Mineralogical Magazine, June 2006, Vol. 70(3), pp. 291–298

Characterization of fluoro-edenite by μ-Raman and μ-FTIR spectroscopy

C. RINAUDO[1], S. CAIRO[1], D. GASTALDI[1], A. GIANFAGNA[2], S. MAZZIOTTI TAGLIANI[2], G. TOSI[3] AND C. CONTI[3]

[1] Department of Environmental and Life Science, University of Eastern Piedmont 'A. Avogadro' – V. Bellini 25/G, 15100 Alessandria, Italy
[2] Department of Earth Science, University of Rome 'La Sapienza', P. le Aldo Moro 5, 00185 Roma, Italy
[3] Department of Earth and Material Sciences, Università Politecnica delle Marche, 60100 Ancona, Italy

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 μ-Raman and μ-FTIR spectroscopy. The wavenumbers at which the bands are detected in the μ-Raman and μ-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*., 2004*a,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: $^{A}(Na_{0.56}K_{0.15})^{B}(Na_{0.30}Ca_{1.62}Mg_{0.03}Mn_{0.05})^{C}(Mg_{4.68}Fe^{2+}_{0.19}Fe^{3+}_{0.10}Ti^{4+}_{0.03})^{T}(Si_{7.42}Al_{0.58})O_{22}{}^{O3}(F_{1.98}Cl_{0-0.2})_2$.

In this study, we measure the μ-Raman and μ-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 μ-Raman spectrometry (Rinaudo *et al*., 2003, 2004).

The advantage of using μ-Raman or μ-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.

* E-mail: caterina.rinaudo@mfn.unipmn.it
DOI: 10.1180/0026461067030332

© *2006 The Mineralogical Society*

Experimental

For μ-Raman analysis, prismatic crystals of fluoro-edenite shown in Fig. 1 were analysed under a Jobin Yvon LabRAM HR800 μ-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 cm^{-1}. The correct calibration of the instrument was obtained by checking the position of the Si band at ±520.6 cm^{-1}.

The 3500–200 cm^{-1} spectral region was considered, but only in the part of the spectrum corresponding to the lattice modes (1200–200 cm^{-1}) were Raman bands observed. At higher frequencies, a large and very pronounced hump owing to the fluorescence emission of the sample prevented analysis of the region corresponding to OH^- vibrations. The spectra were processed using the curve fit tool of the OPUS software program.

A number of μ-FTIR reflectance spectra were registered on fluoro-edenite shown in Fig. 1 and on tremolite samples previously studied by μ-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 cm^{-1} using a resolution of 4 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.

FIG. 1. Optical micrograph of fluoro-edenite studied by μ-Raman and μ-FTIR spectroscopy.

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

F-edenite (cm^{-1}) this study	Tremolite (cm^{-1}) Rinaudo *et al*. (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

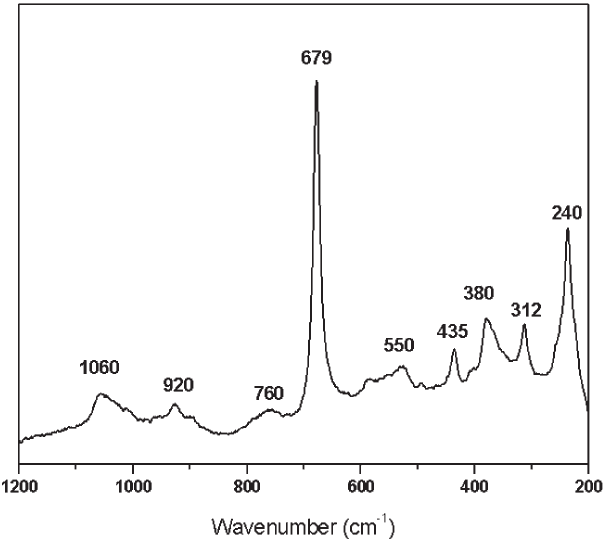

FIG. 2. A μ-Raman spectrum from the fluoro-edenite sample in the region 1200–200 cm^{-1}.

