

Micro-Raman spectroscopy applied on oriented crystals of fluoro-edenite amphibole

ELISA FORNERO¹, MARIO ALLEGRINA¹, CATERINA RINAUDO^{1,*}, SIMONA MAZZIOTTI-TAGLIANI²
and ANTONIO GIANFAGNA²

¹ Dipartimento di Scienze dell'Ambiente e della Vita, Università degli Studi del Piemonte Orientale "Amedeo Avogadro"-
Via Bellini, 25/g - 15100 Alessandria

² Dipartimento di Scienze della Terra, Università degli Studi di Roma "La Sapienza", P.le A. Moro, 5 - 00185 Roma

ABSTRACT. — Fluoro-edenite crystals from Biancavilla, a mineral characterized by various cations in different crystallographic sites, have been studied with Electron Microprobe Analysis (EMPA) and micro-Raman spectroscopy. The spectroscope used in this study was fitted with an optical microscope equipped with two polarizers and a rotating plate with a vernier, allowing precise orientation of the sample. The Raman spectra were acquired after precisely aligning the crystals with respect to the incident laser beam. The spectra recorded are discussed in relation to the chemical data from EMPA analyses. This investigation suggests that a similar methodological approach can be used to discriminate other fibrous amphiboles which can be difficult to identify by conventional techniques.

RIASSUNTO. — Tramite microsonda elettronica EMPA e spettroscopia micro-Raman sono stati studiati cristalli di fluoro-edenite provenienti da Biancavilla, specie minerale caratterizzata da variabilità cationica nei diversi siti cristallografici. Lo spettroscopio utilizzato in questo lavoro è munito di microscopio ottico dotato di due polarizzatori e di un piatto rotante con nonio, accessori che permettono

una precisa orientazione del campione in esame. E' stato così possibile acquisire spettri Raman su cristalli ugualmente orientati rispetto al fascio laser incidente. Gli spettri registrati sui cristalli esaminati sono discussi in relazione alla composizione chimica determinata mediante la microsonda EMPA. Questa metodologia potrebbe essere estesa all'analisi degli anfiboli fibrosi, spesso difficili da identificare con le tecniche convenzionali.

KEY WORDS: *Fluoro-edenite, micro-Raman spectroscopy, amphiboles, EMPA*

INTRODUCTION

The identification of the Raman spectra of minerals defined as "asbestos" has demonstrated that Raman spectroscopy is a powerful technique to identify the mineral phases even in minerals very close mineralogically and chemically (Blaha and Rosasco, 1978; Wang *et al.*, 1988a; 1988b; Lewis *et al.*, 1996; Bard *et al.*, 1997). Recently, micro-Raman spectroscopy has been applied to mineral associations where different phases are strongly intergrown (micro-crystal associations, mineral fibres, etc.) and to thin sections obtained from rock samples (Rinaudo *et al.*, 2003a; 2003b;

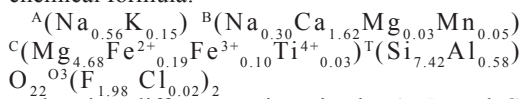
* Corresponding author, E-mail:
caterina.rinaudo@mfn.unipmn.it

2004; 2005; 2006; Groppo *et al.*, 2006; Belluso *et al.*, 2007). The technique is certainly very useful when applied to crystals non-embedded in resins or other materials as all observed bands may be ascribed only to the examined mineral with no interference from glue, sample holders or similar. On the other hand, when analyzing prepared samples, thin sections or crystals glued to a sample holder, particular care must be taken to distinguish the spectrum contribution of the mineral from the other components. In fact all chemical bonds which change their polarizability after interaction with the laser incident beam are Raman-active.

The intensity of the Raman bands depends on the orientation of the sample with respect to the laser incident beam. Usually this orientation is uncontrolled, therefore the intensity of the resultant Raman bands is not indicative of the amounts of the different chemical components in the studied mineral. The amphibole silicates show mostly complex chemical formulas and different electrovalence substitutions in equivalent crystallographic sites. In particular, a correct assignment of the bands is very difficult in the spectral region $<600\text{ cm}^{-1}$, where the vibrational modes of the cations occurring in octahedral or cubic coordination are active, because in this spectral region also lie the bending modes of the SiO_4 tetrahedra and the vibrations of the OH-groups.

