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Quantitative chemistry and compositional variability of fluorine fibrous amphiboles from Biancavilla (Sicily, Italy)

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Abstract. — Compositional variability of the new fluorine fibrous amphiboles (fluoro-edenite) from the volcanic area of Biancavilla (Sicily, Italy) is reported here for the first time. Quantitative chemical analysis of a suite of four samples was performed by a standardized SEM-EDS microanalysis method, previously developed and tested on different typologies of fibrous amphiboles. The results highlighted compositional differences, especially concerning Si, Ca, Fe, and Na contents, both within the same and among the different samples. Compared to the previously investigated fluoro-edenite prismatic variety, the fluorine fibrous amphiboles showed average values of Si and Fe contents always higher, whereas Ca was significantly lower, which we consider a distinctive character for the fluorine fibrous variety. The Fe^{3+}/Fe_{tot} ratios, evaluated by Mössbauer spectroscopy, reflected different iron oxidation states: Fe^{3+} was always more prevalent than Fe^{2+}, which was very low for two of the four samples analyzed. Employing the Leake classification, all the analyzed fluorine amphibole fibers showed an edenite-winchite trend, with a non negligible content of tremolite component. Both the fluorine amphibole fibers and the prismatic fluoro-edenite from Biancavilla may be correlated with the same genetic process, but the compositional variability reflect different growth conditions. The large variation observed for Fe^{3+}/Fe_{tot} ratios in the amphibole fibers is probably due to local variations of oxygen fugacity during crystallization. A workable hypothesis is that a hot metasomatizing fluid, enriched in fluorine and other incompatible elements, altered the volcanic rocks and caused the crystallization of either the fibrous fluorine amphiboles, by a very fast cooling, or the prismatic fluoro-edenite, by slow cooling.

Riassunto. — Viene riportata la variabilità composizionale di alcuni campioni di anfiboli fibrosi (fluoro-edenite) di Biancavilla (Sicilia, Italia), analizzati per la prima volta in modo quantitativo tramite microanalisi SEM-EDS standardizzata, un metodo sviluppato e testato in precedenza dagli stessi autori su diverse tipologie di anfiboli fibrosi. I risultati hanno evidenziato differenze composizionali relative, in particolare, ai contenuti di Si, Ca, Fe e Na, sia all'interno dello stesso campione che tra i diversi campioni analizzati. Un carattere composizionale distintivo tra questi anfiboli fibrosi e la fluoro-edenite prismatica precedentemente studiata è il contenuto sempre più basso di Ca e sempre più alto di Si e Fe nella varietà fibrosa. Inoltre i rapporti Fe^{3+}/Fe_{tot} ottenuti sui campioni di fibre tramite spettroscopia Mössbauer hanno evidenziato differenti stati di ossidazione del

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ferro, con il Fe^{3+} sempre prevalente sul Fe^{2+}. Secondo la classificazione di Leake, le fibre di anfibolo analizzate mostrano un andamento composizionale edenite-winchite, con un contenuto di tremolite non trascurabile. La variabilità composizionale riscontrata indica pertanto condizioni di crescita differenti, sebbene il processo genetico che ha portato alla formazione delle fibre potrebbe essere lo stesso processo che ha permesso la cristallizzazione della fluoro-edenite prismatica. L'ampia variazione del rapporto Fe^{3+}/Fe_{tot} riscontrata nelle fibre di anfibolo sembrerebbe associata a variazioni locali della fugacità di ossigeno durante la loro cristallizzazione. Sulla base delle indicazioni acquisite è ipotizzabile che un fluido caldo, ricco in F ed altri elementi incompatibili, abbia metasomatizzato le rocce vulcaniche preesistenti e facilitato la cristallizzazione di anfiboli fibrosi (raffreddamento veloce) e di fluoro-edenite prismatica (raffreddamento lento).