Results and discussion

In Fig. 2 a typical μ-Raman spectrum recorded on the prismatic fluoro-edenite shown in Fig. 1 is reported. The spectrum exhibits a very intense band at 679 cm^{-1} and less intense and broad bands near 1060, 920, 550, 380 and 240 cm^{-1}, the profile fitting of which is displayed in Fig. 3*a*–*e*. The assignation 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 cm^{-1} and is therefore ascribed to ν_1 (A_g) symmetric stretching modes of the Si–O_b–Si bridges. The band near 1060 cm^{-1} (Fig. 2), formed by two bands lying at 1061 and 1041 cm^{-1} (Fig. 3*a*), is assigned to antisymmetric stretching vibrations, ν_{as}, of the Si–O_b–Si linkages; the band near 920 cm^{-1} (component bands at 929 and 899 cm^{-1}, Fig. 3*b*) is produced by symmetric stretching modes, ν_s, of the O–Si–O bonds; and finally, the band at 760 cm^{-1} (Fig. 2) can be ascribed to ν_s vibrations of the Si–O_b–Si bridges. In the <650 cm^{-1} spectral region, the assignation 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 (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

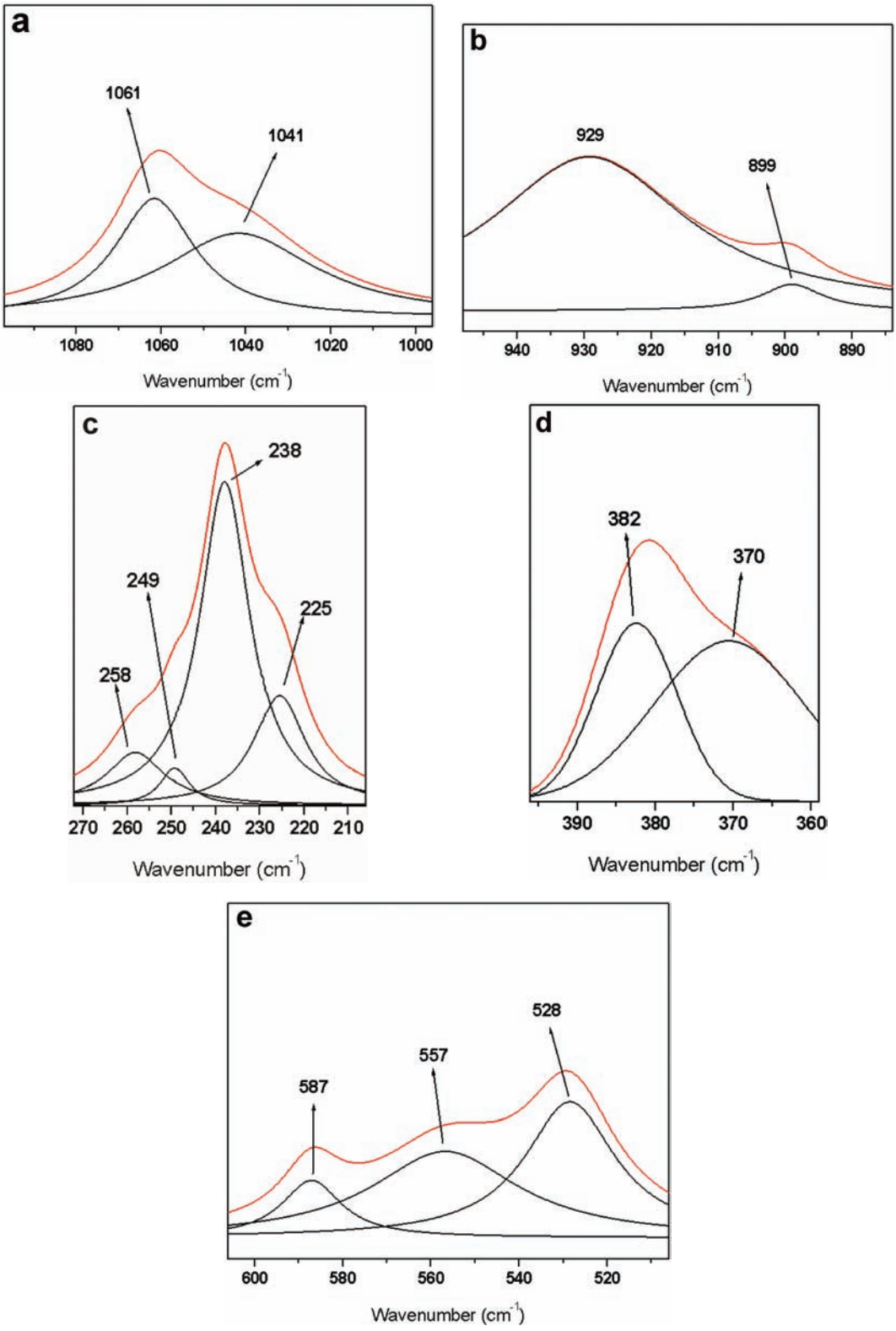

FIG. 3(a–e). Individual band-fitting profiles detected in the spectral regions near 1050, 920, 550, 380 and 236 cm^{-1}, respectively.

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

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 ν_1 (A_g) symmetric stretching modes of the $Si-O_b-Si$ bridges vibrate in fluoro-edenite at slightly higher wavenumbers than in tremolite (679 *vs.* 676 cm^{-1}); (2) the ν_{as} modes of the $Si-O_b-Si$ linkages produce two distinct bands at 1062 and 1031 cm^{-1} on tremolite and one broad band, formed by two components lying at 1061 and 1041 cm^{-1}, on fluoro-edenite; (3) the

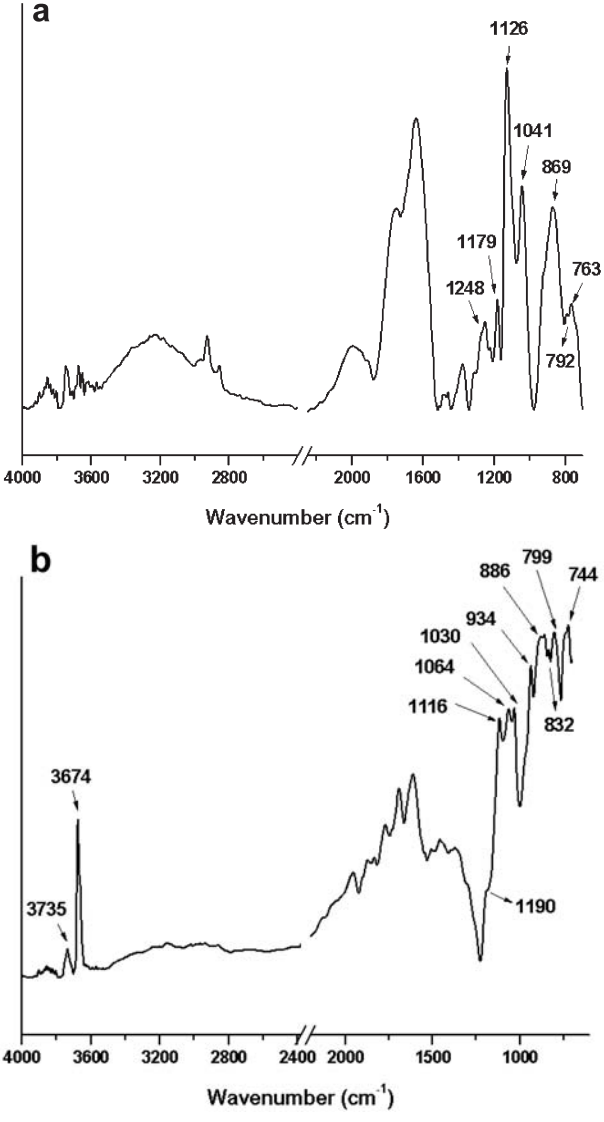

FIG. 4. (*a*) μ-FTIR spectrum of fluoro-edenite in the region 4000−700 cm^{-1}. (*b*) μ-FTIR spectrum of tremolite in the region 4000−700 cm^{-1}.

