*American Mineralogist, Volume 84, pages 86–91, 1999*

# Near-infrared study of short-range disorder of OH and F in monoclinic amphiboles

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

[1]Centre de Recherche sur la Synthèse et la Chimie des Minéraux, and FR 09, CNRS, 1A, rue de la Férollerie, 45071 Orléans Cedex 2, France

[2]Dipartimento di Scienze Geologiche, Università di Roma Tre, Largo S. Leonardo Murialdo 1, I-00146 Rome, Italy

[3]Department of Geological Sciences, University of Manitoba, Winnipeg, Manitoba, Canada R3T 2N2

## ABSTRACT

Amphiboles were synthesized along the joins tremolite–fluorotremolite, richterite–fluororichterite and potassic-richterite–potassic-fluororichterite at 750 °C and 1 kbar $P(H_2O)$. Infrared spectra of the amphiboles were recorded in the principal OH-stretching region. Amphiboles of the tremolite–fluorotremolite series show one-mode behavior, a single band due to a local MgMgMg-OH-$^{A}\square$ ($\square$ = vacancy) arrangement; this behavior is consistent with no coupling between NNN (next-nearest-neighbor) O3 anions either through the O3-O3 edge or across the vacant A-site cavity. The amphiboles of the richterite-fluororichterite and potassic-richterite–potassic-fluororichterite series show two-mode behavior, two bands due to the local arrangements MgMgMg-OH-$^{A}$Na-OH and MgMgMg-OH-$^{A}$Na-F (and their K equivalents); this behavior is consistent with coupling between NNN O3 anions across the filled A-site cavity through Na or K that occupies the A-site. A mathematical model is developed to describe local (OH,F) ordering in amphiboles as a function of F content. The variation in infrared band intensities is consistent with complete short-range disorder of OH and F in the synthetic amphiboles of the richterite-fluororichterite and potassic-richterite-potassic–fluororichterite series.

## INTRODUCTION

In the last fifteen years, crystal-structure research on amphiboles has provided a fairly good knowledge of long-range order (LRO). However, our knowledge of short-range order (SRO) is negligible owing to the fact that we still need to develop methods that can easily characterize SRO in rock-forming minerals. Infrared spectroscopy in the OH-stretching region is sensitive to both LRO and SRO, and has great potential in this regard for OH-bearing minerals (Della Ventura 1992; Della Ventura et al. 1996; Hawthorne et al. 1996a). Nominal fluorine end-member amphiboles have been widely used in thermodynamic (Westrich and Navrotsky 1981; Graham and Navrotsky 1986) and crystal-structure studies (Cameron et al. 1983; Raudsepp et al. 1987a, 1987b, 1991; Welch et al. 1994; Boschmann et al. 1994; Oberti et al. 1995), but little is known about OH-F ordering in intermediate compositions. Here, we apply IR spectroscopy in the OH-stretching region to the problem of characterizing SRO of OH and F in the amphibole structure.

## EXPERIMENTAL METHODS

The amphiboles were synthesized at 750 °C, 1 kbar $P(H_2O)$ by Robert et al. (1989). These synthetic richterite crystals are elongated, with a length generally not exceeding 20 μm, and with a length/diameter ratio around ten (Della Ventura et al. 1993a). Previous HRTEM examinations showed that these amphiboles are essentially free of chain-multiplicity and chain arrangement faults (Hawthorne et al. 1997). WDS electron-microprobe analysis (EMPA) for F was done with a CAMECA SX 50 operated at 15 kV, 6 nA beam current, for a counting time of 10 s, both on peak and on background. Natural topaz was used as a standard. Samples were prepared by embedding a few milligrams of run product in epoxy resin. After polishing, enough crystals were found to be suitable for EMPA. Powder infrared spectra were recorded at room temperature on a Nicolet 800 spectrophotometer, equipped with a $CaF_2$ beamsplitter and a nitrogen-cooled MCT detector operating at a nominal resolution of 2 $cm^{-1}$. The conventional KBr pellet method was used, with a sample/KBr ratio of 0.1, for a total of 150 mg. Details of sample preparation may be found in Robert et al. (1989). Thirty-two scans were averaged for each spectrum.