KEY WORDS: *fluorine fibrous amphiboles, compositional variability, fluoro-edenite, Biancavilla.*

INTRODUCTION

After the studies of Gianfagna *et al.* (2003) and Gianfagna *et al.* (2007), the present work represents a further step in the characterization of the new fluorine-bearing fibrous amphiboles found in the volcanic area of Biancavilla (Sicily, Italy). The quantitative characterization of the mineral fibers, and in particular of the fibrous amphiboles, is a real and actual issue for their environmental and health interest. The Biancavilla samples give a novel opportunity to clarify the classification of the mineral fibers as asbestos, and to enhance understanding of the role of chemical composition in the fiber-lung reactivity mechanisms. Residents of this volcanic area experienced unexpected cases of pleural mesothelioma, a distinctive lung specific pathology, which was found to be related to the widespread occurrence of amphibole fibers (Paoletti *et al.*, 2000; Comba *et al.*, 2003; Burragato et al, 2005). Recent in vitro studies of these amphibole fibers showed that their toxicity is strongly related to chemical composition, with particular relevance of the Fe content and its oxidation state (Soffritti *et al.*, 2004; Cardile *et al.*, 2004; Pugnaloni *et al.*, 2007). The mineralogical approach is essential in accurately characterizing mineral fibers: their study is difficult because of their extremely small size, and in fact only few works report quantitative chemistry of fibrous minerals. However, Meeker *et al.*(2003), Gunter at al. (2003), Gunter *et al.* (2007), and Gianfagna *et al.* (2007), have studied winchite, tremolite, and fluoro-edenite fibers, suggesting specific analytical procedures.

Mineralogical, genetic and environmental aspects of the fluorine-rich amphiboles from Biancavilla were recently described by Mazziotti-Tagliani (2007) and by Mazziotti-Tagliani *et al.* (2007). Previous qualitative chemical studies by Bruni *et al.* (2006) showed compositional differences in fibrous amphiboles as compared to the prismatic fluoro-edenite, while Gianfagna *et al.* (2007) utilized a semi-quantitative chemical characterization employing an innovative SEM-EDS "overlapping" analytical method. The method was able to distinguish between prismatic and fibrous fluoro-edenite compositions.

In this work we perform a quantitative chemical characterization of a suite of fluorine-rich fibrous amphiboles coming from the locality of "Il Calvario", utilizing the quantitative analytical method described in detail by Paoletti *et al.* (2008). This method is a SEM-EDS technique standardized with powdered prismatic crystals similar in composition to the fibers.

MATERIALS AND ANALYTICAL METHODS

Materials

Next to the eastern part of Biancavilla there is a quarry area called "Il Calvario", which was mined extensively for a sandy volcanic material for local buildings. After Romano (1982), this area was geologically reinterpreted as a series of domes and dikes associated with "autoclastic breccia", a fine grained material (Burragato *et al.*, 2005). Previous mineralogical investigations identified in the area the new amphibole end-member *fluoro-edenite* (Gianfagna & Oberti, 2001), which displays prismatic, acicular, and fibrous morphologies.

The discovery of the fibrous amphibole, recognized as the cause of the pathology in this area (Paoletti *et al.*, 2000; Comba *et al.*, 2003), made necessary further mineralogical and environmental studies. The volcanological and mineralogical investigations identified the presence of fibrous amphiboles inside and outside the quarry (Burragato *et al.*, 2005). The fibrous morphology was found in the metasomatized benmoretic lava (sodian latite) both in the fractures and cavities in association with prismatic fluoro-edenite, and in the autoclastic breccia (Fig. 1). The aerial photograph of the Biancavilla area showing the location of the sampling points of the four samples is reported in Fig. 2.