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. 4*a*,*b*. The broad, strong multicomponent band in the 2000–1300 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 cm^{-1} region are analysed by fitting their profile and the results are reported in Figs 5*a*, 6*a* for fluoro-edenite and in Figs 5*b*, 6*b* 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 OH^- stretching modes in the spectrum from fluoro-edenite (Fig. 4*a*) whereas in the tremolite spectrum (Fig. 4*b*), strong bands produced by the OH^- stretching modes are observed at 3735 and 3674 cm^{-1}; (2) the broad band at 1248 cm^{-1} (component bands at 1274, 1249 and 1220 cm^{-1}, Fig. 5*a*) is absent from the tremolite spectrum (Fig. 5*b*); it may be assigned to ν_{as} O–Si–O

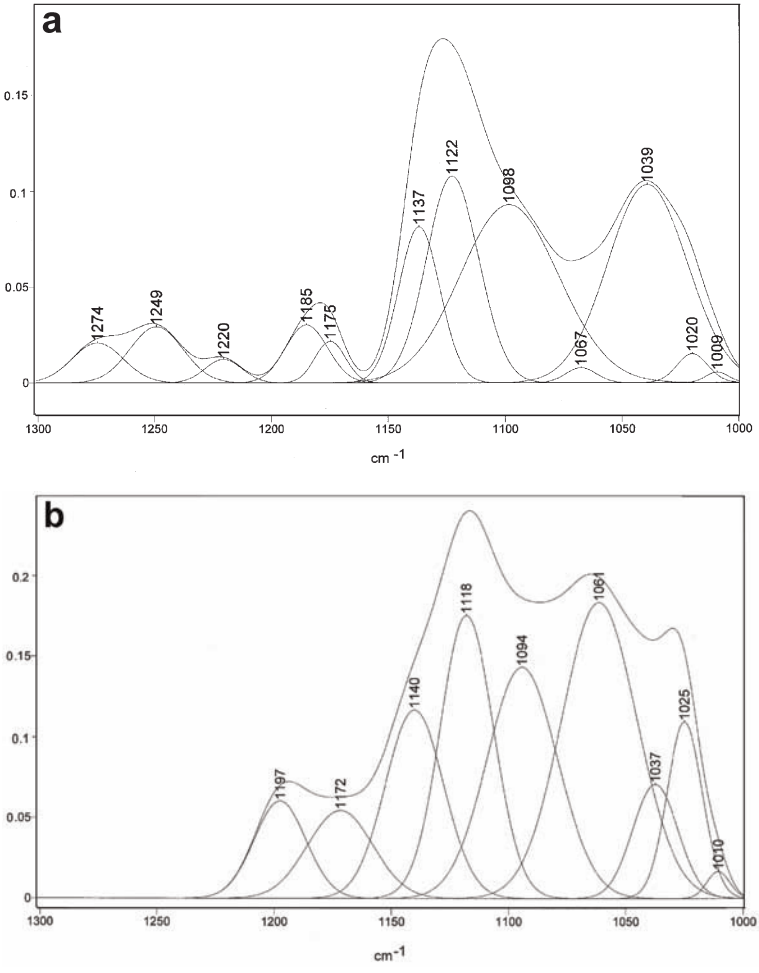

FIG. 5. Individual band-fitting profiles of fluoro-edenite (*a*) and tremolite (*b*) in the spectral region 1300–1000 cm^{-1}.

