

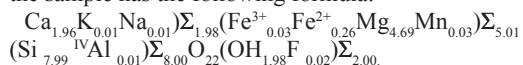
Crystal chemical and structural characterization of fibrous tremolite from Ala di Stura (Lanzo Valley, Italy)

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ABSTRACT. — The present work reports new chemical and structural data of fibrous tremolite from Ala di Stura (Lanzo Valley, Piedmont, Italy). From the toxicological point of view, this fibrous tremolite species exhibited high carcinogenicity in previous intraperitoneal injection experiments with rats. Crystal-chemical data were obtained by electron microprobe and ICP-MS analysis, Mössbauer and FT-IR spectroscopy, and parallel-beam X-ray powder diffraction. Fe²⁺ occurs at the [M(1)+M(3)] and M(2) sites, and Fe³⁺ is present only in M(2) site. No evidence of a split M(4) site was observed. The presence of Fe²⁺ at both M(1) and M(3) sites was confirmed by FT-IR spectroscopy, with M(1) = 0.09 apfu and M(3) = 0.05 apfu. The cell volume, 909.07(2) Å³, is higher than that for the end-member (Ca/Mg = 2/5) tremolite, in accord with the presence of small amount of Fe; the sample has the following formula:

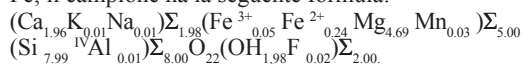


RIASSUNTO. — Il presente lavoro riporta nuovi dati chimici e strutturali della tremolite fibrosa di Ala di Stura (Valle di Lanzo, Piemonte, Italia). Da un punto di vista tossicologico, questa tremolite ha già mostrato

una elevata cancerogenicità in precedenti studi con iniezioni intraperitoneali su ratti.

I dati cristallografici chimici qui riportati sono stati ottenuti tramite Microsonda Elettronica, ICP-MS, spettroscopie Mössbauer e FT-IR, e diffrazioni di raggi-X a fascio parallelo su polveri.

Il Fe²⁺ occupa i siti [M(1)+M(3)] e M(2), mentre il Fe³⁺ è presente esclusivamente nel sito M(2). Nessuna evidenza è stata invece osservata per uno "split" del sito M(4). La presenza di Fe²⁺ in entrambi i siti M(1) e M(3) è stata confermata dalla spettroscopia FT-IR, con M(1) = 0,09 apfu e M(3) = 0,05 apfu. Il volume della cella elementare di 909,07(2) Å³ è più grande di quello del termine estremo di tremolite (Ca/Mg = 2/5) in accordo con la presenza di un basso contenuto di Fe; il campione ha la seguente formula:



KEY WORDS: *fibrous tremolite; crystal chemistry; Mössbauer spectroscopy; Rietveld method; Ala di Stura, Valle di Lanzo, Piedmont, Italy.*

INTRODUCTION

Tremolite is a monoclinic (C2/m) calcic amphibole with ideal formula Ca₂Mg₅Si₈O₂₂(OH)₂.

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In addition to the prismatic variety, the fibrous variety is very common, and belongs to the regulated asbestos minerals, together with actinolite, amosite, antophyllite riebeckite, and crocidolite. Crystal-chemical characterization of fibrous amphiboles is extremely relevant for environmental and health issues. Although the crystal chemistry of the amphibole prismatic varieties has been well described in the literature, the corresponding fibrous varieties have not been properly characterized. Due to difficulties in the experimental approach, detailed work on fibrous amphiboles has appeared only recently (Sokolova *et al.*, 2000, 2003; Gunter *et al.*, 2003; Gianfagna *et al.*, 2003, 2007; Ballirano *et al.*, 2008). The effects of asbestos on human health have been recognised since the beginning of the last century. Toxicological studies showed that interaction between fibrous material and biological materials are strongly dependent on both the morphology/crystal habit and the crystal chemistry of the mineral fibers (Fubini, 1993, 1996; Gilmour *et al.*, 1997). Fibers of tremolite from Ala di Stura (Lanzo Valley, Piedmont) were used in an intraperitoneal injection experiment with male SPF Wistar rats. The tremolite sample showed high carcinogenicity and very long incubation times of the mesothelioma. (Davis *et al.*, 1991; Addison and McConnel, 2005). Conversely, cytotoxicity of Lanzo tremolite on A549 lung cells was recently shown to be very low compared to tremolite fibers

from the nearby Susa and Ossola Valleys (Gazzano *et al.*, 2007; Turci *et al.*, 2007). The specimen studied in this work comes from the serpentinites of the Ultrabasic Lanzo Massif in the Occidental Alps (Lanzo Valley, Piedmont). The Lanzo Massif is part of the innermost part of “Zona Piemontese”; part of the sub-continental lithosphere emplaced at shallow levels during the opening of the Mesozoic Piemontese-Ligurian basin and subsequently involved in the subduction processes associated with ocean closure (Piccardo, 2004). The tremolite occurs in veins associated with extensional fault movement. The hand-sample is composed of tremolite, calcite and serpentine.