The starting material utilized for this work was the autoclastic grained material, made of lava pieces scattered in a fine matrix, which contained the mineral assemblage with micrometrical and sub-micrometrical dimensions (Fig. 1b). The extremely small dimensions of the fibers and their associated minerals made the mineralogical studies difficult. To avoid or at least reduce any influence of other minerals on the experimental data, samples enriched in amphibole fibers were prepared, according to the procedure reported in Gianfagna *et al.* (2007). Briefly, this method allows a fiber enrichment of >90% through a simple sedimentation in water, and a withdraw of the surnatant solution after 30 to 35 hours. In the SEM photographs of Fig. 3 two examples of the fibrous amphiboles analyzed in the present work are displayed. These fluorine-rich fibrous amphiboles generally show a thickness lower than 1 μm (200 to 600 nm) and a variable length, until to 100-150 μm. In particular, sample 1, 2, and 3, are characterized by an acicular-fibrous morphology and shorter fibers (medium length ≅ 50 μm), while sample 4 shows a more filamentous-asbestiform morphology with length up to 150 μm.

Quantitative SEM-EDS chemical characterization

Because of the extremely reduced dimensions of the fibers, chemical analysis by Electron Microprobe (EMP) was not possible, therefore quantitative chemical analyses were obtained by utilizing the standardization procedure on SEM-EDS instrument, as reported in Paoletti *et al.* (2008). To address the problem of the small dimensions of the fibers, fragments of the prismatic fluoro-edenite, previously analysed by EMP, were utilized as a compositional reference. The operating conditions of the instrumental equipment were: 15 keV beam energy, 10 mm working distance, 0° tilt angle. A variable number of fibers (from 40 to about 60, with diameter between 0.2 and 0.9 μm) for each of the four samples were analyzed (Table 1). Sample 2 comes from Poggio Mottese locality, north of the "Il Calvario" quarry area, and is the same sample previously studied in Gianfagna *et al.*

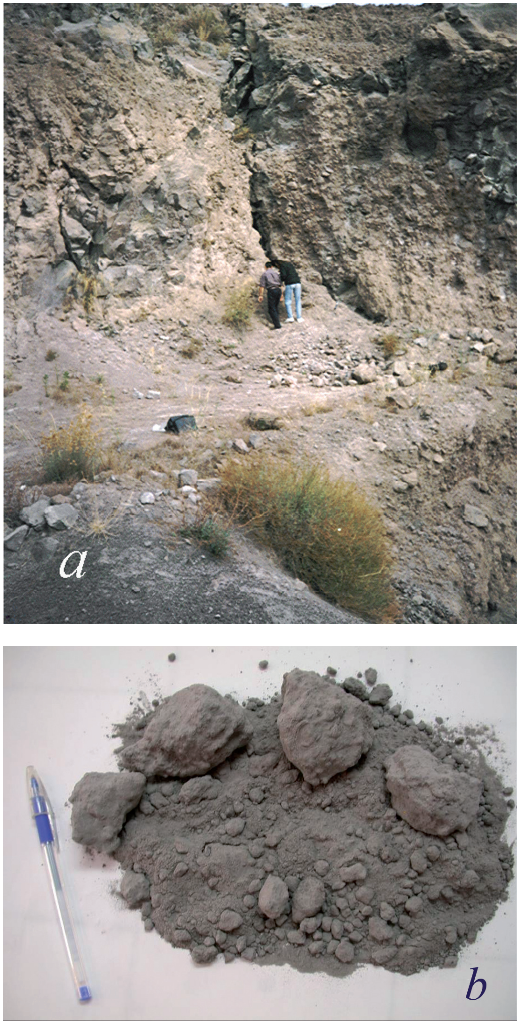

Fig. 1 – a) Extractive front of the "Il Calvario" quarry, where the vertical fractures present superficial mineralization of prismatic yellow fluoro-edenite amphibole; b) fine grained volcanic material of the "autoclastic breccia" (fractured and crumbled benmoreite lava) containing the fluorine fibrous amphiboles.

