

# Characterization of fluoro-edenite by $\mu$ -Raman and $\mu$ -FTIR spectroscopy

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## ABSTRACT

The prismatic variety of fluoro-edenite, a new amphibole found in lavas from Mt Etna in Biancavilla (Catania Province, Sicily, Italy), has been characterized by  $\mu$ -Raman and  $\mu$ -FTIR spectroscopy. The wavenumbers at which the bands are detected in the  $\mu$ -Raman and  $\mu$ -FTIR spectra are compared with tremolite, asbestos the chemical and crystallographic characteristics of which are very similar to those of fluoro-edenite.

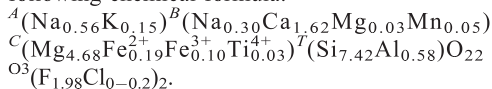
**KEYWORDS:** Raman spectroscopy, IR spectroscopy, fluoro-edenite, tremolite.

## Introduction

FLUORO-EDENITE, a new amphibole end-member of the edenite series (Gianfagna and Oberti, 2001), is rarely found in nature, probably because edenite corresponds, in the amphiboles field, to an unstable composition and therefore it can appear only as a non-predominant component (Leake *et al.*, 1997; Raudsepp *et al.*, 1991). Nevertheless, abundant quantities of well developed yellow fluoro-edenite crystals, showing prismatic, acicular and fibrous habits, were recently detected in autoclasts of grey-red benmoreitic lavas at Mt Calvario, in the Etnean Volcanic Complex (Catania Province, Sicily, Italy) (Gianfagna *et al.*, 1997, 2003). Material extracted from the Mt Calvario quarry site was widely used as building material in the 1960s and the 1970s, and a cluster of malignant pleural mesothelioma cases detected in Biancavilla, a village located in the Etnean Volcanic Complex, has been ascribed to fluoro-edenite with an elongated or fibrous habit (Paoletti *et al.*, 2000; Comba *et al.*, 2003; Gianfagna *et al.*, 2003; Burragato *et al.*, 2005). Moreover, it has been demonstrated that mouse (Cardile *et al.*, 2004a,b) and human (Soffritti *et*

*al.*, 2004) lung cells treated with fluoro-edenite exhibit functional modifications and changes in biochemical parameters.

The chemical and crystallographic characteristics of prismatic fluoro-edenite were determined by Gianfagna and Oberti (2001) who proposed the following chemical formula:



In this study, we measure the  $\mu$ -Raman and  $\mu$ -IR spectra of the same type of crystals, with the additional aim of determining whether these spectroscopic techniques allow fluoro-edenite to be easily distinguished from tremolite, which is legally defined as 'asbestos' and is more commonly found in natural outcrops. This builds on previous works demonstrating that the various mineral phases of the asbestos amphibole can easily be distinguished by  $\mu$ -Raman spectrometry (Rinaudo *et al.*, 2003, 2004).

The advantage of using  $\mu$ -Raman or  $\mu$ -FTIR spectroscopy is that neither requires sample preparation: the spectrum is acquired by placing the sample directly in the path of the laser beam in the spectroscope. This may be a crucial factor when asbestiform fluoro-edenite must be detected in building materials or in the environment.

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## Experimental

For  $\mu$ -Raman analysis, prismatic crystals of fluoro-edenite shown in Fig. 1 were analysed under a Jobin Yvon LabRAM HR800  $\mu$ -spectrometer equipped with a CCD air-cooled detector, an Olympus BX41 microscope, a television camera and a 20 mW HeNe laser operating at 632.8 nm. The spectra were registered at a resolution of  $1\text{ cm}^{-1}$ . The correct calibration of the instrument was obtained by checking the position of the Si band at  $\pm 520.6\text{ cm}^{-1}$ .