ANALYTICAL METHODS

Scanning Electron Microscopy (SEM), Electron Microprobe (EMP) analysis and Inductively Coupled Plasma-Mass Spectrometry (ICP-MS)

SEM was performed using a ZEISS DSM 940A equipped with a LINK EDS system. Images were obtained from a fragment of the hand specimen mounted on a sample stub and carbon coated (about 0.05 μm of thickness). Analytical conditions were 15 kV accelerating voltage and 3.4 μA beam current. The acicular morphology and fiber bundles are shown in Fig. 1. The chemical composition of the tremolite fibers was determined using a

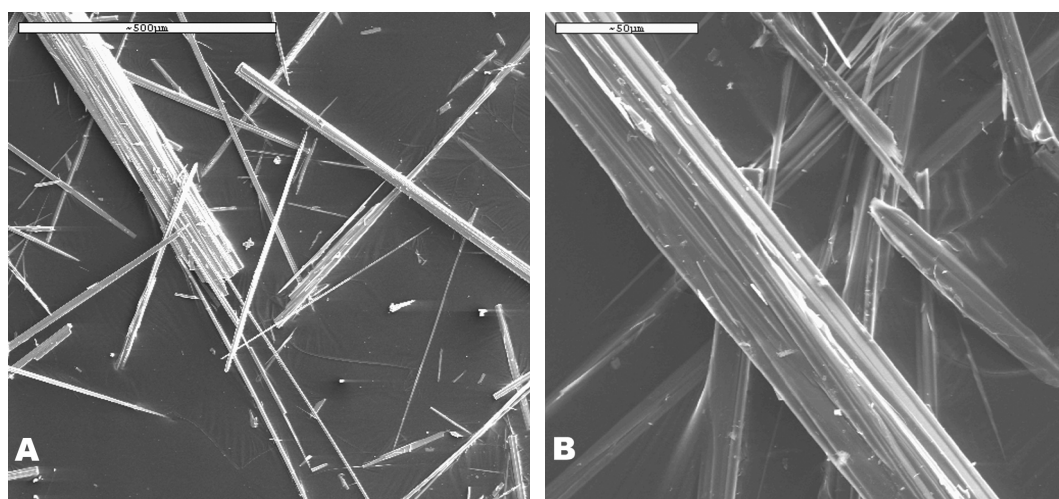


Fig. 1 - SEM images of fibrous Ala di Stura tremolite: a) dimension bar 500 μm ; b) dimension bar 50 μm .

Cameca SX-50 electron microprobe equipped with five wavelength-dispersive spectrometers using the following conditions: excitation voltage 15 kV, specimen current 15 nA, beam diameter 5 μm , 20 s count time (peak), 10 s count time (background). The following standards were used: wollastonite (Si $K\alpha$, Ca $K\alpha$), rutile (Ti $K\alpha$), corundum (Al

$K\alpha$), magnetite (Fe $K\alpha$), metallic Mn (Mn $K\alpha$), periclase (Mg $K\alpha$), orthoclase (K $K\alpha$), jadeite (Na $K\alpha$), metallic Cr (Cr $K\alpha$), fluorophlogopite (F $K\alpha$), and sylvite (Cl $K\alpha$).

Table 1 shows the average chemical composition, observed ranges (min-max), and crystal-chemical formula normalized on the basis of 24 (O+F+Cl).

TABLE 1
Chemical composition obtained by EMP (14 analytical points) and ICP-MS analysis, min-max ranges and mean crystal-chemical formula of fibrous Ala di Stura tremolite

Oxides	EMP wt(%)	ICP-MS wt(%)	Range	Sites	apfu
SiO ₂	57.50(36)	-	57.09 - 58.45	Si	7.994
TiO ₂	0.02(2)	0.02	0.00 - 0.05	^{IV} Al	0.009
Al ₂ O ₃	0.05(1)	0.04	0.03 - 0.07	ΣT	8.002
Cr ₂ O ₃	0.01(1)	-	0.00 - 0.04		
MgO	22.64(22)	28.01	22.22 - 23.06		
CaO	13.14(13)	15.79	12.96 - 13.35	^{VI} Al	0.000
MnO	0.26(5)	0.19	0.20 - 0.35	Ti	0.002
FeO _{tot}	2.42(25)	2.27	1.98 - 2.81	Cr	0.001
Na ₂ O	0.06(2)	0.03	0.03 - 0.08	Fe ³⁺	0.025
K ₂ O	0.03(1)	0.02	0.01 - 0.05	Mg	4.691
F	0.04(5)	-	0.00 - 0.15	Fe ²⁺	0.256
Cl	0.01(1)	-	0.00 - 0.04	Mn	0.03
H ₂ O*	2.13			ΣC	5.005
	98.30				
F ₃ Cl=O	0.02			Ca	1.957
Total	98.28			Na	0.015
				K	0.006
				ΣB	1.978
**Fe ₂ O ₃	0.24				
**FeO	2.20				
				OH	1.978
				F	0.017
				Cl	0.002
				ΣO_3	1.997

Note: estimated standard deviations in brackets. * estimated from stoichiometry.

** measured by Mössbauer spectroscopy.

Cations are reported in atoms per formula unit (apfu) and were assigned following Hawthorne (1981) and Leake *et al.* (1997). Table 1 also shows the results of an ICP-MS analysis on bulk separate.

⁵⁷Fe Mössbauer Spectroscopy

The amphibole fibers were gently ground in an agate mortar with acetone and mixed with a powdered acrylic resin to avoid (or reduce) preferred orientations. About 100 mg of sample were available, and FeO total content was close to 2.5 wt. %, so that the absorber was within the limits for the thin absorber thickness described by Long *et al.* (1983).