Fig. 2 – Aerial photograph of Biancavilla area, showing the "Il Calvario" quarry (central zone) and the related sampling points of the four samples of fibrous amphiboles. The red circle represents prismatic fluoro-edenite location. (Modified after Burragato et al., 2005).

(2007). This sample was reanalyzed here to verify the analytical consistence of the method and the differences between the original semi-quantitative and the present quantitative SEM-EDS method.

^{57}*Fe Mössbauer spectroscopy*

The enriched amphibole fiber samples were ground gently in an agate mortar with acetone and mixed with a powdered acrylic resin to avoid (or reduce) preferred orientation. Due to different Fe contents and, above all, the scarcity of the samples, an amount variable between 10 and 70 mg was selected. This corresponds to a maximum of 2 mg Fe/cm^2 and is well below an absorber density where thickness effects affect Mössbauer results, as reported by Long *et al.* (1983). The spectra were collected at room temperature (RT) by using a conventional spectrometer system operated in constant acceleration mode with a ^{57}Co source of nominal strength of 50 mCi in a rhodium matrix. The spectral data were recorded in a multichannel analyser by using 512 channels in the velocity range -4 to 4 mm/s. To obtain good counting statistics, up to 9×10^6 counts per channel were collected and excellent signal-to-noise ratios were obtained. After velocity calibration against a spectrum of high-purity α-Fe foil (25 µm thick) taken at RT, the raw data were folded to 256 channels. The spectra were fitted assuming Lorentzian peak shape and using the commercial fitting program Recoil 1.04 described by Lagarec and Rancourt (1988). The reduced χ^2 was used to evaluate statistical best fit, and uncertainties were calculated using the covariance matrix. Full spectral details and fitting strategies are discussed elsewhere (Andreozzi *et al.*, submitted).

RESULTS AND DISCUSSION

The average chemical compositions of the four samples analysed in the present work are reported in Table 1. For each sample, oxide contents (wt

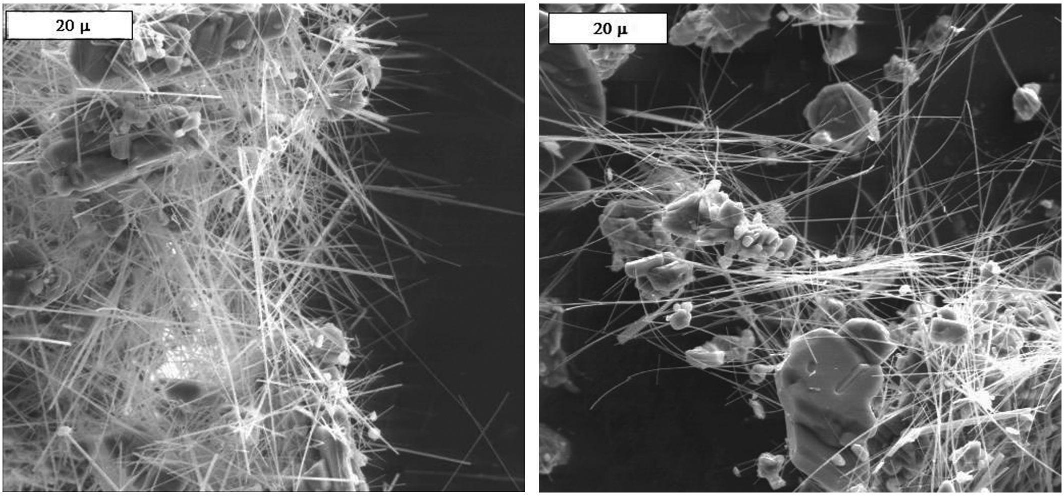

Fig. 3 – SEM photographs of two examples of fibrous amphiboles from Biancavilla: sample 3 (left), and sample 4 (right). The other associated minerals prevalently are alkali-feldspars, clinopyroxenes, fluorapatite and Fe-Ti oxides.