Spectra were fitted by interactive optimization followed by least-squares refinement using symmetrical Gaussian line-shapes, following the method described in Della Ventura et al. (1996). There are two prominent peaks in the spectra of end-member OH-richterites, and there are three prominent peaks in the spectra of F-bearing richterites, here labeled A, B and C (Fig. 1). The results of the peak fitting are in Table 1.

* E-mail: jlrobert@cnrs-orleans.fr

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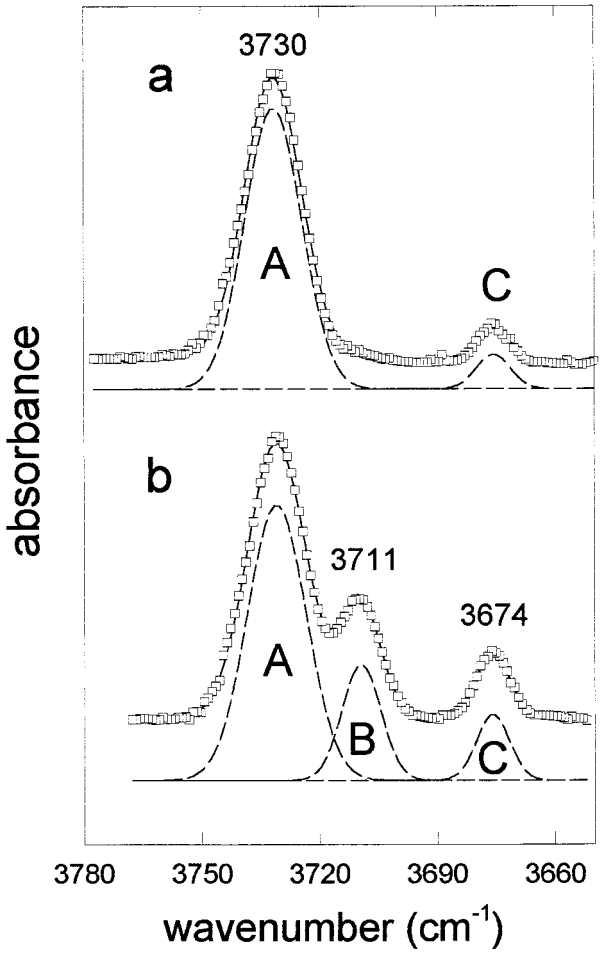



**FIGURE 1.** Peak fits to the IR spectra of synthetic end-member richterite (**a**) and fluororichterite (**b**) with nominal F = 1.2 apfu. Absorbance in arbitrary scale. Pots = spectral data. Dashed lines = Gaussian components. Solid line = sum of Gaussians. Band nomenclature: A = OH group facing Na at A-site, in OH-Na-HO configuration; B = OH group facing Na at A-site, in OH-Na-F configuration; and C = OH group pointing toward a vacant A-site.

## MICROPROBE ANALYSIS

The F content (Fig. 2) could be measured by EMPA for the Na-(OH-F) series only. Among several point analyses done on each sample, only those giving total oxides ≥93 wt% were considered reliable. EMP analyses show that the measured F content is systematically lower than the nominal one, especially for high F contents in the system. This discrepancy is typical of F-bearing silicates grown under hydrothermal conditions (Robert et al. 1989, 1993).

## INFRARED SPECTROSCOPY

### (OH,F)-tremolite

Figure 3 shows the OH-stretching spectra of tremolite with differing (OH,F) content. For increasing amounts of F in the amphibole, no new bands are observed in the OH-stretching region; the single band at 3674 $cm^{-1}$ simply decreases in intensity.