Data were collected at room temperature, using a conventional spectrometer operated in constant acceleration mode, with a ⁵⁷Co source of nominal strength of 50 mCi in a rhodium matrix, and recorded in a multichannel analyzer using 512 channels for the velocity range -4 to 4 mm/s.

About 3.5 million counts per channel were collected. After velocity calibration against a spectrum of high-purity α -iron foil (25 μ m thick), the raw data were folded to 256 channels. The spectrum was fitted using the Recoil 1.04 fitting program (Lagarec and Rancourt, 1988). Pure Lorentian line shape were fitted, and results were satisfactory (reasonable parameters and reduced $\chi^2 = 0.71$). On this basis, more complex fitting, involving quadrupole splitting distributions was considered unnecessary. A model based on three doublets, with two doublets for Fe²⁺ and one doublet for Fe³⁺ was chosen. Uncertainties were calculated using the covariance matrix and the errors were estimated to be approximately $\pm 3\%$ for both Fe²⁺ and Fe³⁺ (Table 2).

X-ray Powder Diffraction

Powder diffraction data were collected on a fully-automated parallel-beam Bruker AXS D8 Advance diffractometer, operating in transmission mode and equipped with a Position Sensitive Detector (PSD) VÅNTEC-1. Fibers were ground with ethanol in agate mortar and the powder mounted in a 0.7 mm diameter borosilicate glass capillary. Preliminary evaluation of the diffraction pattern indicated the presence of serpentine (a reflection at $12.5^\circ 2\theta$ was removed from the refinement).

Rietveld refinement was carried out with the GSAS (Larson and Von Dreele, 1994) and the EXPGUI graphical interface (Toby, 2001). The background was fitted with a 36-term Chebyshev polynomial of the first kind to better model the bump arising from the incoherent scattering from the capillary.

Peak-shapes were fitted with the TCH pseudo-Voigt function (Thompson *et al.*, 1987) modified for asymmetry (Finger *et al.*, 1994). Refined variables were the GW (angle-independent) Gaussian parameter, LX and LY (1/cos θ and tan θ dependent) Lorentzian parameters, and S/L and H/L asymmetry parameters (constrained to be equal in magnitude). **Starting structural data were from Yang and Evans (1996).** Isotropic displacement parameters were kept fixed throughout the refinement because of the strong correlations with the site occupancies.

Cell parameters, fractional coordinates for all atoms, and site scattering for M(1), M(2), M(3), M(4) and M(4⁺) were refined. Structural soft constraints were also imposed: T-O x 8 = 1.625(25) Å, O-O x 12 = 2.655(40) Å, M(1)-O x 6 = 2.08(1) Å, M(2)-O x 6 = 2.08(5) Å, M(3)-O x 6 = 2.07(1) Å, M(4)-O x 8 = 2.51(15) Å, M(4⁺)-O x 8 = 2.55(35) Å

TABLE 2
Room temperature Mössbauer parameters for the fibrous Ala di Stura tremolite

δ	ΔE_Q	Γ	Assignment	Area (%)	χ^2
1.14	2.92	0.32	Fe ²⁺	51	
1.16	1.89	0.32	Fe ²⁺	38	0.71
0.28	1.17	0.6	Fe ³⁺	11	

Note: δ = centre shift (with respect to α iron); ΔE_Q = quadrupole splitting; Γ = full width half maximum.

with an initial weight on the constraints of 1000. The weight was then reduced to 2 in the last stages of the refinement.

Attempts to refine the M(4') site resulted in the y coordinate of M(4') moving toward M(4) with a corresponding reduction of the occupancy to zero, indicating a single M(4) site.

Attempts to model the presence of preferred orientation by means of the generalised spherical harmonics description of Von Dreele (1997) produced a minor improvement in the fit with an index J of 1.042. Convergence was reached with the agreement factors reported in Table 3. Experimental details and miscellaneous data are reported in Table 3. Fractional coordinates and

isotropic displacement parameters are instead reported in Table 4. Selected bond distances and angles are reported in Table 5, unit-cell parameters and site scattering (s.s.) values in Table 6.

The experimental and calculated patterns with the relative differences curve are shown in Fig. 2.

Fourier Transform InfraRed (FT-IR) Spectroscopy

FT-IR data were collected on a Nicolet MAGNA 760 over the range 4000-400 cm^{-1} : 32 scans at a nominal resolution of 4 cm^{-1} were averaged. The instrument was equipped with a KBr beamsplitter and a TGS detector. The powdered samples were mixed in a 2:100 ratio with 200 mg of KBr in order

TABLE 3

Experimental details of the X-ray diffraction data collection and miscellaneous data of the refinement. Statistical descriptors as defined by Young (1993)

Instrument	Siemens D8 Advance
X-ray tube	CuK α at 40 kV and 40 mA
Incident beam optic	Multilayer X-ray mirrors
Sample mount	Rotating capillary (60 rpm)
Soller slits	2 (2.3° divergence + radial)
Divergence and antivergence slits	0.6 mm
Detector	Position Sensitive Detector (PSD) VÅNTEC-1 opening window 6° 2 θ .
2 θ range (°)	5-140
Step size (°)	0.02
Counting time (s)	10
R _p (%); R _{wp} (%); R _F ² (%)	2.19; 3.49; 6.02
Reduced χ^2	14.91
Restraints contribution to χ^2	76.7
Refined parameters	87
Peak-cut-off (%)	0.05
J	1.042
GW	18.9(3)
LX; LY	0.7(1); 9.0(2)
S/L=H/L	0.0273(3)

