# CRYSTAL CHEMISTRY AND REACTIVITY OF FIBROUS AMPHIBOLES OF ENVIRONMENTAL AND HEALTH INTEREST

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The present study was devoted to the full characterization of amphibole fibers by means of a well tested multi-analytical approach with the aim to correlate crystal chemistry with chemical reactivity and toxicity. The studied specimens are tremolite fibers from ophiolitic outcrops at different Italian localities such as (from north to south): 1) Ala di Stura (Lanzo Valley, Piedmont); 2) Mt. Rufeno (Acquapendente, Latium); 3) Castelluccio Superiore (Potenza, Basilicata); 4) S. Mango (Catanzaro, Calabria). A sample of fibrous tremolite from the ophiolite complex outcropping in Montgomery County, Maryland (USA) was also studied. In addition, samples of non-regulated fibrous amphiboles from Biancavilla (Catania, Sicily) and from Libby (Montana, USA) were studied for comparison. The detailed crystal chemical characterization was carried out by combining Inductively Coupled Plasma-Mass (ICP-MS) spectrometry, Electron Microprobe Analysis (EMPA), Scanning Electron Microscopy (SEM) with microanalysis system, parallel-beam X-Ray Powder Diffraction (XRPD), $^{57}$Fe Mössbauer spectroscopy (MS) and Fourier-Trasform Infra-Red (FT-IR) spectroscopy. Beside the mineralogical characterization, the surface chemistry and surface reactivity of some samples have been also investigated. The surface chemistry of the fibers was studied by X-Ray Photoelectron Spectroscopy (XPS) with specific attention to the surface iron content and its oxidation state. Electron Paramagnetic Resonance (EPR) Spectroscopy was used to characterize the HO° hydroxyl radicals and the measurement of their absolute concentration. In addition, tests of lipid peroxidation in the presence of hydrogen peroxide were performed to identify and distinguish their reactivity, and the degradation of linolenic acid in conditions similar to those found in pulmonary alveoli was monitored. The products of degradation of linolenic acid were studied by UV-visible spectroscopy. The surface chemistry and the reactivity of a sample of crocidolite UICC (Union Internationale Contre le Cancer, Johannesburg, South Africa) and a sample of calcite (Iceland spar variety) were also investigated as positive and negative references, respectively. Finally, full characterization of fibrous amphiboles (morphology, crystal chemistry, crystal structure, cation site partitioning, $Fe^{3+}/Fe_{tot}$ ratio of the bulk and surface, surface chemistry and reactivity) was coupled with cytotoxicity tests *in vitro* (MTT test on A 559 and MeT-5A cells) performed on the same samples.

This work required the use of several complementary disciplines from mineralogy to chemistry and biology. Therefore, the collaboration between the Sapienza University of Rome and the University of Pierre et Marie Curie of Paris VI was the underlying framework of such a challenging and interdisciplinary work.

## STATE OF THE ART

Exposure to asbestos has been linked to numerous health problems and respiratory diseases. Today, three principal diseases are linked to asbestos exposure: asbestosis, lung cancer, and mesothelioma. (1) *Asbestosis* is a non-malignant diffuse interstitial fibrosis of the lung tissue. High asbestos exposure can cause scarring of the lung tissue (fibrosis), causing it to become stiff, resulting in a restriction in pulmonary function and reduction in the lung's ability to exchange carbon dioxide for oxygen. (2) *Lung cancers* related to asbestos exposure are bronchogenic carcinomas, which include squamous cell carcinomas, small- and large-cell carcinoma, and adenocarcinomas. Cancers that arise in other parts of the lung, such as alveolar carcinomas and sarcomas, are rare and are not known to be caused by asbestos. (3) *Mesothelioma* is a cancer which mainly develops in the pleura (outer lining of the lungs and internal chest wall), but it may also occur in the pericardium and peritoneum, lining of heart and abdominal cavities, respectively.

The mechanism through which asbestos fibers may give rise to disease is not yet completely clear. Many authors agree in attributing to mineral fibers the formation of Reactive Oxygen Species (ROS) that determine a strong release of HO° free radicals by partially dissolving into biological fluids participing in Fenton chemistry (Fubini & Otero Aréan, 1999; Kamp & Weitzman, 1999; Robledo & Mossman, 1999). Toxicological studies evidenced that interactions between fibrous material and biological environment are strongly dependent on both the geometry and the crystal chemistry of mineral fibers (Stanton *et al.*, 1981; Fubini, 1993, 1996). In particular, the presence and the bioavailability of Fe received considerable attention by the biomedical community. It was proposed that both the presence and structural coordination of Fe are important factors in the toxicity of asbestos (Fubini *et al.*, 2001) and, furthermore, that only the Fe exposed on the fiber surface is relevant in the ROS production (Gazzano *et al.*, 2005).