In our laboratory the Raman spectroscopy is equipped with an optical microscope, two polarizers and a rotating plate with a vernier, which allows us to obtain spectra from different samples placed in exactly the same orientation with respect to the laser incident beam; therefore the intensity of the Raman bands in spectra observed from different crystals may be considered orientation independent. In order to study the effect of substitutions in different crystallographic sites on the intensity and wavenumbers of the Raman bands, we applied the technique to single crystals of fluoro-edenite, an amphibole found in the etnean volcanic complex (Gianfagna *et al.*, 2003; Burrigato *et al.*, 2005). This mineral grows with both fibrous or prismatic habit as described by Gianfagna and Oberti (2001). The chemical and structural characteristics of prismatic samples have been studied by Gianfagna

and Oberti (2001), who determined the following chemical formula:



showing different cations in the A, B and C sites. The Raman and IR spectra of the same type of crystals studied by Gianfagna and Oberti (2001) have been determined and discussed by Rinaudo *et al.* (2006) on non-prepared samples and with random orientations with respect to laser incident beam. A more thorough chemical characterization by Electron Microprobe Analysis (EMPA) of several samples of prismatic fluoro-edenite demonstrated a variability in the content of the cations occupying the A, B, C and T sites. We collected the Raman spectra from the same set of samples with the hope to correlate the bands observed in the Raman spectra with the differences in chemical compositions and site occupancy. In this study we describe the results whilst remaining conscious that a theoretical approach to calculate the wavenumbers of the different vibrational modes would be a more conventional method. Nevertheless, the calculations of the vibration modes is challenging and significant differences are observed between the calculated and observed wavenumbers (Pascale *et al.*, 2004; Prencipe *et al.*, 2006) for minerals involving various cations, also heterovalent, in a crystallographic site and in sites different from a crystallographic point of view.

In addition, for environmental and health issues, it is extremely important to correctly identify and characterize the amphibole samples (Gianfagna *et al.*, 2003; Gunter *et al.*, 2003; Meeker *et al.*, 2003; Soffritti *et al.*, 2004; Bruni *et al.*, 2006; Gianfagna *et al.*, 2007; Gunter *et al.*, 2007). Accurately interpreted micro-Raman spectroscopy is proving to be a useful method to discriminate fibrous minerals with similar structure and/or chemical composition (i.e. serpentine minerals) not easily identifiable using other techniques such as X-Ray Powder Diffraction and Analytical Scanning Electron Microscopy. Micro-Raman spectroscopy might also prove a useful method when dealing with mineral mixtures and helping to verify results from other analytical methods.

METHODS and TECHNIQUES

The prismatic fluoro-edenite crystals studied in this work originate from the Biancavilla area (in the region of Mount Etna, Sicily), with their first reported occurrence as secondary mineral in the lava fissures. Gianfagna and Oberti (2001) structurally characterized these fluoro-edenite samples and described their chemical variability, proving heterovalent substitutions in the different crystallographic sites.

In the present work, a suite of prismatic fluoro-edenite crystals are characterized by Electron Microprobe (EMPA) and micro-Raman Spectroscopy. 54 millimetric-sized single crystals were previously prepared in thin section (enclosed in resin directly on slide, thinned, polished and graphitized). Selected single crystals, like that represented in Fig. 1, were analyzed by EMPA to assess the differences in the chemical composition. Elemental composition of the studied crystals was obtained with a Cameca SX-50 electron microprobe (IGAG, Rome "La Sapienza") under the following operating conditions: 15 kV accelerating voltage, 15 nA beam current, 3 μm beam size, 20 s peak count-time and 10 s background count-time. Calibration was performed using the following standards: wollastonite (Si K_{α} , Ca K_{α}), rutile (Ti K_{α}), corundum (Al K_{α}), magnetite (Fe K_{α}), metallic Mn (Mn K_{α}), orthoclase (K K_{α}), jadeite (Na K_{α}), fluorophlogopite (F K_{α}) and sylvite (Cl K_{α}).

Some samples, chemically analysed by EMPA, were then characterized by micro-Raman under

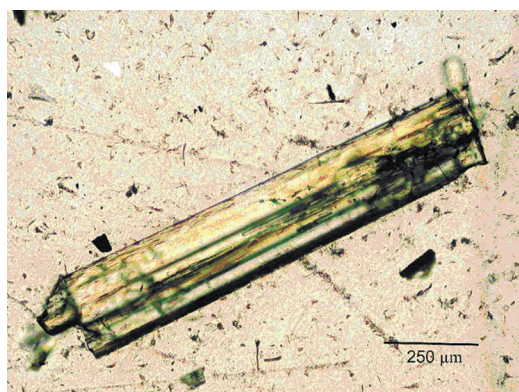


Fig. 1 – Polarized light image of a selected fluoro-edenite crystal.