The  $3500\text{--}200\text{ cm}^{-1}$  spectral region was considered, but only in the part of the spectrum corresponding to the lattice modes ( $1200\text{--}200\text{ cm}^{-1}$ ) were Raman bands observed. At higher frequencies, a large and very pronounced hump owing to the fluorescence



FIG. 1. Optical micrograph of fluoro-edenite studied by  $\mu$ -Raman and  $\mu$ -FTIR spectroscopy.

emission of the sample prevented analysis of the region corresponding to  $\text{OH}^-$  vibrations. The spectra were processed using the curve fit tool of the OPUS software program.

A number of  $\mu$ -FTIR reflectance spectra were registered on fluoro-edenite shown in Fig. 1 and on tremolite samples previously studied by  $\mu$ -Raman spectroscopy by Rinaudo *et al.* (2004). The instrument used was a Perkin Elmer FTIR Spectrum GX1 Spectrometer interfaced to a Perkin Elmer Autoimage microscope, equipped with a Mercury Cadmium Telluride (MCT) detector mounted on the infrared microscope. The spectra were scanned from  $4000$  to  $700\text{ cm}^{-1}$  using a resolution of  $4\text{ cm}^{-1}$ . The baseline was measured in each case, and component bands of interest were isolated using Second Derivative, Fourier Self Deconvolution and Curve-Fitting (Gaussian character) procedures. Spectrum 3.03 (Perkin Elmer) and Grams AI (Galactic Corp.) were used for managing the data.

TABLE 1. List of the Raman bands ( $\text{cm}^{-1}$ ) detected in fluoro-edenite (this study) and in tremolite (reported by Rinaudo *et al.*, 2004).

| F-edenite ( $\text{cm}^{-1}$ )<br>this study | Tremolite ( $\text{cm}^{-1}$ )<br>Rinaudo <i>et al.</i> (2004) |
|--|--|
| 1061   | 1062   |
| 1041   | 1031   |
|  | 950  |
| 929  | 932  |
| 899  |  |
| 760  | 751  |
| 679  | 676  |
| 587  | 531  |
| 557  | 516  |
| 528  |  |
| 435  | 438  |
|  | 418  |
|  | 396  |
| 382  |  |
| 370  | 373  |
|  | 355  |
| 312  |  |
|  | 306  |
| 258  | 254  |
| 249  |  |
| 238  | 234  |
| 225  | 225  |

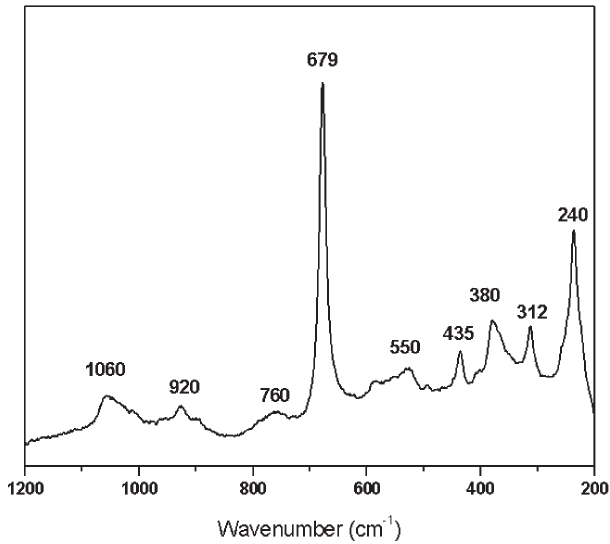


FIG. 2. A  $\mu$ -Raman spectrum from the fluoro-edenite sample in the region 1200–200  $\text{cm}^{-1}$ .