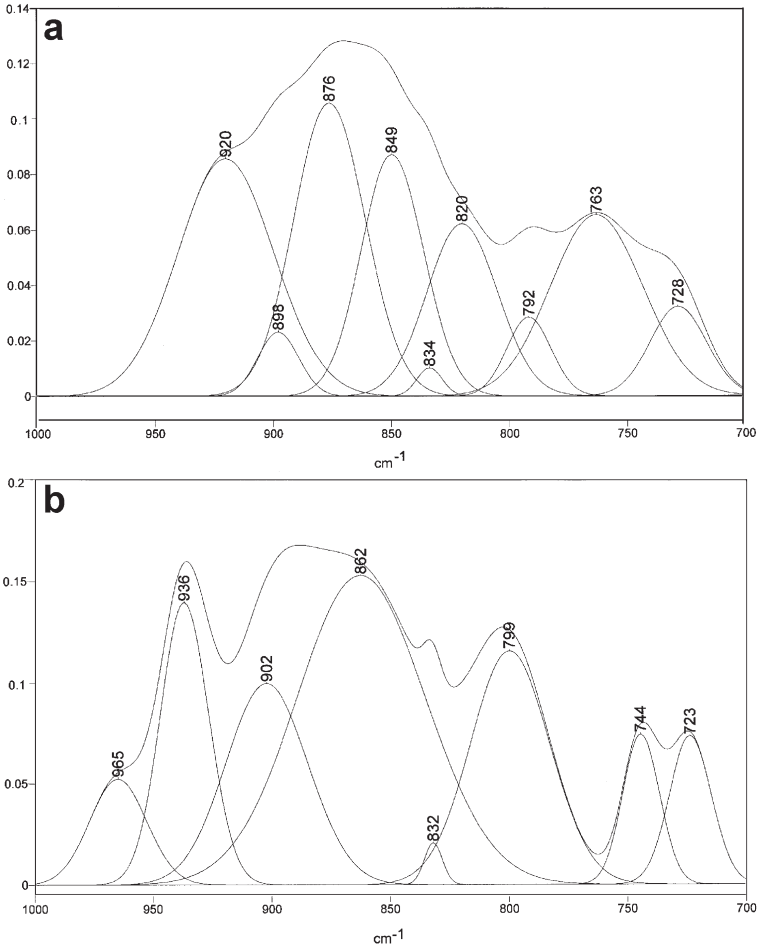

FIG. 6. Individual band-fitting profiles of fluoro-edenite (*a*) and tremolite (*b*) in the spectral region 1000−700 cm^{-1}.

modes; (3) the fluoro-edenite samples (Figs 4*a*, 5*a*) show bands at 1179 cm^{-1} (component bands at 1185, 1175 cm^{-1}), at 1126 cm^{-1} (component bands at 1137, 1122, 1098 and 1067 cm^{-1}) and at 1041 cm^{-1} (component bands at 1039, 1020 and 1009 cm^{-1}), which can be ascribed to ν_{as} vibrations of the Si−O_b−Si bridges. The corresponding vibrational modes appear on the tremolite spectrum (Figs 4*b*, 5*b*) at 1190 cm^{-1} (component bands at 1197 and 1172 cm^{-1}), at 1116 cm^{-1} (component bands at 1140, 1118 and 1094 cm^{-1}), at 1064 cm^{-1}, and at 1030 cm^{-1} (component bands at 1061, 1037, 1025 and 1010 cm^{-1}); (4) in the ~900−800 cm^{-1} spectral region, where ν_s stretching modes of the O−Si−O can be observed, the fluoro-edenite spectrum shows a broad band near 869 cm^{-1} (component bands at 920, 898, 876, 849, 834 and 820 cm^{-1}) and a weak band at 792 cm^{-1} (Fig. 6*a*,*b*), whereas tremolite exhibits bands at 934 cm^{-1} (component bands at 965 and 936 cm^{-1}), at 886 cm^{-1} (component bands at 902 and 862 cm^{-1}), at 832 and 804 cm^{-1}; (5) the ν_s modes of the Si−O_b−Si linkages appear in the fluoro-edenite spectrum at 763 cm^{-1} (component bands at 763 and 728 cm^{-1}) (Figs 4*a*, 6*a*); in tremolite at 744 cm^{-1} and 723 cm^{-1} (Figs 4*b*, 6*b*).

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

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

Acknowledgements

This work was supported by a contribution from the Italian project 'Spectroscopic and computational characterization of fibrous minerals not classified asbestos' PRIN 2004.

References

Bard, D., Yarwood, J. and Tylee, B. (1997) Asbestos fibre identification by Raman microspectroscopy. *Journal of Raman Spectroscopy*, **28**, 803–809.

Blaha, J.J. and Rosasco, G.J. (1978) Raman microprobe spectra of individual microcrystals and fibers of talc, tremolite, and related silicate minerals. *Analytical Chemistry*, **50**, 892–896.

Burragato, F., Comba, P., Baiocchi, V., Palladino, D.M., Simei, S., Gianfagna, A., Paoletti, L. and Pasetto, R. (2005) Geo-volcanological, mineralogical and environmental aspects of quarry materials related to pleural neoplasm in the area of Biancavilla, Mount Etna (Eastern Sicily, Italy). *Environmental Geology*, **47**, 855–868.

Cardile, V., Renis, M., Scifo, C., Lombardo, L., Gulino, R., Mancari, B. and Panico, A.M. (2004a) Behaviour of the new asbestos amphibole fluoro-edenite in different lung cell systems. *The International Journal of Biochemistry & Cell Biology*, **36**, 849–860.