a Jobin Yvon HR800 LabRam μ -spectrometer, equipped with an Olympus BX41 microscope, a rotating plate with vernier, a HeNe 20 mW laser working at 632.8 nm and a CCD air-cooled detector. The calibration of the instrument was obtained by checking not only the position of the Si band at $\pm 520.6 \text{ cm}^{-1}$, but also its intensity, taking particular care to register all spectra starting with the same initial intensity, measured on a Si standard sample. In order to balance the signal against noise, 10 cycles of 200 scans were performed on each sample. During preparation of the thin sections all the fluoro-edenite crystals were positioned with the hk0 faces, which are also cleavage planes, parallel to the slice, therefore we analyzed in EMPA and micro-Raman cleavages of the starting samples. After EMPA analyses, six selected crystals were separated from the section and taped onto a slide. In order to verify the crystallographic orientation of the crystals selected for Raman analysis, an optical study under a polarized mineralogical microscope was also performed. By the observed interference figures (off-centered optical axes), it was confirmed that all crystals were lying on the cleavage hk0 planes. For the Raman characterization, all the crystals were oriented exactly in the same position with respect to the elongation axis. Raman spectra were initially registered with the crystals positioned with the elongation axis parallel to the N-S direction of the cross-hair of the ocular lens of the microscope, then at 90° with respect to the previous orientation and finally at 45° . In this final position, the most defined and intense Raman bands were observed, therefore in the remainder of the work the spectra were described on crystals placed with their elongation at 45° with respect to N-S direction of the cross-hair of the ocular lens. The Raman region corresponding to the lattice modes, 1200–200 cm^{-1} , was analyzed in detail. In order to obtain better comparisons of the collected spectra, the raw spectra are shown (i.e., they have not been processed).

RESULTS and DISCUSSION

Table 1 shows the average chemical composition of the 54 crystals studied herein. Despite significant compositional variations of SiO_2 , Al_2O_3 , MgO and CaO contents, all the crystals may be classified

TABLE 1 – Results of quantitative analyses of fluoro-edenite crystals from Biancavilla

	3	4	9	10	31	48	Average*	Average**
SiO ₂	51.58	52.47	53.93	51.91	52.92	51.46	52.38	52.38
TiO ₂	0.61	0.59	0.04	0.73	0.55	0.62	0.52	0.57
Al ₂ O ₃	4.50	4.17	3.04	4.07	3.87	4.41	4.01	4.07
FeO _{tot}	2.58	2.32	2.49	2.48	2.34	2.59	2.47	2.39
MnO	0.46	0.53	0.47	0.54	0.48	0.57	0.51	0.51
MgO	22.45	22.61	23.05	22.63	22.78	22.6	22.69	22.66
CaO	11.05	11.07	10.36	10.87	11.03	10.77	10.86	11.01
Na ₂ O	3.12	3.07	3.28	3.18	3.03	3.25	3.15	3.10
K ₂ O	0.92	0.81	0.84	0.86	0.84	0.83	0.85	0.85
F	4.43	4.56	4.63	4.35	4.28	4.55	4.46	4.49
Cl	0.07	0.07	0.09	0.08	0.06	0.09	0.08	0.08
Total	101.78	102.27	102.24	101.71	102.22	101.75	102.00	102.15
-(F+Cl=O)	1.88	1.93	1.97	1.85	1.82	1.93	1.90	1.91
Total	99.90	100.33	100.27	99.86	100.41	99.82	100.10	100.23

* Derived from 6 analyses of prismatic fluoro-edenite

** Drived from 54 analyses of prismatic fluoro-edenite

as “edenite”. For the presented study six crystals, considered representative for the entire suite, were selected.

The six crystals, labeled: 3, 4, 9, 10, 31 and 48 are shown plotted in Fig. 2 in the Leake diagram (Leake *et al.*, 1997).

Sample 3 shows the highest content of Al₂O₃, primarily located in the T sites. Crystal 4 represents a halfway point between samples 9 and 31. Sample 9 is characterized by the highest amount in SiO₂, MgO and Na₂O, the lowest content in CaO, sodium content higher in the B sites than in the A sites and potassium content comparable with those detected in the other studied crystals. Crystal 31 is very close to the average composition for the six samples described in this work. Sample 48 is the crystal with the lowest amount of SiO₂. In addition, samples 10 and 48 exhibit a high content in Na₂O, TiO₂ and MnO. These crystals have the highest occupancy of the A sites, as a consequence of both high content in calcium and high $\Delta C_{(Mn, Fe^{2+}, Mg)}$ value, see Table 2. Despite samples 10 and 48 showing a similar average composition, we included both samples because sample 10

shows a wide compositional range, while 48 is more chemically homogeneous.

Table 2 shows the chemical formulas for the six crystals calculated on the basis of 24 (O + F + Cl) apfu and Fe³⁺/ΣFe_{tot} determined by Mössbauer Spectroscopy.