## Results and discussion

In Fig. 2 a typical  $\mu$ -Raman spectrum recorded on the prismatic fluoro-edenite shown in Fig. 1 is reported. The spectrum exhibits a very intense band at 679  $\text{cm}^{-1}$  and less intense and broad bands near 1060, 920, 550, 380 and 240  $\text{cm}^{-1}$ , the profile fitting of which is displayed in Fig. 3a–e. The assignment of the detected bands is proposed on the basis of the analyses of the IR spectra of the amphiboles (Lazarev, 1972; Farmer, 1974), of the Raman bands of holmquistite, a Li-bearing amphibole (Kloprogge *et al.*, 2001), and of the Raman bands of the amphibole asbestos (Rinaudo *et al.*, 2004). The most intense band in Fig. 2 lies at 679  $\text{cm}^{-1}$  and is therefore ascribed to  $\nu_1$  ( $A_g$ ) symmetric stretching modes of the Si–O<sub>b</sub>–Si bridges. The band near 1060  $\text{cm}^{-1}$  (Fig. 2), formed by two bands lying at 1061 and 1041  $\text{cm}^{-1}$  (Fig. 3a), is assigned to antisymmetric stretching vibrations,  $\nu_{as}$ , of the Si–O<sub>b</sub>–Si linkages; the band near 920  $\text{cm}^{-1}$  (component bands at 929 and 899  $\text{cm}^{-1}$ , Fig. 3b) is produced by symmetric stretching modes,  $\nu_s$ , of the O–Si–O bonds; and finally, the band at 760  $\text{cm}^{-1}$  (Fig. 2) can be ascribed to  $\nu_s$  vibrations of the Si–O<sub>b</sub>–Si bridges. In the <650  $\text{cm}^{-1}$  spectral region, the assignment of the observed bands is problematic due to the coupling of the vibrations of the  $MO_6$  and  $MO_8$  polyhedra ( $M$ : cations in octahedral or cubic sites), of the deformation modes of the  $(Si_4O_{11})_\infty$  ribbons and

TABLE 2. IR band positions ( $\text{cm}^{-1}$ ) observed in fluoro-edenite and in tremolite spectra.

| Fluoro-edenite | Tremolite |
|----------------|-----------|
|                | 3735      |
|                | 3674      |
| 1274           |           |
| 1249           |           |
| 1220           |           |
| 1185           | 1197      |
| 1175           | 1172      |
| 1137           | 1140      |
| 1122           | 1118      |
| 1098           | 1094      |
| 1067           | 1061      |
| 1039           | 1037      |
| 1020           | 1025      |
| 1009           | 1010      |
| 920            | 965       |
| 898            | 936       |
| 876            | 902       |
| 849            | 862       |
| 834            | 832       |
| 820            |           |
| 792            | 799       |
| 763            | 744       |
| 728            | 723       |