Cardile, V., Proietti, L., Panico, A.M. and Lombardo, L. (2004b) Nitric oxide production in fluoro-edenite treated mouse monocyte-macrophage cultures. *Oncology Reports*, **12**, 1209–1215.

Comba, P., Gianfagna, A. and Paoletti, L. (2003) Pleural mesothelioma cases in Biancavilla are related to a new fluoro-edenite fibrous amphibole. *Archives of Environmental Health* **58**, 229–232.

Farmer, V.C. (1974) *The Infrared Spectra of Minerals*. Monograph **4**, Mineralogical Society, London.

Gianfagna, A. and Oberti, R. (2001) Fluoro-edenite from Biancavilla (Catania, Sicily, Italy): crystal chemistry of a new amphibole end-member. *American Mineralogist*, **86**, 1489–1493.

Gianfagna, A., Paoletti, L. and Ventura, P. (1997) Segnalazione di fibre di amianto anfibolico nei prodotti lavici metasomatizzati di Monte Calvario (Biancavilla, Sicilia Orientale). *Plinius, Suppl. EJM*, **18**, 117–119.

Gianfagna, A., Ballirano, P., Bellatreccia, F., Bruni, B., Paoletti, L. and Oberti, R. (2003) Characterization of amphibole fibres linked to mesothelioma in the area of Biancavilla, Eastern Sicily, Italy. *Mineralogical Magazine*, **67**, 1221–1229.

Kloprogge, J.T., Case, M.H. and Frost, R.L. (2001) Raman microscopic study of the Li amphibole holmquistite, from the Martin Marietta Quarry, Bessemer City, NC, USA. *Mineralogical Magazine*, **65**, 775–785.

Lazarev, A.N. (1972) *Vibrational Spectra and Structure of Silicates.* Consultants Bureau, New York and London, p. 1.

Leake, B.E., Woolley, A.R., Arps, C.E., Birch, W.D., Gilbert, M.C., Grice, J.D., Hawthorne, F.C., Kato, A., Kisch, H.J., Krivovichev, V.G., Linthout, K., Laird, J., Mandarino, J.A., Maresch, W.V., Nickel, E.H., Rock, N.M.S., Schumacher, J.C., Smith, D.C., Stephenson, N.C.N., Ungaretti, L., Whittaker, E.J.W. and Youzhi, G. (1997) Nomenclature of amphiboles: report of the subcommittee on amphiboles of the International Mineralogical Association, Commission on New Minerals and Mineral Names. *Mineralogical Magazine*, **61**, 295–321.

Lewis, I.R., Chaffin, N.C., Gunter, M.E. and Griffiths, P.R. (1996) Vibrational spectroscopic studies of asbestos and comparison of suitability for remote analysis. *Spectrochimica Acta A*, **52**, 315–328.

Paoletti, L., Batisti, D., Bruno, C., Di Paola, M., Gianfagna, A., Mastrantonio, M., Nesti, M. and Comba, P. (2000) Unusually high incidence of malignant pleural mesothelioma in a town of eastern Sicily: an epidemiological and environmental study. *Archives of Environmental Health*, **55**, 392–398.

Raudsepp, M., Turnock, A.C. and Hawthorne, F.C. (1991) Amphibole synthesis at low pressure: what grows and what doesn't. *European Journal of Mineralogy*, **3**, 983–1004.

Rinaudo, C., Gastaldi, D. and Belluso, E. (2003) La spettroscopia Raman: tecnica di identificazione rapida di fibre di asbesto. *Siti Contaminati*, **2**, 116–120.

Rinaudo, C., Belluso, E. and Gastaldi, D. (2004) Assessment of the use of Raman spectroscopy for the determination of amphibole asbestos. *Mineralogical Magazine*, **68**, 455–465.

Soffritti, M., Minardi, F., Bua, L., Degli Esposti, D. and Belpoggi, F. (2004) First experimental evidence of peritoneal and pleural mesotheliomas induced by fluoro-edenite fibres present in Etnean volcanic material from Biancavilla (Sicily, Italy). *European Journal of Oncology*, **9**, 169–175.

[*Manuscript received 6 February 2006: revised 1 July 2006*]