Unfortunately, the small dimensions of the individual fluoro-edenite crystals used for Raman analysis prevented determination of the Fe³⁺/ΣFe_{tot} ratio for each sample and a mean value, obtained by Mössbauer Spectroscopy on ~20 mg of powdered crystals (Gianfagna *et al.*, 2007), was necessarily considered. However in the six analyzed samples the total FeO content is very close (Table 1), and the partition between Fe²⁺ and Fe³⁺ in the respective crystal chemical formula (Table 2) may be considered reliable.

As described earlier, the spectroscopic data were collected on hk0 cleavages, always oriented with their elongation axis at 45° with respect to the N-S direction of the ocular lens cross-hair. Three to four Raman spectra were collected on each sample with the same orientation but directing the laser beam to different areas, however no differences

in wavenumbers and intensity of the bands were detected; thus, on the same crystal and along a same crystal direction the results are reproducible. In Figs. 3 a-f a Raman spectrum from the six fluoro-edenite crystals is shown. Spectral artifacts, attributable to the adhesive tape used to fix the thin sections to the support glass, were sometimes detected on sample 48 and always on sample 4. On these crystals bands at 1166, 1114, 1073, 910, 878, 847, 653, 516 cm^{-1} , never observed on non-prepared samples (Rinaudo *et al.*, 2006), appear on the spectra, Fig. 3b. Moreover, the band near 1040 cm^{-1} shows an anomalous intensity. Raman spectra, from the glass and from the glass on which the adhesive tape was added, were collected.

The result from the last test is shown in Fig. 4, proving that when the amphibole crystal is more transparent, as on samples 4 or 48, the contribution of the foreign materials is detectable on the Raman spectrum. It should be noted that the spectrum for sample 48, reported in Fig. 3f, was chosen where the scattering from the material used to fix the crystal was less strong.

Based upon the spectra shown in Figs. 3a-f and the chemical data in Table 1, we can determine the following relationships between Raman spectra and chemical composition:

- in respect of the amount of Si and Al, cations in tetrahedral sites, sample 9 represents the crystal with the highest content of SiO_2 – almost 1%

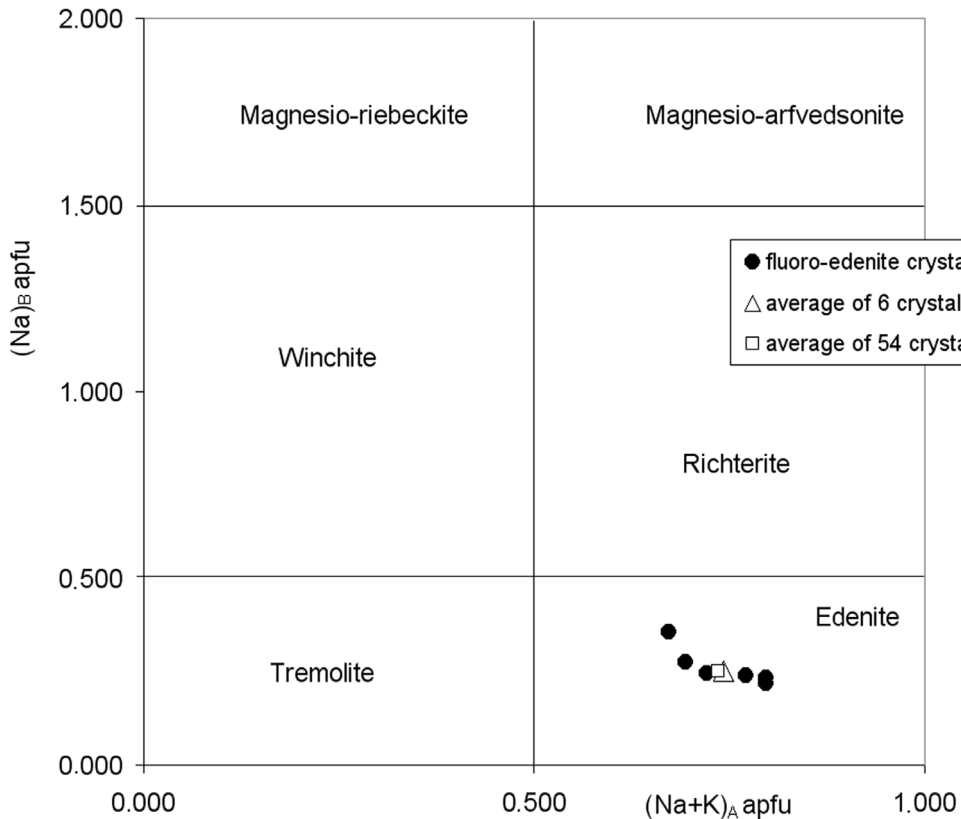


Fig. 2 – Classification graph plotting the composition of the six crystals analyzed in this work. The average chemical compositions for these 6 samples and for all 54 crystals are also reported; modified by Leake *et al.* (1997).