TABLE 4

Fractional coordinates and isotropic displacement parameters (not refined) for fibrous Ala di Stura tremolite

Site	x	y	z	U _{iso} (Å ²)
O(1)	0.1161(6)	0.08577(29)	0.2190(14)	0.008
O(2)	0.1180(7)	0.17225(33)	0.7233(14)	0.008
O(3)	0.1086(7)	0	0.7144(19)	0.008
O(4)	0.3648(6)	0.24733(27)	0.7863(17)	0.008
O(5)	0.3431(7)	0.13367(29)	0.0944(15)	0.008
O(6)	0.3460(7)	0.11632(25)	0.5980(16)	0.008
O(7)	0.3426(7)	0	0.2929(20)	0.008
T(1)	0.28274(33)	0.08374(15)	0.2978(8)	0.005
T(2)	0.2886(4)	0.17043(14)	0.8018(8)	0.005
M(1)	0	0.08811(23)	0.5	0.006
M(2)	0	0.17708(23)	0	0.006
M(3)	0	0	0	0.006
M(4)	0	0.27735(15)	0.5	0.008
H*	0.206	0	0.771	0.03

* kept fixed throughout the refinement

to obtain transparent pellets. Measurements were done in air at room temperature.

RESULTS AND DISCUSSIONS

Comparison between ICP-MS and the EMP results (Table 1) shows differences observed between MgO and CaO far larger than their standard deviations and are related to the presence of calcite and serpentine in the hand sample as revealed by the results of the previous XRPD experiments. EMP analyses suggest chemical homogeneity of the fibers. The FeO_{tot} content varies from 1.98 to 2.81 wt % and is not related to the Ca content. The Mössbauer pattern is typical of a paramagnetic material without impurities (Fig 3). The spectrum

is nicely reproduced by means of three quadrupole doublets: the first two show isomer shift (IS) values about 1.1 mm/s and quadrupole splitting (QS) values of about 1.9 mm/s and 2.9 mm/s, and were assigned Fe²⁺; the other one shows IS of about 0.28 mm/s and QS of about 1.2 mm/s and was assigned to Fe³⁺. The Fe³⁺ content is 11% Fe_{tot} from direct area measurement, and 9% when adjusting for the recoil-free fraction, as suggested by Dyar *et al.* (1993). In the series tremolite-actinolite, Burns and Greaves (1971) attributed the Fe²⁺ doublets with QS of 1.7-1.9 mm/s and 2.8-2.9 mm/s to the presence of ^{M(2)}Fe²⁺ and ^{M(1)}Fe²⁺, respectively. More recently, many authors have assigned the doublet with the lowest QS to ^{M(2)}Fe²⁺, but different assignments have been proposed for the doublets with higher QS, suggesting an irresolvable combination of

TABLE 5

Selected bond distances (\AA) and polyhedral distortion ($\Delta \times 10^4$) for fibrous Ala di Stura tremolite. Reference data of Yang and Evans, 1996 (Y&E96) from single-crystal and those of Ballirano *et al.*, 2008 (Ball08) from Rietveld refinement are shown for comparison

	This work	Y&E96	Ball08		This work	Y&E96	Ball08
T(1)-O(1)	1.587(5)	1.600(1)	1.592(4)	T(2)-O(4)	1.591(5)	1.587(1)	1.598(4)
T(1)-O(7)	1.627(3)	1.619(1)	1.630(2)	T(2)-O(2)	1.624(5)	1.612(1)	1.627(4)
T(1)-O(5)	1.627(6)	1.633(2)	1.624(5)	T(2)-O(6)	1.656(7)	1.676(1)	1.656(5)
T(1)-O(6)	1.658(8)	1.630(2)	1.649(5)	T(2)-O(5)	1.643(8)	1.656(2)	1.654(6)
<T(1)-O>	1.625	1.620	1.624	<T(2)-O>	1.629	1.633	1.634
Δ	2.4	0.6	1.6	Δ	2.3	4.6	2.1
M(1)-O(3) x 2	2.085(5)	2.087(1)	2.071(4)	M(2)-O(4) x 2	2.037(7)	2.019(1)	2.028(5)
M(1)-O(1) x 2	2.091(7)	2.067(1)	2.080(5)	M(2)-O(2) x 2	2.087(6)	2.088(1)	2.074(5)
M(1)-O(2) x 2	2.088(6)	2.081(1)	2.081(5)	M(2)-O(1) x 2	2.167(6)	2.134(1)	2.133(5)
<M(1)-O>	2.088	2.078	2.079	<M(2)-O>	2.097	2.080	2.078
Δ	0	0.2	0.1	Δ	6.5	5.2	4.3
M(3)-O(3) x 2	2.058(9)	2.062(2)	2.060(6)	M(4)-O(4) x 2	2.297(7)	2.327(1)	2.306(5)
M(3)-O(1) x 4	2.092(6)	2.073(1)	2.093(4)	M(4)-O(2) x 2	2.378(7)	2.405(1)	2.375(5)
<M(3)-O>	2.081	2.069	2.082	M(4)-O(6) x 2	2.580(6)	2.535(2)	2.565(4)
Δ	0.6	0.1	0.6	M(4)-O(5) x 2	2.808(7)	2.766(1)	2.784(5)
				<M(4)-O>	2.516	2.508	2.508
T(1)-O(5)-T(2)	139.4(5)			Δ	62	44	55
T(1)-O(6)-T(2)	136.4(5)						
T(1)-O(7)-T(1)	137.0(6)						

Note: Polyhedron distortion Δ as defined by Brown and Shannon (1973): $\Delta = (1/n)\Sigma[(R_i - R)/R]^2$ where n is the number of ligands. R is the average bond length and R_i an individual bond length.