%), compositional range (min-max), and number of atoms per formula unit (*apfu*) are showed. Moreover, an averaged crystal-chemical formula has been calculated and reported. Oxides sum is always 100 % due to the SEM-EDS micro-analysis normalization. Because the difficulty in analyzing F and Cl at low concentrations with SEM-EDS instrument, their contents were fixed to 4.40 and 0.06 wt%, respectively, because these two values represent the average contents generally encountered in the fluoro-edenite amphiboles from Biancavilla analyzed by EMPA (Gianfagna & Oberti, 2001; Gianfagna et al., 2003). Fe^{2+} and Fe^{3+} quantification was obtained by Mössbauer Spectroscopy and utilized for the formula calculation on the basis of 24 (O+F+Cl).

The large number of analyses and the analytical method here employed contributed to a highly reliable chemical characterization of all the analyzed samples. This is particularly evident for sample 2, reanalyzed here, which shows values of iron oxides (Fe_2O_3 4.45, FeO 1.97, wt %) which are different from those (Fe_2O_3 3.17, FeO 1.39 wt %) previously reported in Gianfagna *et al.* (2007). However, even though the oxide contents of Fe^{2+} and Fe^{3+} are different, the Fe^{3+}/Fe_{tot} ratio is the same.

As shown by chemical results reported in Table 1, and clearly evident from plotting on the $^{A}(Na+K)/^{B}Na$ graphs (Leake *et al.*, 1977) in Fig. 4, the four samples show reasonably similar, but slightly different compositional trends. The point analyses of the four samples fall next to the line 1:1 edenite-winchite. However, a tremolite composition is always present in all samples. We would like to highlight the similarity of sample 1 and sample 4 compositional trends, characterized by higher winchite component with respect to the samples 2 and 3, which have more significant tremolite contents. In particular, sample 2 shows the highest Ca and minor Na contents in the A structural site (see formulae in Table 1 subset). Fibers of sample 3 are mainly edenites (nominally fluoro-edenite) with a small tremolite component. Notably, samples 2 and 3 have a compositional range more restricted than samples 1 and 4. Sample 3 is the closest in composition to the prismatic fluoro-edenite studied by Gianfagna & Oberti (2001). Moreover, sample 2 shows a parallel trend with respect to the previous study, (Gianfagna *et al.*, 2007) with higher tremolite component due to higher Fe content and lower Si, Mg, and Na contents. The observed compositional differences are related to the different analytical SEM-EDS method here adopted, which takes into account a significant error factor correction (Paoletti *et al.*, 2008) not previously considered.

The Fe content and oxidation state are not easily related to compositional trends, since samples 2 and 3, the two samples with minor

Table 1
Chemical composition of the four samples of fibrous amphiboles from Biancavilla

	Sample 1		Sample 2		Sample 3		Sample 4	
# Analyses	52		40		42		58	
Oxides (wt%)	Average	Range	Average	Range	Average	Range	Average	Range
SiO_2	54.12	52.39 - 56.70	52.66	50.61 - 55.19	53.49	51.47 - 55.56	53.86	51.68 - 55.92
TiO_2	0.03	0.00 - 0.06	0.03	0.01 - 0.05	0.02	0.00 - 0.06	0.03	0.00 - 0.06
Al_2O_3	1.95	1.38 - 3.28	2.91	1.96 - 3.81	2.51	1.56 - 3.27	2.31	1.52 - 3.32
MgO	21.34	19.28 - 23.11	20.50	19.07 - 21.36	22.63	21.21 - 24.19	21.94	20.56 - 23.39
CaO	8.48	7.03 - 9.88	10.20	9.01 - 11.32	9.19	7.62 - 10.84	8.59	7.22 - 10.58
MnO	0.56	0.00 - 1.06	0.45	0.18 - 0.79	0.49	0.23 - 0.78	0.44	0.00 - 1.00
FeO_{tot}	5.43	3.74 - 6.68	5.98	4.36 - 7.28	3.59	1.88 - 5.18	5.03	3.41 - 6.74
Na_2O	3.10	2.30 - 3.82	2.29	1.49 - 3.10	3.08	2.02 - 3.80	2.78	2.09 - 3.76
K_2O	0.53	0.18 - 1.30	0.52	0.00 - 0.79	0.55	0.11 - 1.02	0.54	0.16 - 1.04
[a]F	4.40		4.40		4.40		4.40	
[a]Cl	0.06		0.06		0.06		0.06	
[b]Total	100.00		100.00		100.00		100.00	
[c]Fe_2O_3	3.26		4.45		3.67		5.25	
[c]FeO	2.50		1.97		0.29		0.30	