TABLE 2 – *Crystal-chemical formulae of the six prismatic crystals analyzed by micro-Raman spectroscopy, calculated on the basis of 24 apfu (O + F + Cl)*

	3	4	9	10	31	48	Average *	Average **
Si	7.216	7.287	7.469	7.262	7.348	7.203	7.298	7.289
^{IV} Al	0.742	0.681	0.496	0.672	0.619	0.728	0.659	0.667
ΣT	7.958	7.970	7.965	7.933	7.982	7.931	7.956	7.957
^{VI} Al	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
†Fe ³⁺	0.277	0.246	0.264	0.265	0.249	0.278	0.263	0.255
†Fe ²⁺	0.025	0.023	0.024	0.024	0.023	0.025	0.024	0.023
Mg	4.682	4.682	4.759	4.720	4.716	4.715	4.712	4.701
Ti	0.064	0.062	0.004	0.077	0.058	0.065	0.055	0.060
Mn	0.055	0.062	0.055	0.064	0.056	0.067	0.060	0.060
ΣC	5.104	5.077	5.107	5.151	5.115	5.150	5.117	5.099
ΔC(Mn, Fe ²⁺ , Mg)	0.104	0.077	0.107	0.151	0.115	0.151	0.117	0.105
Ca	1.657	1.648	1.537	1.630	1.641	1.615	1.621	1.642
Na	0.240	0.275	0.356	0.220	0.244	0.234	0.261	0.253
ΣB	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000
Na	0.607	0.551	0.523	0.642	0.573	0.649	0.591	0.584
K	0.164	0.144	0.149	0.154	0.149	0.149	0.151	0.151
ΣA	0.770	0.695	0.672	0.796	0.722	0.797	0.742	0.736

* Derived from 6 analyses of prismatic fluoro-edenite

** Derived from 54 analyses of prismatic fluoro-edenite

† Fe³⁺/Fetot was evaluated by Mössbauer Spectroscopy

higher than in the other samples. Therefore the Al-Si substitutions in the tetrahedral sites are lowest in this sample. In the Raman spectra (Fig. 3c), the most intense band, assigned to symmetric stretching modes (ν_s) A_{1g} of the Si-O_b-Si linkages, lies at 679 cm⁻¹ and the bands at 1061 and 1042 cm⁻¹, ascribed to antisymmetric stretching vibrations (ν_{as}) of the Si-O_b-Si linkages appear as two distinct bands. Finally the band at 929 cm⁻¹, ν_s modes of

the O-Si-O bonds, is better defined than in the spectra from all the other samples. In considering the spectra from samples 48 and 3, Figs. 3f and 3a respectively, corresponding to samples with the lowest amount of SiO₂ (see Tables 1 and 2) the (ν_s) A_{1g} modes lie at 678 cm⁻¹ and the band at 1061 cm⁻¹ disappears. Moreover the band near 925 cm⁻¹, produced by the ν_s modes of the O-Si-O bonds, appears large and convoluted;

