely, could involve a possible difference in molar absorptivity (Skogby & Rossman 1991) between the local richterite-like (Al-free) and the pargasite-like (Al-rich) environments.

Despite these problems, it is apparent from the spectra of Figure 2 that there is strong short-range order involving F, giving rise to the band at 3710 cm^{-1} in the spectrum of PFR. The proposed SRO of H associated to $(Si,Al)_6$ rings of tetrahedra in richterite can be explained by considering the local environment of the OH-group in Al-bearing amphiboles. In pargasite, the H atom is in such a position to form a H-bond with the closest O(7) anion (Hawthorne 1983); in fact, it is the strength of this interaction that causes the frequency of the OH-stretching vibration to be lower than for the corresponding OH groups associated with Si_6 rings (Della Ventura *et al.* 1997). Therefore, in a structure with mixed Si_6 and $(Si,Al)_6$ environments of tetrahedra, H will associate preferentially with $(Si,Al)_6$ rings such as to provide extra bond-valence contribution *via* a weak H-bond to O(7) bridging Al–O–Si linkages. Although this is a relatively small effect, it may be sufficiently significant to lead to local H–$(Si,Al)_6$ SRO. Short-range ordering of OH and F is therefore likely to be relevant to the majority of (OH,F)-amphiboles, as also suggested by preliminary spectroscopic data collected on synthetic (OH,F)-pargasite (Robert *et al.* 1995b; M. Welch, pers. commun.).

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