[a]fixed values for all samples (see text); [b]normalized analyses; [c]Obtained through Mössbaur investigation

content of winchite component in the Leake graphs, show the highest and the lowest content of total iron, respectively. The same applies for Fe^{2+} contents (0.296 and 0.034 *apfu*, respectively) (Table 2).

Summarizing the compositional characters of these amphibole fibers, we can say that they are all fluorine dominant, in which Ca and Fe^{3+}/Fe_{tot} values result variable. With respect to the previously investigated fluoro-edenite prismatic variety, the fluorine fibrous amphiboles showed average values of Si and Fe contents always higher, whereas Ca was significantly lower, which we consider a distinctive character for the fluorine fibrous variety.

On the basis of this upgraded chemical evidence, we distinguish the several fluorine-rich fibrous amphiboles from Biancavilla in three different varieties represented by:

1) samples 1 and 4, characterized by high winchite component and similar total Fe contents (but different oxidation state);

Table 1
continued...

Chemical formulae on the basis of 24 (O+ F+Cl)

apfu	**1**	**2**	**3**	**4**
Si	7.676	7.495	7.544	7.587
Ti	0.003	0.003	0.002	0.003
Al	0.326	0.488	0.417	0.384
Fe^{3+}	0.348	0.477	0.389	0.557
Fe^{2+}	0.297	0.235	0.034	0.035
Mn	0.067	0.054	0.059	0.053
Mg	4.51	4.35	4.758	4.607
Ca	1.289	1.556	1.389	1.297
Na	0.852	0.632	0.842	0.762
K	0.096	0.094	0.099	0.097
F	1.974	1.981	1.963	1.96
Cl	0.014	0.014	0.014	0.014

1 $^{T}(Si_{7.676}{}^{IV}Al_{0.324})_{\Sigma 8.000}\,{}^{C}({}^{VI}Al_{0.002}Fe^{3+}_{0.348}Fe^{2+}_{0.297}Mg_{4.283}Ti_{0.003}Mn_{0.067})_{\Sigma 5.000}$
$^{B}(Mg_{0.227}Ca_{1.289}Na_{0.484})_{\Sigma 2.000}\,{}^{A}(Na_{0.368}K_{0.096})_{\Sigma 0.464}\,{}^{O3}(F_{1.974}Cl_{0.014})_{\Sigma 1.988}$

2 $^{T}(Si_{7.495}{}^{IV}Al_{0.488})_{\Sigma 7.984}\,{}^{C}(Fe^{3+}_{0.477}Fe^{2+}_{0.235}Mg_{4.229}Ti_{0.003}Mn_{0.067})_{\Sigma 5.000}$
$^{B}(Mg_{0.121}Ca_{1.555}Na_{0.324})_{\Sigma 2.000}\,{}^{A}(Na_{0.307}K_{0.094})_{\Sigma 0.401}\,{}^{O3}(F_{1.981}Cl_{0.014})_{\Sigma 1.995}$