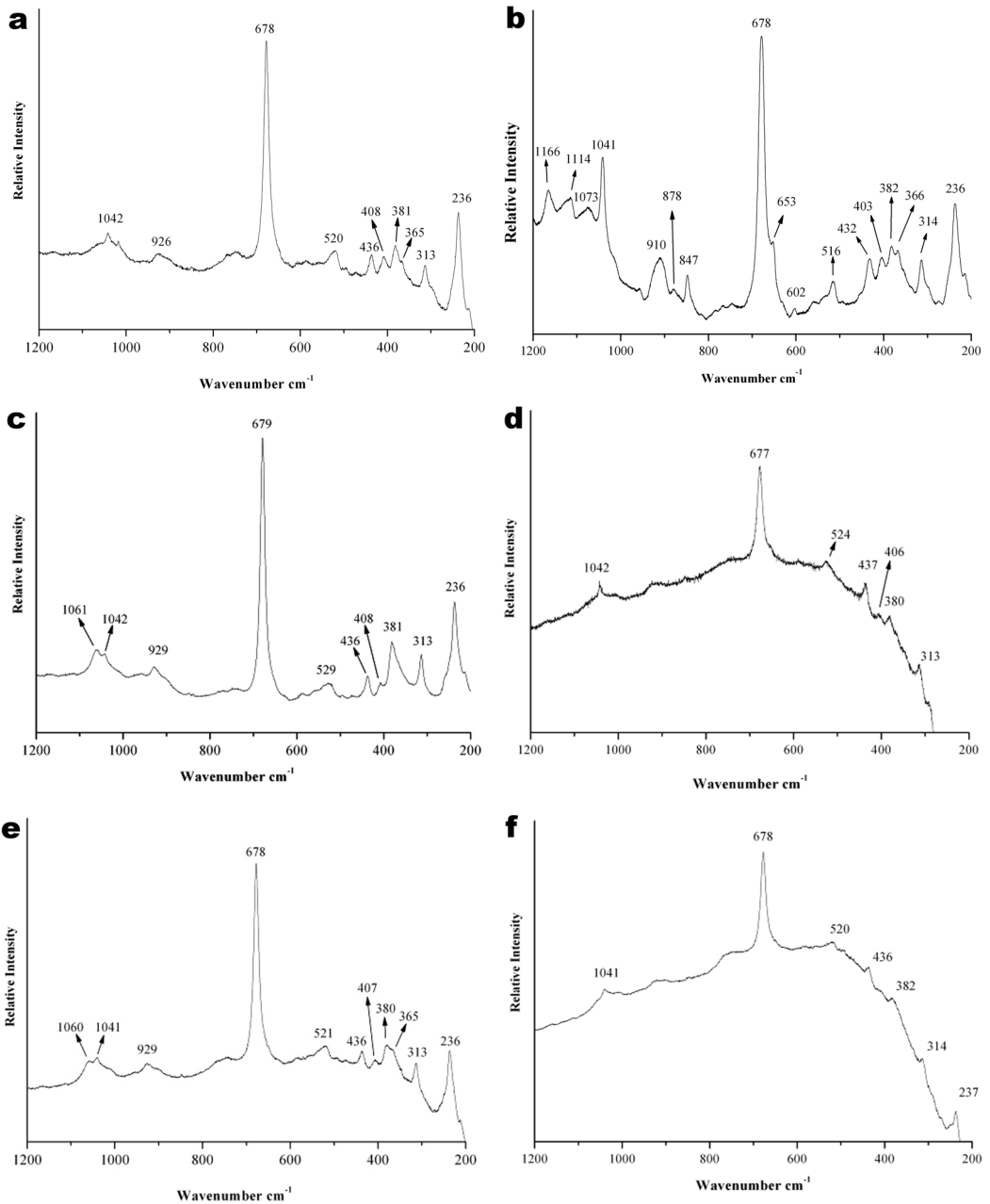


Fig. 3 a - f – Raman spectra of fluoro-edenite samples in the region 1200-200 cm^{-1} . From a to f: sample 3, 4, 9, 10, 31 and 48 respectively.

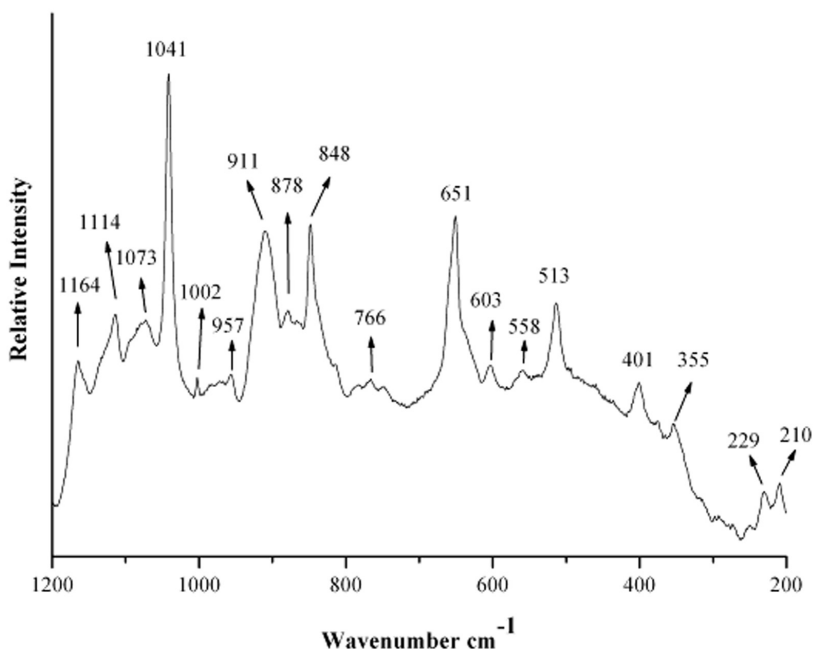


Fig. 4 – Raman spectrum registered on the glass on which adhesive tape was added.