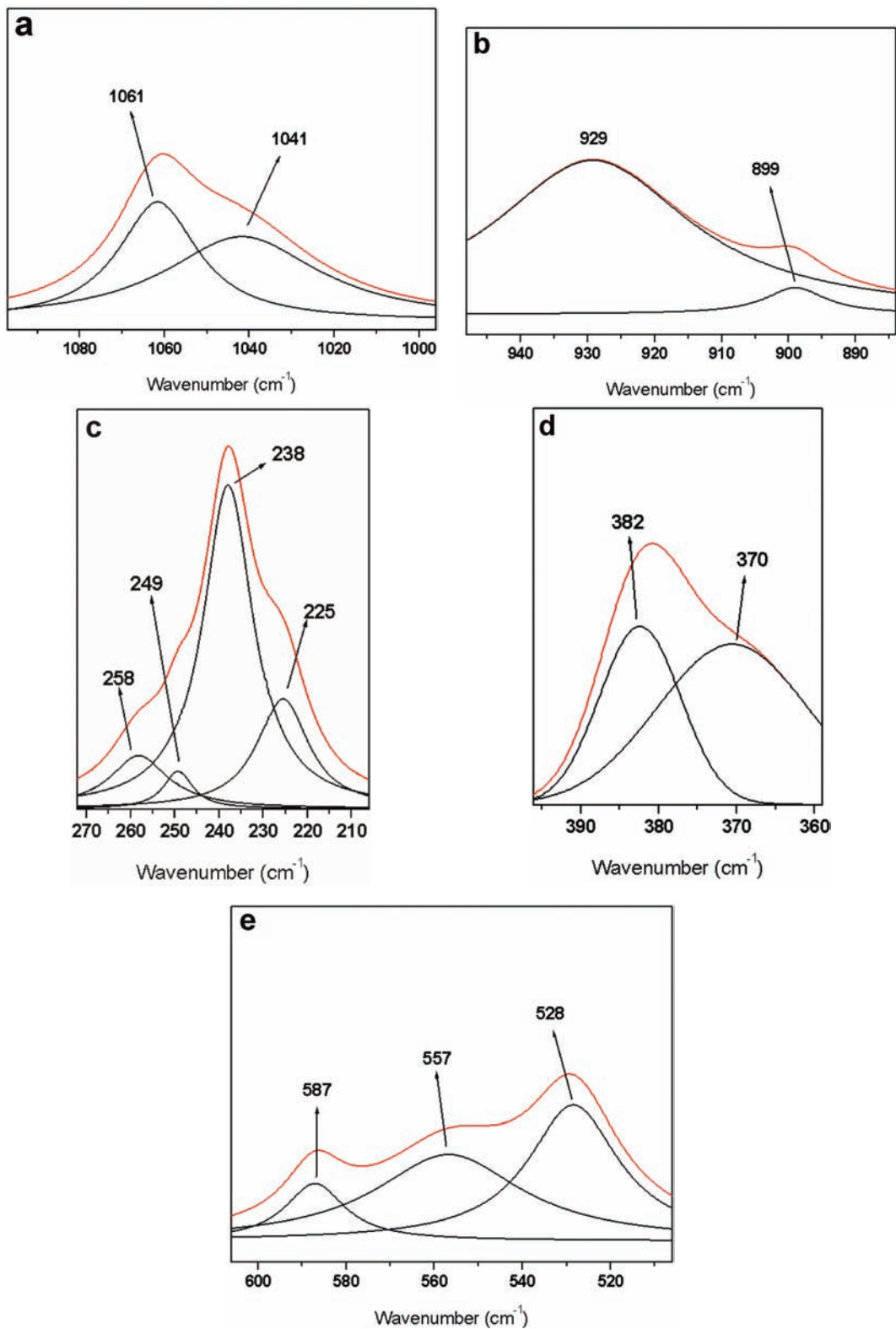


FIG. 3(a–e). Individual band-fitting profiles detected in the spectral regions near 1050, 920, 550, 380 and 236  $\text{cm}^{-1}$ , respectively.

of the F–O bonds. In this part of the spectrum, large asymmetric bands are observed near  $240\text{ cm}^{-1}$ , made up of four component bands at  $258$ ,  $249$ ,  $238$  and  $225\text{ cm}^{-1}$  (Fig. 3c); near  $380\text{ cm}^{-1}$ , band components at  $382\text{ cm}^{-1}$  and at  $370\text{ cm}^{-1}$  (Fig. 3d); in the  $550\text{--}530\text{ cm}^{-1}$  region, component bands lying at  $587$ ,  $557$  and  $528\text{ cm}^{-1}$  (Fig. 3e).

When the Raman spectrum registered on fluoro-edenite is compared with that of tremolite

(Rinaudo *et al.*, 2003, 2004; Bard *et al.*, 1997; Lewis *et al.*, 1996; Blaha & Rosasco, 1978), we observe: (1) the  $\nu_1$  ( $A_g$ ) symmetric stretching modes of the Si–O<sub>b</sub>–Si bridges vibrate in fluoro-edenite at slightly higher wavenumbers than in tremolite ( $679$  vs.  $676\text{ cm}^{-1}$ ); (2) the  $\nu_{as}$  modes of the Si–O<sub>b</sub>–Si linkages produce two distinct bands at  $1062$  and  $1031\text{ cm}^{-1}$  on tremolite and one broad band, formed by two components lying at  $1061$  and  $1041\text{ cm}^{-1}$ , on fluoro-edenite; (3) the