$M^{(1)+M(3)}Fe^{2+}$ (see Gunter *et al.*, 2003, and references therein).

In the present work, about 40% of the total Fe^{2+} was allocated to M(2) (QS of 1.89 mm/s) and about 60% of the total Fe^{2+} to M(1)+M(3) (QS of 2.92 mm/s). Fe^{3+} was allocated at the M(2) site, as consistently reported by various authors for sodic amphiboles (Ernst and Wai, 1970), strontian potassic-richterite (Sokolova *et al.*, 2000), ferrian winchite (Sokolova *et al.*, 2001), winchite-

richterite (Gunter *et al.* 2003), and fluoro-edenite (Gianfagna *et al.*, 2007).

Thus this sample is compositionally fairly close to an ideal tremolite. The measured cell volume of 909.07(2) \AA^3 is higher than the values of 906.5 \AA^3 (Gottschalk *et al.*, 1999), 906.6 \AA^3 (Verkouteren and Wylie, 2000), 907.0 \AA^3 (Yang and Evans, 1996) reported for pure tremolite, and 907.37 \AA^3 (Ballirano *et al.*, 2008) reported for fibrous tremolite of the Susa Valley. The higher volume is in accord with the presence of 5.4% ferro-actinolite

TABLE 6

Unit-cell parameters and site scattering values (in electrons per formula unit) for fibrous Ala di Stura tremolite obtained from structure refinement. Possible population are the result of combining chemical, Mössbauer and Rietveld refinement data

	Refinement	Possible site partition	Chemical data
a (Å)	9.8424(1)		
b (Å)	18.0712(2)		
c (Å)	5.28354(7)		
β (°)	104.680(1)		
V (Å ³)	909.07(2)		
M(4)	39.08(20)		
B site sum	39.08(20)	Ca _{1.96} ; Na _{0.01} ; K _{0.01}	39.50
M(1)	24.86(17)	Mg _{1.88} ; Fe ²⁺ _{0.09} ; Mn _{0.03}	25.65
M(2)	25.46(17)	Mg _{1.86} ; Fe ³⁺ _{0.03} ; Fe ²⁺ _{0.12}	26.1
M(3)	12.48(12)	Mg _{0.95} ; Fe ²⁺ _{0.05}	12.7
C sites sum	62.80(27)		64.57

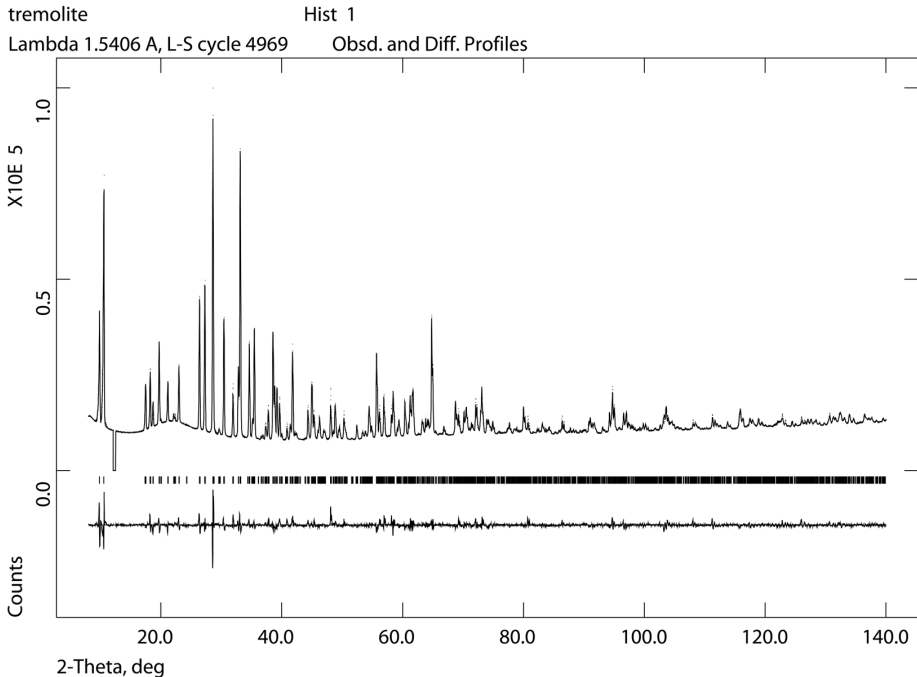


Fig. 2 - Experimental (dots) and calculated (line) Rietveld plots for fibrous Ala di Stura tremolite. The difference profile is showed at the bottom. Vertical markers refer to the positions of the calculated Bragg reflections for tremolite.