- in the spectra of samples 10 and 48 (Figs. 3d and 3f) a large fluorescence hump occurs underlying the Raman bands. It can also be noted that these samples correspond to fluoro-edenite with an higher amount of $\text{FeO}+\text{MnO}+\text{TiO}_2$ (3.75 and 3.78, respectively) substituting MgO in the C sites;

- considering now the band near 380 cm^{-1} , where no interference of adhesive tape is seen, we observe that in the sample 9 (Fig. 3c), corresponding to the lowest amount of CaO and the highest content of Na_2O , a convoluted band at 381 cm^{-1} was detected. In samples with increasing CaO concentrations, a band near 365 cm^{-1} appears more and more distinct until sample 4 (Fig. 3b), where two separated bands at 382 and 366 cm^{-1} were visible.

For all crystals, the Raman spectrum in the region corresponding to OH^- vibrations was registered although no bands were observed, confirming the chemical data of Table 1 concerning the presence of F^- and Cl^- substituting the OH^- .

The present work would be a contribution to the understanding of the effects of cation substitutions in the wavenumbers of the Raman

bands in amphibole minerals. Chemical analyses and Raman spectroscopy have been carried out on the same samples of fluoro-edenite. The coupling of the optical microscope with a rotating plate allowed consistent orientations for each sample with respect to the incident laser beam. Although at the moment the technique seems more sensitive to tetrahedral substitutions, many other spectroscopic studies must be performed on crystals on which quantitative chemical analyses have been carried out. Use of a spindle-stage equipped microscope could allow collection of Raman spectra along the principal vibration directions of optically anisotropic crystals as discussed in Gunter *et al.* (2005) and Gunter and Twamley (2001) or along their crystallographic directions as discussed in Gunter and Twamley (2001).

Nevertheless, an important observation can be drawn from this study when Raman spectroscopy is applied on samples that use some type of mounting media: every foreign material may be Raman active and therefore its contribution to the observed bands must be considered. New Raman bands or those of

anomalous intensity must be carefully studied in order to be sure that they are not produced by the mounting media, by the materials used to prepare the sample, or by the use of a particular excitation source. From these considerations it is obvious that Raman spectrum must be collected from samples which have undergone no prior sample preparation, thus eliminating the extraneous bands in the spectra.

Finally, this study on the prismatic fluoro-edenite represents a first step to study the amphibole fibres from Biancavilla which exhibit compositional variation. Specific investigations on the fibrous phases could demonstrate the presence of different compositions in the fibres in the geological setting.

ACKNOWLEDGEMENTS

The authors wish to thank Prof. G. Della Ventura and Prof. M. E. Gunter for the helpful suggestions and the “Ministero dell’Università e della Ricerca” of Italy for financial support (PRIN 2004 project: “Spectroscopic and computational characterization of fibrous minerals not classified asbestos”).