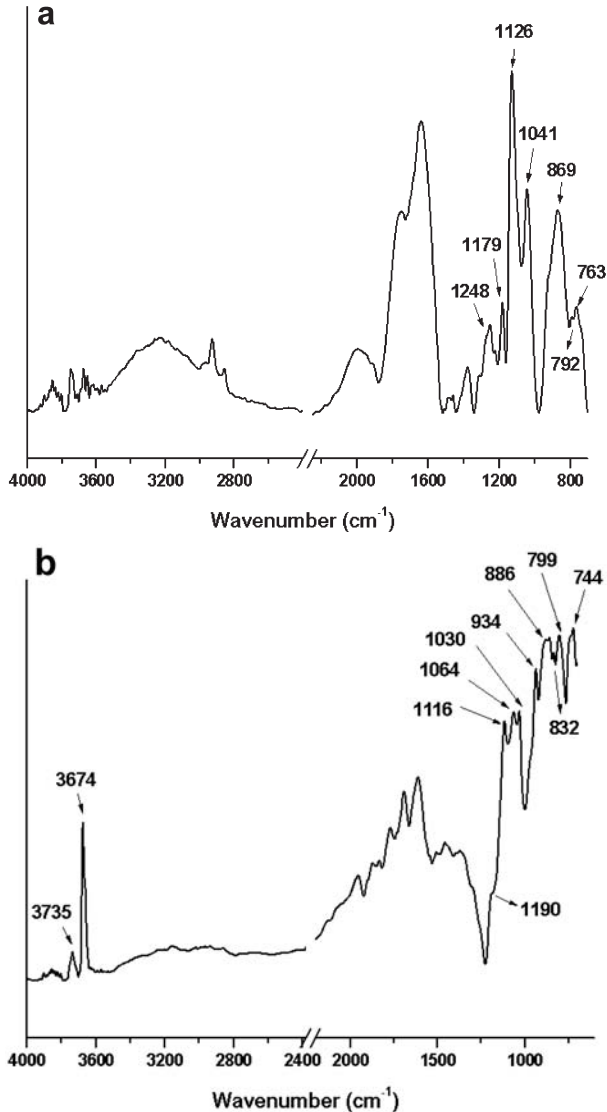


FIG. 4. (a)  $\mu$ -FTIR spectrum of fluoro-edenite in the region  $4000\text{--}700\text{ cm}^{-1}$ . (b)  $\mu$ -FTIR spectrum of tremolite in the region  $4000\text{--}700\text{ cm}^{-1}$ .

Raman spectrum of tremolite exhibits narrow and well defined bands, whereas the bands in fluoro-edenite are broad and convoluted, perhaps as a consequence of a more complex chemical composition and frequent substitutions in the different structural sites (Gianfagna and Oberti, 2001).

The results of the micro-FTIR analysis of the fluoro-edenite and of the tremolite studied by Rinaudo *et al.* (2004) are reported in Table 1 and the spectra are shown in Fig. 4a,b. The broad, strong multicomponent band in the 2000–1300  $\text{cm}^{-1}$  region is, in our opinion, the result of specular reflections, as demonstrated by the fact that it disappears when the spectrum is registered on samples mixed with KBr matrix

(Lewis *et al.*, 1996; Tosi *et al.* unpublished results, 2005). The bands detected in the 1300–700  $\text{cm}^{-1}$  region are analysed by fitting their profile and the results are reported in Figs 5a, 6a for fluoro-edenite and in Figs 5b, 6b for tremolite. By comparing the spectra of the two minerals, the following may be suggested: (1) as expected, no significant absorption appears in the region of the  $\text{OH}^-$  stretching modes in the spectrum from fluoro-edenite (Fig. 4a) whereas in the tremolite spectrum (Fig. 4b), strong bands produced by the  $\text{OH}^-$  stretching modes are observed at 3735 and 3674  $\text{cm}^{-1}$ ; (2) the broad band at 1248  $\text{cm}^{-1}$  (component bands at 1274, 1249 and 1220  $\text{cm}^{-1}$ , Fig. 5a) is absent from the tremolite spectrum (Fig. 5b); it may be assigned to  $\nu_{\text{as}}$  O–Si–O