**TABLE 1.** Relative intensities of the principal OH-stretching bands

| $F_{nom}$ | A | B | C |
|---|---|---|---|
| 0.0* | 0.94 | 0.00 | 0.06 |
| 0.2* | 0.71 | 0.20 | 0.09 |
| 0.4* | 0.51 | 0.40 | 0.09 |
| 0.6* | 0.33 | 0.58 | 0.09 |
| 0.8* | 0.18 | 0.72 | 0.09 |
| 1.0* | 0.04 | 0.90 | 0.06 |
| 0.0† | 0.94 | 0.00 | 0.06 |
| 0.2† | 0.72 | 0.23 | 0.05 |
| 0.4† | 0.55 | 0.41 | 0.04 |
| 0.6† | 0.37 | 0.59 | 0.04 |
| 0.8† | 0.18 | 0.75 | 0.06 |
| 1.0† | 0.08 | 0.84 | 0.08 |

*Notes:* A, B, C nomenclature refers to Figure 1.
* Synthetic amphiboles along the richterite–fluororichterite series as a function of the nominal F content, F(nom) in apfu.
† Along the potassic-richterite–fluoro-potassic-richterite series.

### (OH,F)-richterites

The OH-stretching spectra of end-member richterite and potassic-richterite are well known (Robert et al. 1989; Della Ventura and Robert 1990; Della Ventura et al. 1991). There is a main band at 3735 or 3730 $cm^{-1}$ for K or Na at the A-site, respectively, plus a weaker band at 3675 $cm^{-1}$. The high-wavenumber band is assigned to an O-H dipole directed toward the A-cation, and the low-wavenumber band is assigned to an O-H dipole directed toward a vacant A-site (Robert et al. 1989). The presence of this second component in all spectra of synthetic and natural richterites indicates that richterite invariably departs from its ideal end-member composition (Hawthorne 1996; Hawthorne et al. 1997) of $Na_2CaMg_5Si_8O_{22}(OH)_2$.

For synthetic (OH,F)-richterites, the FTIR spectra in the OH-stretching region as a function of F content have been shown by Robert et al. (1989). When F replaces OH at the O3 site, a new band appears in the spectrum at 3714 or 3711 $cm^{-1}$, respectively, for $^{[A]}K$ or $^{[A]}Na$ (Fig. 1). The position of this new band is constant for any (OH,F) composition, and its relative intensity is a linear function of the F content of the amphibole (Robert et al. 1989). This behavior indicates the existence of two distinct configurations in the structure, and these must be assigned to local arrangements involving OH and F, as this is the only variable in the system.

## INTERPRETATION OF THE SPECTRA

The O3 site occurs on a mirror plane and is coordinated by two M1 and one M3 cations. When O3 is occupied by OH, the O-H bond is approximately orthogonal to (100). For the amphiboles examined here, M1 = M3 = Mg, and the nearest-neighbor environment is the same: MgMgMg-OH. Hence any spectral differences in these amphibole series must be due to differences in the next-nearest-neighbor environment. Two points need to be ad-

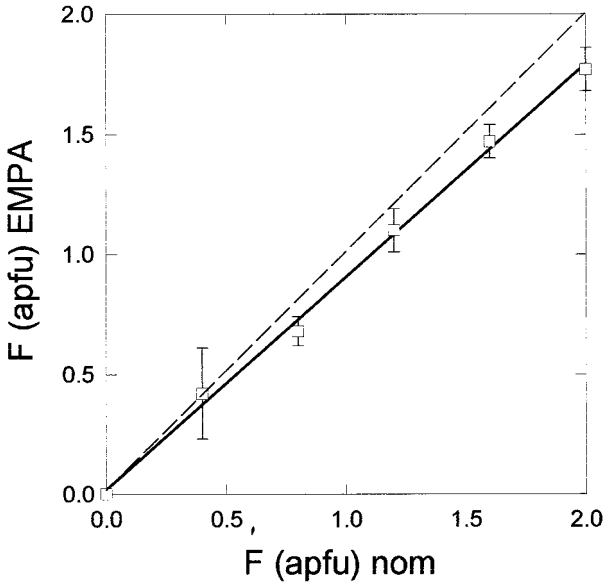



**FIGURE 2.** Relation between the nominal and EPM F contents for synthetic amphiboles for the (OH,F)-richterite series. The error bars are the uncertainties in the EMPA F content; the broken line is the 1:1 line and the bold line is the regression line to the data points.

dressed: (1) the different behavior of the OH-stretching bands of richterite and tremolite with respect to the OH/F substitution; and (2) the variation of the relative band intensities in the spectra of (OH,F)-tremolite and (OH,F)-richterite.