REFERENCES

- BARD T., YARWOOD J. and TYLEE B. (1997) - *Asbestos fiber identification by Raman microspectroscopy*. J. Raman Spectrosc., **28**, 803-809.
- BELLUSO E., FORNERO E., ALBERTAZZI G., CAIRO S. and RINAUDO C. (2007) - *Use of micro-Raman spectroscopy to distinguish carlosturanite from the serpentine minerals*. Can. Mineral., **45**, 1495-1500.
- BLAHA J.J. and ROSASCO G.J. (1978) - *Raman microprobe spectra of individual microcrystals and fibres of talc, tremolite, and related silicate minerals*. Anal. Chem., **50**, 892-896.
- BRUNI B.M., PACELLA A., MAZZIOTTI-TAGLIANI S., GIANFAGNA A. and PAOLETTI L. (2006) - *Nature and extent of exposure to fibrous amphiboles in Biancavilla*. Sci. Total Environ., **370**, 9-16.
- BURRAGATO F., COMBA P., BAIOCCHI V., PALLADINO D.M., SIMI 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)*. Environ. Geol., **47**, 855-868.
- GIANFAGNA A., ANDREOZZI G., BALLIRANO P., MAZZIOTTI-TAGLIANI S. and BRUNI B.M. (2007) - *Structural and chemical contrasts between prismatic and fibrous fluoro-edenite from Biancavilla Sicily, Italy*. Can. Mineral., **45**, 249-262.
- GIANFAGNA A., BALLIRANO P., BELLATRECCIA F., BRUNI B.M., PAOLETTI L. and OBERTI R. (2003) - *Characterisation of amphibole fibres linked to mesothelioma in the area of Biancavilla, Eastern Sicily, Italy*. Mineral. Mag., **67(6)**, 1221-1229.
- GIANFAGNA A. and OBERTI R. (2001) - *Fluoro-edenite from Biancavilla (Catania, Sicily, Italy): Crystal chemistry of a new amphibole end-member*. Am. Mineral., **86 (11-12)**, 1489-1493.
- GROPPA C., RINAUDO C., GASTALDI D., CAIRO S. and COMPAGNONI R. (2006) - *Micro-Raman spectroscopy for a quick and reliable identification of serpentine minerals from ultramafics*. Eur. J. Mineral., **18**, 319-329.
- GUNTER M.E., BELLUSO E. and MOTTANA A. (2007) - *Amphiboles: Environmental and health concerns*. Hawthorne F. C., Oberti R., Della Ventura G. and Mottana A. Eds. The Mineralogical Society of America - Chantilly (USA), 545 pp.
- GUNTER M.E., DOWNS R.T., BARTELMES K.L., EVANS S.H., POMMIER C.J.S., GROW J.S., SANCHEZ M.S., and BLOSS F.D. (2005) - *Optic properties of centimeter-sized crystals determined in air with the spindle stage using EXCALIBUR*. Am. Mineral., **90**, 1648-1654.
- GUNTER M.E., DYAR M.D., TWAMLEY B., FOIT F.F. and CORNELIUS S. (2003) - *Composition Fe³⁺/Σ Fe, and crystal structure of non-asbestiform and asbestiform amphiboles from Libby, Montana, U.S.A*. Am. Mineral., **88(12)**, 1970-1978.
- GUNTER M.E. and TWAMLEY B. (2001) - *A new method to determine the optical orientation of biaxial minerals: A mathematical approach*. Can. Mineral., **39**, 1701-1711.
- LEAKE B.E., WOOLLEY A.R., ARPS C.E.S., BIRCH W.D., GILBERT M.C., GRICE J.D., HAWTHORNE F.C., KATO A., KISCH H.J., KRIVOVICHEV V.G., LINTHOUT K., LAIRD J.O., MANDARINO J.A., MARESH V.W., NICKEL E.H., ROCK N.M.S., SCHUMACHER J.C., SMITH D.C., STEPHENSON N.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*. Am. Mineral., **82**, 1019-1037.
- 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*. Spectrochim. Acta A, **52**, 315-328.
- MEEKER G.P., BERN A.M., BROWNFIELD I.K., LOWERS H.A., SUTLEY S.J., HOEFEN T.M. and VANCE J.S. (2003) - *The Composition and Morphology of Amphiboles from the Rainy Creek Complex, Near Libby, Montana*. Am. Mineral., **88(12)**, 1955-1969.
- PASCALÉ F., TOSCONI S., ZICOVICH-WILSON C., UGLIENGO P., ORLANDO R. and DOVESI R. (2004) - *Vibrational spectrum of brucite, Mg(OH)₂: a periodic ab initio quantum mechanical calculation including OH anharmonicity*. Chem. Phys. Lett., **396**, 308-315.
- PRENCIPE M., NOEL Y., CIVALLERI B., ROETTI C. and DOVESI R. (2006) - *Quantum-mechanical calculation of the vibrational spectrum of beryl (Al₄Be₆Si₁₂O₃₆) at the Γ point*. Phys. Chem. Miner., **33**, 519-532.
- RINAUDO C., BELLUSO E. and GASTALDI D. (2004) - *Assessment of the use of Raman spectroscopy for the determination of amphibole asbestos*. Mineral. Mag., **68(3)**, 455-465.
- RINAUDO C., GASTALDI D., BELLUSO E. and CAPELLA S. (2005) - *Application of Raman Spectroscopy on asbestos fibre identification*. N. Jb. Miner. Abh., **182/1**, 31-36.
- RINAUDO C., GASTALDI D. and BELLUSO E. (2003a) - *Characterization of chrysotile, antigorite and lizardite by FT-Raman Spectroscopy*. Can. Mineral., **41**, 883-890.
- RINAUDO C., GASTALDI D. and BELLUSO E. (2003b) - *La spettroscopia Raman: tecnica di identificazione rapida di fibre di asbesto*. Siti contaminati, **2**, 116-120.
- RINAUDO C., GASTALDI D., CAIRO S., GIANFAGNA A., MAZZIOTTI-TAGLIANI S., TOSI G. and CONTI C. (2006) - *Characterization of fluoro-edenite by μ -Raman and μ -FTIR spectroscopy*. Mineral. Mag., **70(3)**, 291-298.
- 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)*. Eur. J. Oncol., **9**, 169-75.
- WANG A., DHAMELINCOURT P. and TURRELL G. (1988a) - *Raman Microspectroscopic Study of the Cation Distribution in Amphibole*. Appl. Spectrosc., **42**, 1441-1450.
- WANG A., DHAMELINCOURT P. and TURRELL G. (1988b) - *Infrared and Low-Temperature Micro-Raman Spectra of the OH Stretching Vibrations in Cummingtonite*. Appl. Spectrosc., **42**, 1451-1457.