3 $^{T}(Si_{7.544}{}^{IV}Al_{0.417})_{\Sigma 7.961}\,{}^{C}(Fe^{3+}_{0.389}Fe^{2+}_{0.034}Mg_{4.516}Ti_{0.002}Mn_{0.059})_{\Sigma 5.000}$
$^{B}(Mg_{0.242}Ca_{1.389}Na_{0.369})_{\Sigma 2.000}\,{}^{A}(Na_{0.473}K_{0.099})_{\Sigma 0.572}\,{}^{O3}(F_{1.963}Cl_{0.014})_{\Sigma 1.977}$

4 $^{T}(Si_{7.587}{}^{IV}Al_{0.384})_{\Sigma 7.971}\,{}^{C}(Fe^{3+}_{0.557}Fe^{2+}_{0.035}Mg_{4.356}Ti_{0.003}Mn_{0.053})_{\Sigma 5.000}$
$^{B}(Mg_{0.256}Ca_{1.297}Na_{0.447})_{\Sigma 2.000}\,{}^{A}(Na_{0.312}K_{0.097})_{\Sigma 0.409}\,{}^{O3}(F_{1.960}Cl_{0.014})_{\Sigma 1.974}$

2) sample 2, characterized by high tremolite component and the highest Fe content;

3) sample 3, characterized by high edenite (fluoro-edenite) component, and the lowest Fe content.

The compositional variability observed in the analyzed samples may be correlated with small differences in the formation conditions, during the crystallization of the fluorine fibrous amphiboles. Unfortunately, the observed compositional distribution cannot be directly related to the sampling location reported in Fig. 2 because the material in the quarry area is extremely reworked. However, on the basis of the *in situ* observations during the sampling and the additional compositional considerations here obtained, a hypothetic process for the crystallization of prismatic and fibrous fluoro-edenite could be suggested, as already mentioned by Mazziotti-Tagliani (2007).

Hot fluids, enriched in fluorine and other incompatible elements, locally metasomatized the volcanic domes and dike complex present in the