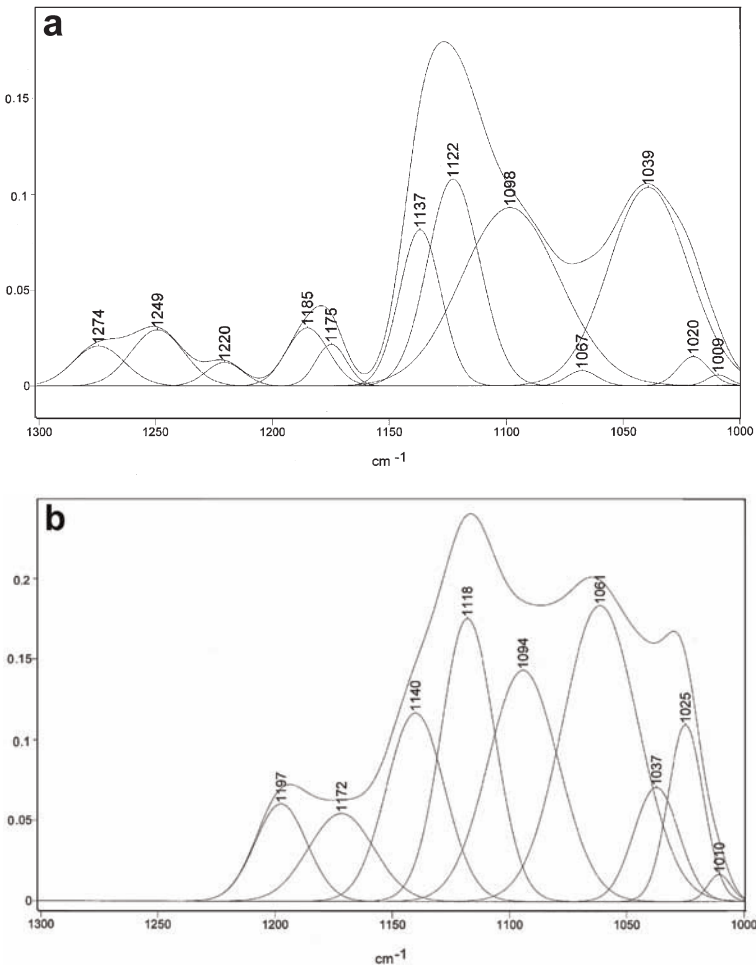


FIG. 5. Individual band-fitting profiles of fluoro-edenite (a) and tremolite (b) in the spectral region 1300–1000  $\text{cm}^{-1}$ .