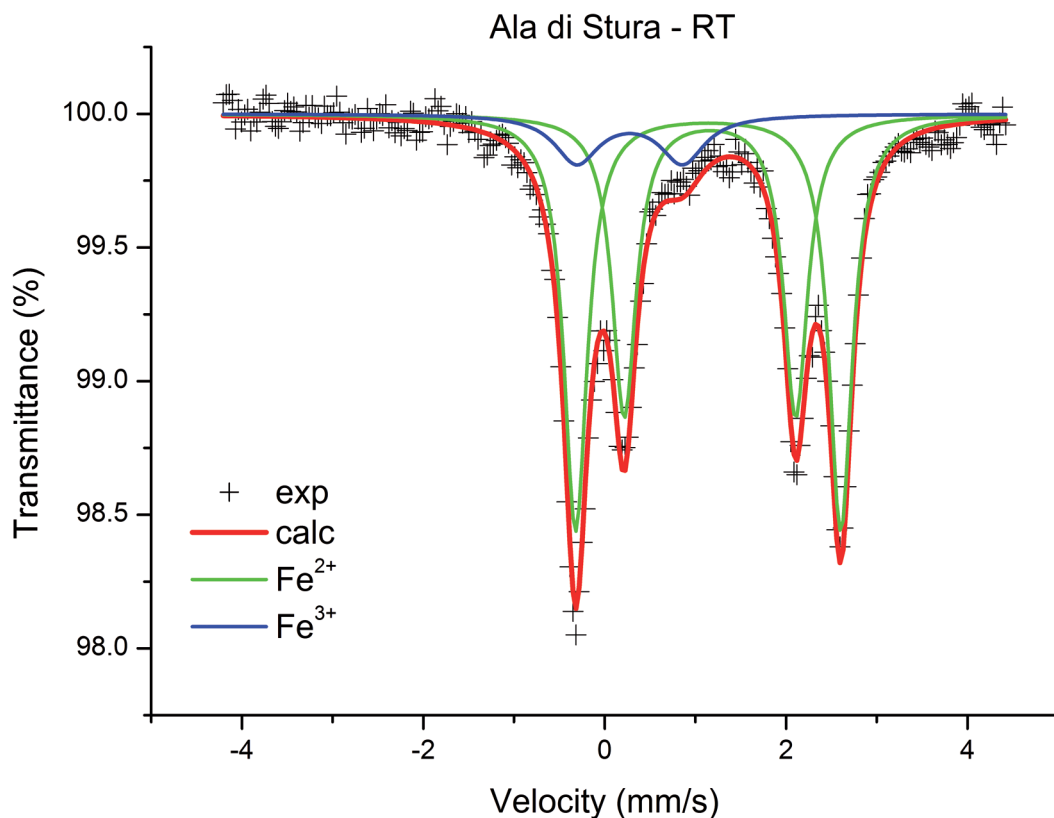


Fig. 3 - Room temperature ^{57}Fe Mössbauer spectrum of fibrous Ala di Stura tremolite.

content $[X_{\text{FeA}} = (\text{Fe}^{2+} + \text{Mn}) / (\text{Fe}^{2+} + \text{Mn} + \text{Mg})]$. Rietveld refinement indicates that the mean $\langle \text{T}(1)\text{-O} \rangle$ distance is slightly smaller than $\langle \text{T}(2)\text{-O} \rangle$ as reported for $C2/m$ amphiboles with no tetrahedrally-coordinated Al (Hawthorne, 1981). Polyhedron distortion Δ shows comparable values for both T(1) and T(2) tetrahedra. Site scattering at M(1), M(2), and M(3) sites indicates the presence of a scatterer heavier than Mg, in agreement with both chemical data and the results of Mössbauer spectroscopy. Good agreement is observed between s.s. derived from Rietveld refinement and those from chemical data, with the largest differences being less than 3% (see Table 6). Site assignment allocates 64% of $^{\text{M}(1)+\text{M}(3)}\text{Fe}^{2+}$ to M(1) and 36% to M(3). Considering the site multiplicities, there are similar Fe^{2+} occupancies at the M(1), M(2), and M(3) sites (Table 6), as observed by Evans and Yang (1998) for tremolite–ferro-actinolite and

Ballirano *et al.* (2008) for tremolite from the Susa Valley. Moreover, the presence of Fe^{2+} at M(1) and M(3) is confirmed by the FT-IR spectrum (Fig. 4). In addition to the absorption band at $3673\text{-}3675\text{ cm}^{-1}$ assigned to the arrangement $^{\text{M}(1)}\text{Mg}^{\text{M}(1)}\text{Mg}^{\text{M}(3)}\text{Mg}$ prominent band is observed at 3660 cm^{-1} and a very weak band at 3645 cm^{-1} , both of which were attributed to $^{\text{M}(1)+\text{M}(3)}\text{Fe}^{2+}$ environment according to results of Skogby and Rossman (1991) and Hawthorne and Della Ventura (2007). Moreover, there is no Fe^{3+} at M(1) or M(3) as shown by the absence of absorption bands at $\Delta = -50\text{ cm}^{-1}$ from the tremolite MgMgMg band (Raudsepp *et al.*, 1987).