## THE BEHAVIOR OF THE OH-STRETCHING BANDS IN TREMOLITE AND RICHTERITES

Figures 1 and 3 reveal a different spectral response to the F → OH substitution for richterites and tremolite. Nominal end-member tremolite has a single OH-stretching band at 3674 $cm^{-1}$. With increasing F → OH substitution, the only change in the spectrum is a monotonic decrease in the intensity of this band; this is known as one-mode behavior (Chang and Mitra 1968). Nominal end-member richterite (potassic-richterite) has two OH-stretching bands at 3730 (3735) and 3674 (3674) $cm^{-1}$, labeled A and C in Figure 1. The A band is associated with an MgMgMg-OH-$^{A}\square$(Na,K) configuration (as in ideal end-member richterite and potassic-richterite) and the C band is associated with an MgMgMg-OH-$^{A}\square$ configuration (as in ideal end-member tremolite). With F → OH substitution, an additional band B appears at 3714 (3711) $cm^{-1}$ and grows in intensity at the expense of band A with increasing F → OH substitution. The response of bands A and B follows two-mode behavior (Chang and Mitra 1968) as an additional band appears with F → OH substitution. Note that band C exhibits one-mode behavior consistent with the behavior of (OH,F)-tremolite (Fig. 3), providing confirmation of the assignment of band C to the tremolite-like configuration MgMgMg-OH-$^{A}\square$.