## CHARACTERIZATION OF FLUORO-EDENITE

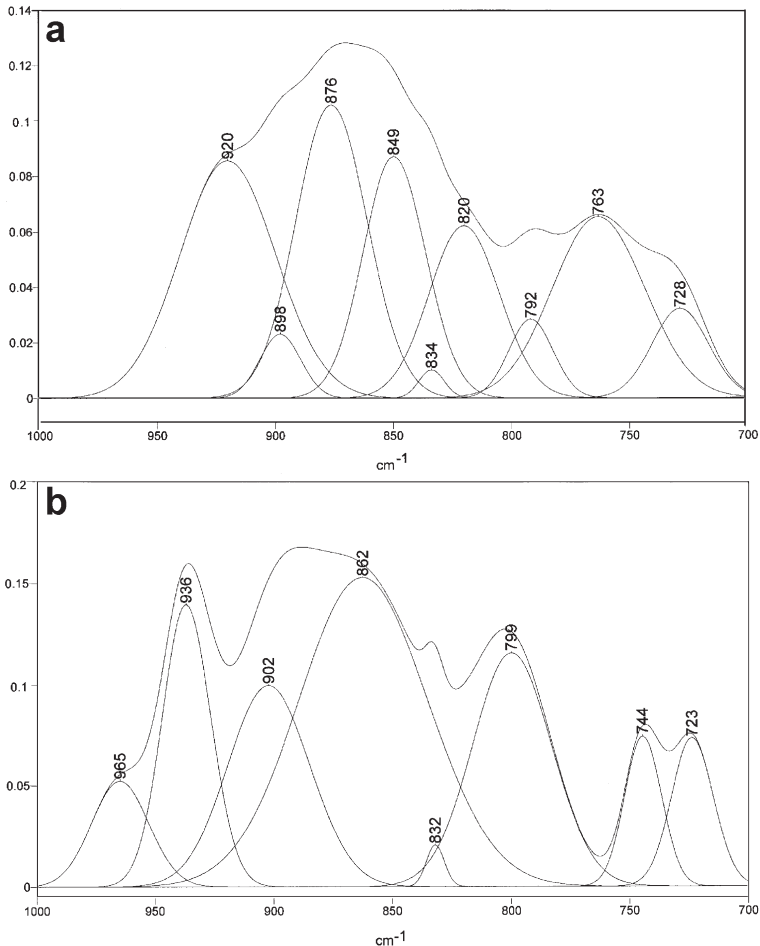


FIG. 6. Individual band-fitting profiles of fluoro-edenite (a) and tremolite (b) in the spectral region 1000–700  $\text{cm}^{-1}$ .

modes; (3) the fluoro-edenite samples (Figs 4a, 5a) show bands at 1179  $\text{cm}^{-1}$  (component bands at 1185, 1175  $\text{cm}^{-1}$ ), at 1126  $\text{cm}^{-1}$  (component bands at 1137, 1122, 1098 and 1067  $\text{cm}^{-1}$ ) and at 1041  $\text{cm}^{-1}$  (component bands at 1039, 1020 and 1009  $\text{cm}^{-1}$ ), which can be ascribed to  $\nu_{\text{as}}$  vibrations of the Si–O<sub>b</sub>–Si bridges. The corresponding vibrational modes appear on the tremolite spectrum (Figs 4b, 5b) at 1190  $\text{cm}^{-1}$  (component bands at 1197 and 1172  $\text{cm}^{-1}$ ), at 1116  $\text{cm}^{-1}$  (component bands at 1140, 1118 and 1094  $\text{cm}^{-1}$ ), at 1064  $\text{cm}^{-1}$ , and at 1030  $\text{cm}^{-1}$  (component bands at 1061, 1037, 1025 and 1010  $\text{cm}^{-1}$ ); (4) in the ~900–800  $\text{cm}^{-1}$  spectral region, where  $\nu_{\text{s}}$  stretching modes of the O–Si–O can be observed, the fluoro-edenite spectrum shows a broad band near 869  $\text{cm}^{-1}$  (component

bands at 920, 898, 876, 849, 834 and 820  $\text{cm}^{-1}$ ) and a weak band at 792  $\text{cm}^{-1}$  (Fig. 6a,b), whereas tremolite exhibits bands at 934  $\text{cm}^{-1}$  (component bands at 965 and 936  $\text{cm}^{-1}$ ), at 886  $\text{cm}^{-1}$  (component bands at 902 and 862  $\text{cm}^{-1}$ ), at 832 and 804  $\text{cm}^{-1}$ ; (5) the  $\nu_{\text{s}}$  modes of the Si–O<sub>b</sub>–Si linkages appear in the fluoro-edenite spectrum at 763  $\text{cm}^{-1}$  (component bands at 763 and 728  $\text{cm}^{-1}$ ) (Figs 4a, 6a); in tremolite at 744  $\text{cm}^{-1}$  and 723  $\text{cm}^{-1}$  (Figs 4b, 6b).

The results, summarized in Tables 1 and 2, demonstrate that fluoro-edenite can be easily identified by using  $\mu$ -Raman or  $\mu$ -FTIR spectroscopy. In fact the  $\mu$ -FTIR spectrum allows fluoro-edenite to be easily distinguished from the other fibrous amphibole through analysis of the spectral region where vibrations of OH<sup>-</sup> groups are

detected at  $>3500\text{ cm}^{-1}$ . On the other hand, the Raman spectrum exhibits bands in the  $1200\text{--}200\text{ cm}^{-1}$  range the profile and wavenumbers of which allow fluoro-edenite to be distinguished from the other fibrous amphiboles, the pure phase  $\mu$ -Raman spectra of which have recently been determined (Rinaudo *et al.*, 2004).

## Acknowledgements

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