With regard to ideal tremolite (Yang and Evans, 1996) and Susa Valley tremolite (Ballirano *et al.*, 2008), the observed increase in $\langle \text{M}(2)\text{-O} \rangle$ distance is consistent with a higher content of Fe^{2+} at M(2). With respect to the ideal tremolite, the increase in

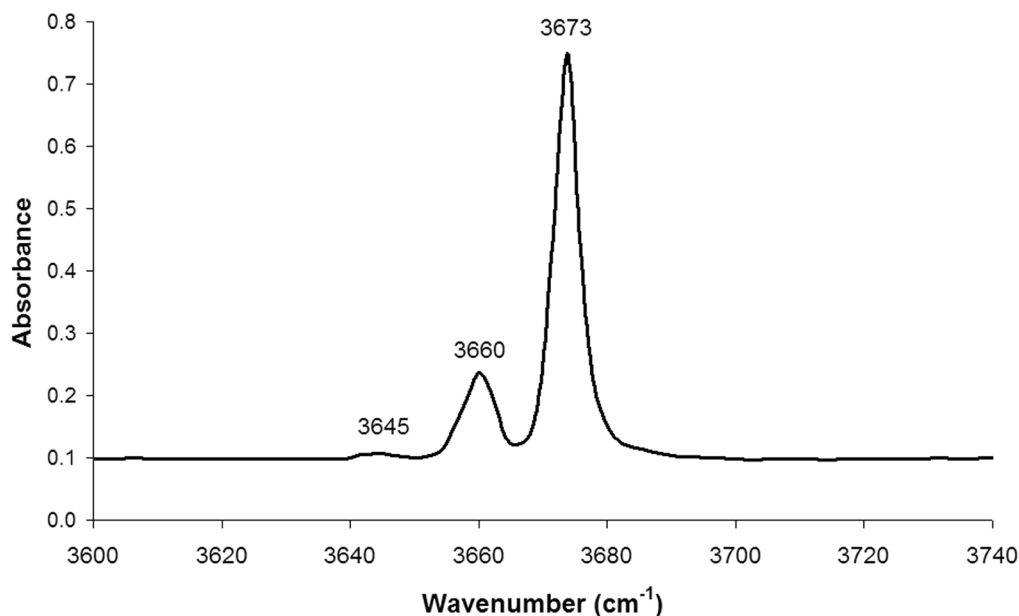


Fig. 4 - FT-IR spectrum in the 3740-3600 cm^{-1} range.

<M(3)-O> is consistent with the presence of minor Fe^{2+} at M(3).

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REFERENCES

- ADDISON J. and McCONNEL E.E. (2005) - *A review of carcinogenicity studies of asbestos and non-asbestos tremolite and other amphiboles*. Intern. Symp. on the Health Hazard Eval. of Fibrous Particles associated with Taconite and the adjacent Duluth Complex. 45 pp.
- BALLIRANO P., ANDREOZZI G.B. and BELARDI G. (2008) - *Crystal chemical and structural characterization of fibrous tremolite from Susa Valley, Italy, with potential harmful effects on human health*. Am. Mineral., **93**, 1023-1033.
- BURNS R.G. and GREAVES C. (1971) - *Correlations of infrared and Mössbauer site population measurements of actinolites*. Am. Mineral., **56**, 2010-2033.
- DAVIS J.M.G., ADDISON J., MCINTOSH C., MILLER B.G. and NIVEN K. (1991) - *Variations in the carcinogenicity of tremolite dust samples of differing morphology*. Ann. N.Y. Acad. Sci., **643**, 473-490.
- DYAR M.D., MACKWELL S.M., MCGUIRE A.V., CROSS L.R. and ROBERTSON J.D. (1993) - *Crystal chemistry of Fe^{3+} and H^+ in mantle kaersutite: Implications for mantle metasomatism*. Am. Mineral., **78**, 968-979.
- ERNST W.G. and WAI C.N. (1970) - *Mössbauer, infrared, X-ray and optical study of cation ordering and dehydrogenation in natural and heat-treated sodic amphiboles*. Am. Mineral., **55**, 1226-1258.
- EVANS B.W. and YANG H. (1998) - *Fe-Mg order-disorder in tremolite-actinolite-ferro-actinolite at*