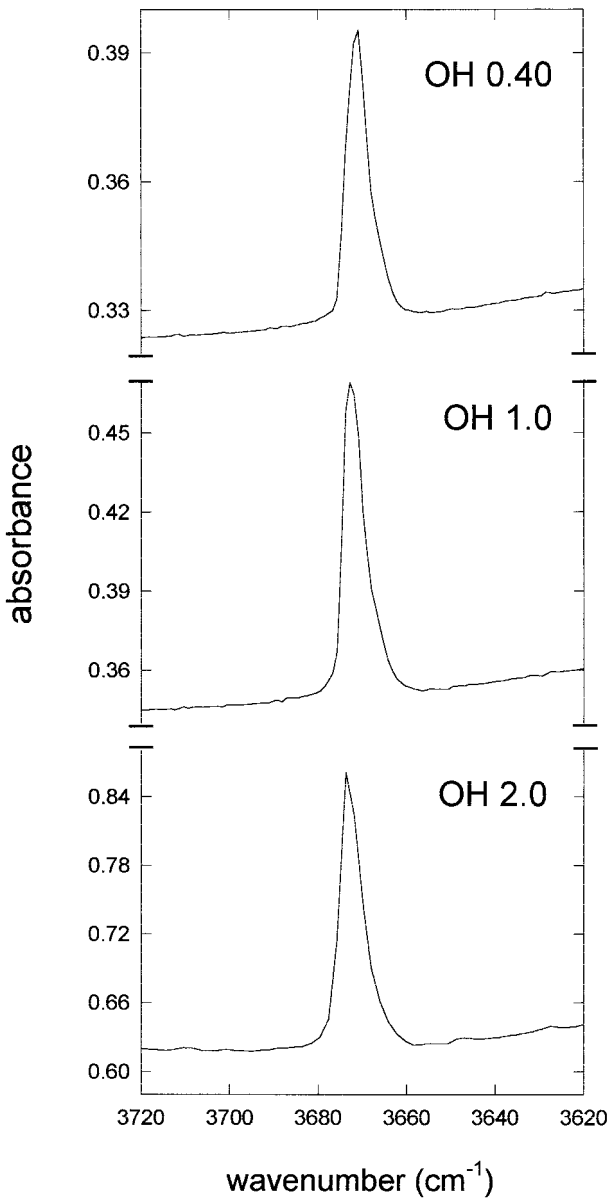



**FIGURE 3.** OH-stretching IR spectra of synthetic tremolites with differing nominal OH F contents (in apfu).

## THE STEREOCHEMISTRY OF LOCAL COUPLING WITHIN THE AMPHIBOLE STRUCTURE

The one-mode behavior of (OH,F)-tremolite indicates that local configurations involving an OH group are not significantly affected by adjacent configurations involving F. Hence we may conclude that there is no coupling between NNN O3 anions either through the O3-O3 edge in the octahedral strip or across the vacant A-site cavity. The two-mode behavior of (OH,F)-richterite and (OH,F)-potassic-richterite indicates that the local configurations involving an OH group in richterites are significantly affected by adjacent configurations involving F. Because the only difference between the tremolite and richterite series

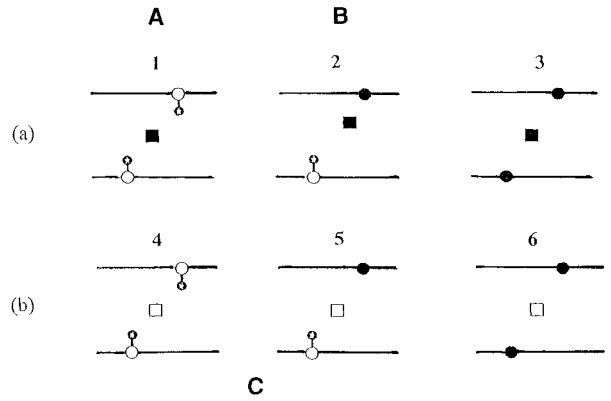



**FIGURE 4.** Local environments involving OH and F in the vicinity of the O3 [= OH] site in (**a**) (OH,F)-richterite; (**b**) (OH,F)-tremolite. Black circles = F; open circles = O; starred circles = H; black square = A-cation; open square = vacant A-site. 1–6 are reference numbers, see text.

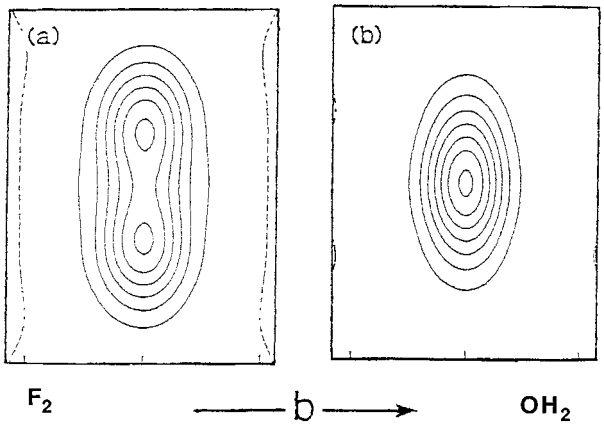



**FIGURE 5.** Electron-density distribution in the A cavity ′ojected onto (-201) in (**a**) fluoro-arfvedsonite, and (**b**) arfvedsonite; from Hawthorne et al. (1996b).

is that the A cation site is empty for tremolite (Fig. 4), we conclude that the two-mode behavior in (OH,F)-richterite must be due to coupling of configurations across the A-site cavity ''through'' Na or K that occupies the A site.