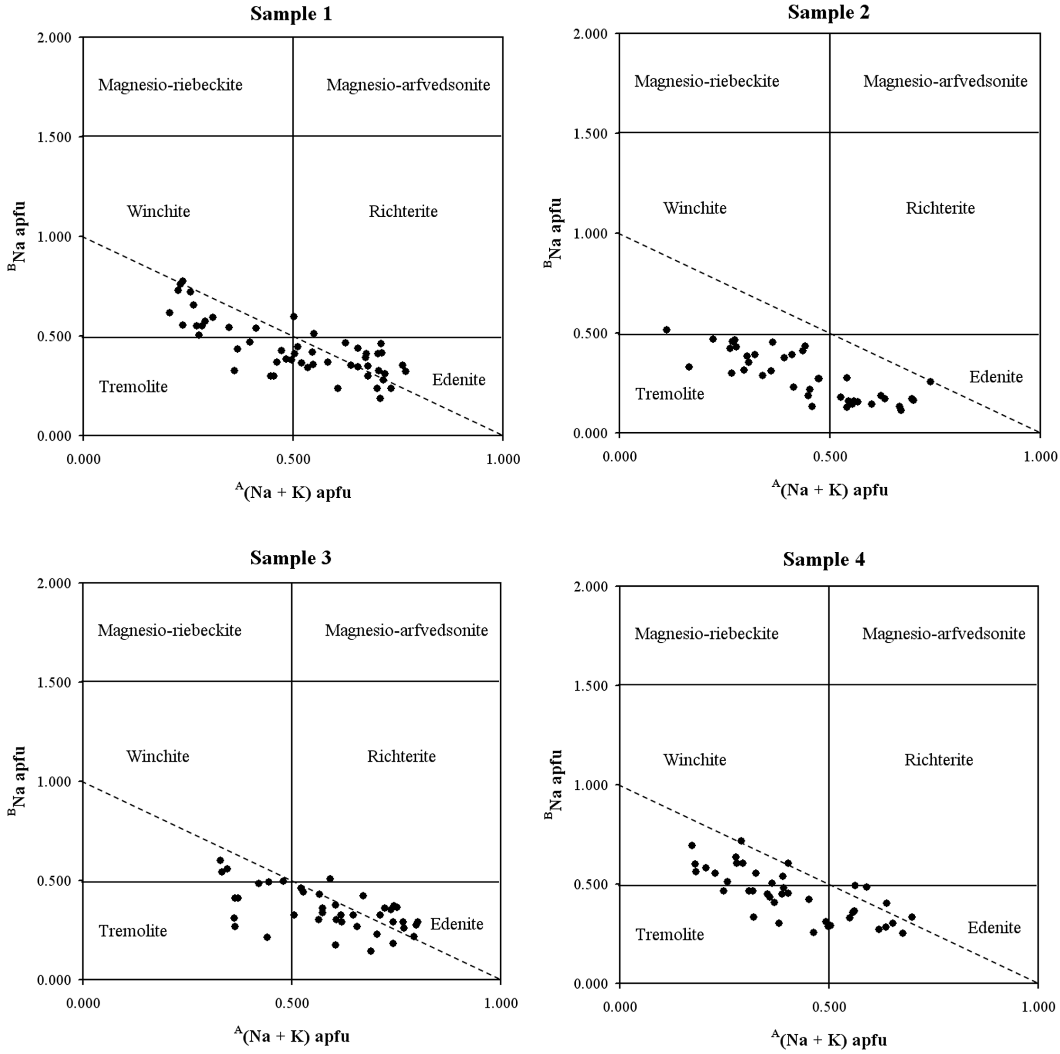

Fig. 4 - All results obtained from the four fibrous amphibole samples from Biancavilla, plotted in the graph A(Na+K)/BNa (Leake et al., 1997).

area (Romano, 1982; Burragato *et al.*, 2005). This caused the crystallization of prismatic and acicular fluoro-edenite, and the coexisting fluorine-rich mineral assemblage, as fluorapatite and fluoroflogopite, in the lava fissures. Fluorapatite (without OH^-) is actually under study for its particular high As content, while fluorophlogopite was recently approved by the IMA commission and published as new fluorine-dominatig mineral (Gianfagna et al, 2007a). In the fine grained material of "autoclastic breccia" abundant amphibole fibers were found, and their dimensions are micrometric to submicrometric (respirable fibers). A workable hypothesis is that the same hot fluid, enriched of F, Cl, Fe, As, REE, etc., (Mazziotti-Tagliani, 2007), contemporarely interacted with both massive and autobrecciated lavas, determining the crystallization of prismatic (in massive lavas)

TABLE 2
Fe^{3+}/Fe_{tot} ratios, and Fe^{2+} and Fe^{3+} contents for the four analyzed samples

Samples	**1**	**2**	**3**	**4**
Fe^{3+}/Fe_{tot}	0.54	0.67	0.92	0.94
Fe^{3+}	0.348	0.477	0.390	0.557
Fe^{2+}	0.296	0.235	0.034	0.036
Total (Fe^{3+}+ Fe^{2+})	**0.644**	**0.712**	**0.424**	**0.593**

and fibrous (in fine grained materials) fluorine amphiboles. Under this hypothesis, the highest cooling path of the fluids in the autoclastic breccia with respect to the dikes is the driving force for the formation of amphibole fibers. Locally different cooling ratios and/or oxygen fugacities should account for the variable Fe^{3+}/Fe_{tot} ratio observed in the four analyzed samples. The suggestion is that the nucleation and crystallization process of the fibers here described could be related to the known phenomenon of the whisker formation, in which the minerals condense directly from vapours or supercritical fluids, as reported for other minerals by several studies (Wiedemann *et al.*, 1974; Macleod and Hall, 1991; Bradley *et al.*, 1996).

The analytical approach here adopted proved to be effective and reliable, and could be also extended to proper characterization of fibers (e.g. asbestos) with high environmental and public health interest.

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