- ambient and high temperature. *Am. Mineral.*, **83**, 458-475.
- FINGER L.W., COX D.E. and JEPHCOAT A.P. (1994) - *A correction for powder diffraction peak asymmetry due to axial divergence*. *J. Appl. Crystallogr.*, **27**, 892-900.
- FUBINI B. (1993) - *The possible role of surface chemistry in the toxicity of inhaled fibers*. In D.B. Wahreit Ed., *Fiber Toxicol.*, **11**, 229257. Academic Press, San Diego.
- FUBINI B. (1996) - *Physico-chemical and cell free assays to evaluate the potential carcinogenicity of fibres*. In A.B. Kane, P. Boffetta, R. Saracci, and J. Wilbourn Eds., *Mec. of Fiber Carcin.*, IARC Scientific Publication 140, International Agency for Research on Cancer, Lyon.
- GAZZANO E., TURCI F., RIGANTI C., TOMATIS M., FUBINI B., BOSIA A. and GHIGO D. (2007) - *La tremolite nelle alpi occidentali: test cellulari con prospettive tossicologiche*. Workshop "Anfiboli fibrosi: nuove problematiche relative al rischio ambientale e sanitario". Roma, 27-28 April 2007, Abstracts, 73-74. (in Italian)
- GIANFAGNA A., BALLIRANO P., BELLATRECCIA F., BRUNI B.M., PAOLETTI L. and OBERTI R. (2003) - *Characterization of amphibole fibers linked to mesothelioma in the area of Biancavilla, Eastern Sicily, Italy*. *Mineral. Mag.*, **67**, 1221-1229.
- GIANFAGNA A., ANDREOZZI G.B., 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.
- GILMOUR P.S., BROWN D.M., BESWIK P.H., MACNEE W., RAHMAN I. and DONALDSON K. (1997) - *Free radical activity of industrial fibers: role of iron in oxidative stress and activation of transcription factors*. *Environ. Health Persp.*, **105** Suppl. 5, 1313-1317.
- GOTTSCHALK M., ANDRUT M. and MELZER S. (1999) - *The determination of the cummingtonite content of synthetic tremolite*. *Eur. J. Mineral.*, **11**, 967-982.
- GUNTER M.E., DYAR M.D., TWAMLEY B., FOIT F.F. JR. and CORNELIUS C. (2003) - *Composition, $Fe^{3+}/\Sigma Fe$, and crystal structure of non-asbestiform and asbestiform amphiboles from Libby, Montana, U.S.A.* *Am. Mineral.*, **88**, 1970-1978.
- HAWTHORNE F.C. (1981) - *Crystal chemistry of the amphiboles*. In D.R. Veblen Ed., *Amphiboles and other hydrous pyriboles Mineralogy*. *Rev. Mineral. Geoch.*, **9A**, 1-102.
- HAWTHORNE F.C. and DELLA VENTURA G. (2007) - *Short range order in amphiboles*. In *Amphiboles: Crystal Chemistry, Occurrence, and Health issues*. *Rev. Mineral. Geoch.*, **67**, 173-222.
- LAGAREC K. and RANCOURT D.G. (1998) - *RECOIL. Mössbauer spectral analysis software for Windows, version 1.0*. Department of Physics, University of Ottawa, Canada.
- LARSON A.C. and VON DREELE R.B. (1994) - *General Structure Analysis System (GSAS)*. Los Alamos National Laboratory Report LAUR 86-748.
- 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., MANDARINO J.A., MARESCH V.W., NICKEL E.H., ROCK N.M.S., SCHUMACHER J.C., SMITH D.C., STEPHENSON N.N., UNGARETTI L., WITHTAKER 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.
- LONG G.J., CRANSHAW T.E. and LONGWORTH G. (1983) - *The ideal Mössbauer effect absorber thickness*. *Möss. Effect Ref. Data J.*, **6**, 42-49.
- MCCONNEL E.E. (1995) - *Advantages and limits of in vivo screeneg tests*. *Ann. Occup. Hyg.*, **39**, 727-735.
- PICCARDO G.B. (1983) - *Genesi delle ofioliti dell'Appennino Settentrionale*. *Mem. Soc. Geol. It.*, **25**, 75-89.
- RAUDSEPP M., TURNOCK A.C., HAWTHORNE F.C., SHERRIFF B.K. and HARTMAN J.S. (1987) - *Characterization of synthetic pargasitic amphiboles ($NaCaMg_4M^{3+}Si_6Al_2O_{22}(OH,F)_2$; $M^{3+}=Al, Cr, Ga, Sc, In$) by infrared spectroscopy, Rietveld structure refinement and ^{27}Al , ^{29}Si , and ^{19}F MAS NMR spectroscopy*. *Am. Mineral.*, **72**, 580-593.
- SKOGBY H. and ROSSMAN G.R. (1991) - *The intensity of amphibole OH bands in the Infrared absorption spectrum*. *Phys. Chem. Min.*, **18**, 64-68.
- SOKOLOVA E.V., KABALOV Y.K., MCCAMMON C., SCHNEIDER J. and KONEV A.A. (2000) - *Cation partitioning in an unusual strontian potassicrichterite from Siberia: Rietveld structure refinement and Mössbauer spectroscopy*. *Mineral. Mag.*, **64**, 19-23.
- SOKOLOVA E.V., HAWTHORNE F.C., MCCAMMON C. and SCHNEIDER J. (2001) - *Ferrian winchite from the Ilmen Mountains, Southern Urals, Russia and some problems with the current scheme of nomenclature*. *Can. Mineral.*, **39**, 171-177.
- THOMPSON P., COX D.E. and HASTINGS J.B. (1987) -

- Rietveld refinement of Debye-Scherrer synchrotron X-ray data from Al₂O₃*. *J. Appl. Crystallogr.*, **20**, 79-83.
- TOBY B.H. (2001) - *EXPGUI, a graphical user interface for GSAS*. *J. Appl. Crystallogr.*, **34**, 210-213.
- TURCI F., GAZZANO E., TOMATIS M., RIGANTI C., GHIGO D. and FUBINI B. (2007) - *La tremolite nelle alpi occidentali: un'analisi chimico-fisica con prospettive tossicologiche*. Workshop "Anfiboli fibrosi: nuove problematiche relative al rischio ambientale e sanitario". Roma, 27-28 April 2007, Abstracts, 68-72.
- VON DREELE R.B. (1997) - *Quantitative texture analysis by Rietveld refinement*. *J. Appl. Crystallogr.*, **30**, 517-525.
- VERKOUTEREN J.R. and WILYE A.G. (2000) - *The tremolite-actinolite-ferro-actinolite series: systematic relationship among cell parameters, composition, optical properties, and habit, and evidence of discontinuities*. *Am. Mineral.*, **85**, 1239-1254.
- YANG H. and EVANS B.W. (1996) - *X-ray structure refinements of tremolite at 140 and 295 K: Crystal chemistry and petrologic implications*. *Am. Mineral.*, **81**, 1117-1125.
- YOUNG R.A. (1993) - *Introduction to the Rietveld method*. In R.A. Young, Ed., *The Rietveld method*, 1-38, Oxford Science, Oxford.