Let us consider the stereochemistry around the A cavity. First, comparison of the principal OH-stretching wavenumber in tremolite (3674 $cm^{-1}$) and richterite (3730 $cm^{-1}$) indicates that there is a strong repulsive interaction between H and $^{A}$Na in richterite. Second, comparison with the electron-density distribution in the A cavity for O3 = OH and O3 = F amphiboles (Fig. 5) indicates that Na occupies a more central position in the cavity when O3 = OH than when O3 = F. In turn, this indicates that an OH group will interact less strongly with $^{A}$Na when the opposing O3 site is occupied by F (Fig. 5a) than when it is occupied by OH (Fig. 5b). Thus, owing to a A–F attraction, the A-cation is displaced along the mirror plane, and this reduces the repulsive A–H interaction between the A-cation and the closest OH group. The OH-$^{A}$Na-F configuration should hence absorb at a lower wavenumber than the OH-$^{A}$Na-OH configuration, as is observed for band B (Fig. 1). This conclusion, that local coupling exist across an occupied A-site but not across an unoccupied A-site or along an O3-O3 edge, is extremely important in understanding the OH-stretching spectra of chemically more complex amphiboles (e.g., Della Ventura et al. 1998).

## LOCAL CONFIGURATIONS IN (OH,F)-RICHTERITES

The variation in relative band-intensities in the spectra of intermediate (OH,F)-richterite must be modeled considering all possible local arrangements around the OH group. All richterite samples have small but appreciable amounts of vacant A-sites in the structure, so that there are six configurations to consider (Fig. 4). Let $X$ = proportion of richterite component; $(1 - X)$ = proportion of tremolite component; $x$ = atomic fraction of F: $x = X_F$ = F/(F + OH); $n_i$ = probability of occurrence of local arrangement, with i = 1 to 6 (Fig. 4), such that $\Sigma n_i = 1$. Assuming no (OH,F) short-range order, the probabilities then can be written as: $n_1 = X(1 - x)^2$; $n_2 = 2X(1 - x)x$; $n_3 = Xx^2$; $n_4 = (1 - X)(1 - x)^2$; $n_5 = 2(1 - X)(1 - x)x$; and $n_6 = (1 - X)x^2$.

Thus, the individual band intensities ($I$) should vary as:

$$I_A \propto 2n_1 = 2X(1 - x)^2 \approx X(1 - x) \quad (1)$$

$$I_B \propto n_2 = 2X(1 - x)x \approx xX \quad (2)$$

$$I_C \propto 2n_4 + n_5 = 2(1 - X)(1 - x)^2 + 2(1 - X)(1 - x)x \approx 1 - X, \quad (3)$$

where the approximation on the right hand side assumes that the extinction coefficient of bands ABC are equal, i.e., that the total band intensity ($I_A + I_B + I_C$) is $2(1 - x)$. For this approximation, relative intensities must be compared.

## SHORT-RANGE DISORDER IN (OH,F)-RICHTERITES

There are six possible local configurations involving OH, F, $^{A}$(Na,K), and $^{A}\square$ in (OH,F)-richterites (Fig. 4), and derivation of information on their frequency of occurrence is complicated by configurations 3 and 6 being invisible to infrared spectroscopy in the principal OH-stretching region; and configurations 4 and 5 giving rise to degenerate principal OH-stretching bands. Thus, there are six unknown parameters and three observations (the intensities of the bands in the spectrum). In addition, the sum of the relative proportions of configurations 1–6 is constrained to equal unity. However, the equations are not soluble and hence we cannot deductively derive quantitative information on local ordering. Furthermore, there is the additional problem that the potassic-richterite bands (A and B) and the tremolite band (C) have different molar absorptivities (Hawthorne et al. 1997) and hence the intensities of these two sets of bands do not relate to the frequency of occurrence of the bands in the same way;

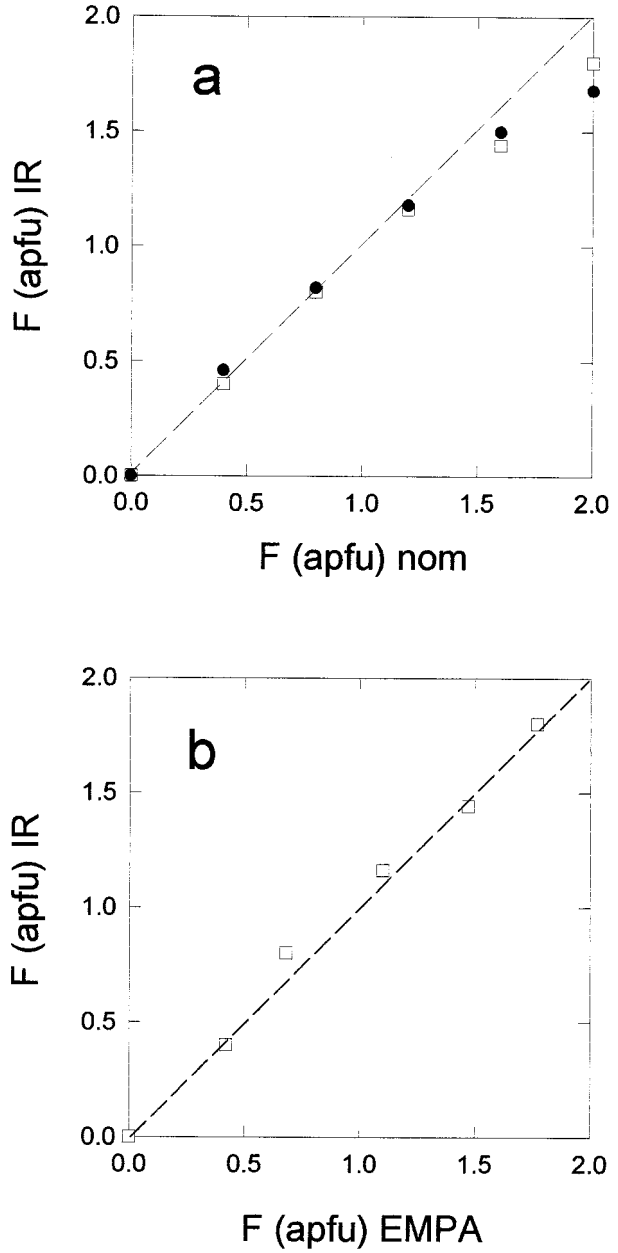



**FIGURE 6.** Comparison between (**a**) nominal- and IR-derived F content in Na-richterites (open symbols) and K-richterites (black dots). (**b**) The F content of Na-richterites measured by EMPA and derived by IR. The broken lines are the 1:1 lines.

the relative intensity of the C band will overestimate the frequency of occurrence of the corresponding local arrangements (4 and 5 in Fig. 4) by a factor ~2.2.

Despite these difficulties, we can test a model involving complete local disorder using the intensities of bands A and B, as the constituent configurations couple through the occupied A-site, and hence have the same molar absorptivity. Although we do not know the exact value of *X*, the variable is not involved in the *relative* intensity of the A and B bands. From Equations 1 to 3,

$$I_A/(I_A + I_B) = X(1-x)/[X(1-x) + Xx] = 1 - x \quad (4)$$

$$I_B/(I_A + I_B) = Xx/[X(1-x) + Xx] = x \quad (5)$$

The calculated and observed intensity ratios are shown in Figure 6a. The agreement is in accord with complete short-range disorder of OH and F in the richterite and potassic-richterite components of the synthetic richterite-fluororichterite and potassic-richterite-fluoro-potassic-richterite series. Figure 6b shows the relation between the F content measured by EMP and the values derived by infrared spectroscopy for the Na series. The excellent agreement between the two sets of data suggests that IR is a reliable tool for measuring OH/F contents, at least in chemically simple systems.

## ACKNOWLEDGMENTS

F.C.H. was supported by an Operating Grant from the Natural Sciences and Engineering Research Council of Canada. Thanks are due to O. Rouer (CRSCM-CNRS, Orléans) for helpful assistance in electron-microprobe analysis and to Mike Carroll for allowing us to use the IR spectrophotometer at the Department of Geology, University of Bristol. The constructive reviews by A. Beran and H. Skogby were greatly appreciated.

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Manuscript received March 30, 1998
Manuscript accepted September 7, 1998
Paper handled by Hans Keppler