Investigations on the relations between asbestos exposure and related diseases have mainly focused on working exposures so far. However, asbestos also occur as accessory minerals in some rocks. In the most abundant of these rocks, the ophiolite complexes, chrysotile, tremolite and actinolite asbestos are frequently found. Ophiolte rocks are used as building and ornamental materials, because of their exceptional physical and mechanical qualities such as strength, durability, variety in appearance and color. Natural asbestos (both chrysotile and amphibole) occurrence represents an environmental problem due to the potential exposure that may result if the asbestos-bearing rocks are disturbed by weathering processes and/or human activities. However, epidemiological studies showed that low to moderate exposure to chrysotile asbestos presents a very low health risk, and this is presumably due to its solubility in the body. On the contrary, the bio-solubility was observed to be very low in the case of amphibole asbestos (Van Oss *et al.*, 1999).

In the Italian peninsula, especially in the Alps and the Apennines, there is a massive presence of ophiolitic outcrops rich in serpentine (chrysotile) and amphibole fibers (tremolite-actinolite and anthophyllite). The Piedmont region (NW Italy) has the largest number of such outcrops such as: the Lanzo Valley and in particular the ex-mine of Balangero, in which chrysotile was mined. Environmental concern was recently caused by the excavations of the Susa Valley railway tunnel (Ballirano *et al.*, 2008). In fact, some high-speed railway lines such as Turin-Lyon and Genoa-Milan involve tunnel excavations occurring in metamorphic formations, such as serpentinites, in which zones containing fibrous tremolite may be found. These excavations give rise to worker health and public environmental issues (Astolfi *et al.*, 1991). Ophiolites hosting fibers of tremolite also outcrop in various localities in the central and southern part of Italy: quarries of ophiolite, widely used in the past, are present in Calabria (Punturo *et al.*, 2002) and Latium (Burragato *et al.*, 2001), but their presence has not been associated with health problems so far. However, in Basilicata, the presence of fibrous tremolite in the soils of Lauria and Castelluccio Superiore Towns (Potenza) was related to some pleural mesothelioma cases occurred in these rural communities (Burragato *et al.*, 2004; Pasetto *et al.*, 2004).

Recently, epidemiological studies revealed cases of environmental contamination of non-regulated fibrous amphiboles. A study on mortality from malignant pleural mesothelioma in Italy evidenced a high and unusual cluster of malignant mesothelioma cases among people living in Biancavilla, a town located on the southwestern side of Etnean volcanic area in Sicily (Di Paola *et al.*, 1996). Environmental and mineralogical surveys in Biancavilla showed no asbestos exposure either from occupational activities or from the use of manufactured products (Paoletti *et al.*, 2000). However, some nearby sites are sources of amphibole minerals of fibrous habit (Paoletti *et al.*, 2000; Gianfagna *et al.*, 2003). The fibrous amphiboles were characterized and the new end-member fluoro-edenite was recognized. On the basis of these results Comba *et al.* (2003) suggested that the unusual cluster of mesothelioma in Biancavilla could be caused by the exposure to such new fibrous amphiboles. From the toxicological point of view, these amphibole fibers showed high carcinogenicity in previous intraperitoneal injection experiments with rats (Soffritti *et al.*, 2004). In addition, recent *in vitro* studies revealed that their toxicity is strongly related to the chemical composition, with particular relevance to the Fe content and its oxidation state (Cardile *et al.*, 2004; Pugnaloni *et al.*, 2007). Another well known case of non-regulated amphibole fiber occurrence is that of Libby (Montana, USA). In this area, an elevated incidence of lung cancer and mesothelioma cases was found in the local miners and millers (McDonald *et al.*, 2002). The local vermiculite mine operated from 1923 to 1990 for the local building industry. Wilye & Verkouteren (2000) and Gunter *et al.* (2001, 2003) demonstrated the presence of fibrous amphiboles, with composition dominantly ranging from winchite to richterite, in the vermiculitic deposits. The environmental survey finally related the diseases to the fibrous amphiboles (Gunter *et al.*, 2003). The above mentioned environmental diseases are related to both regulated and non-regulated amphiboles fibers, and make the study of these minerals a topic of great interest. Although in the scientific literature the crystal-chemistry of the various amphibole prismatic varieties has been described in thousands of works, that of the corresponding fibrous variety has been well characterized just in few cases (Sokolova *et al.*, 2000, 2001; Gunter *et al.*, 2003; Gianfagna *et al.*, 2003, 2007; Ballirano *et al.*, 2008; Pacella *et al.*, 2008, Paoletti *et al.*, 2008).

## RESULTS OBTAINED

The fibrous amphiboles here studied showed $Fe_{tot}$ contents spanning a range from *ca.* 0.24 to *ca.* 0.71 apfu, with the minimum and maximum contents observed for Castelluccio tremolite and sample 2 from Biancavilla, respectively. Tremolites showed the lowest $Fe_{tot}$ content, being on average below *ca.* 0.34 apfu, except for Maryland tremolite (*ca.* 0.52 apfu). Fibrous amphiboles from Biancavilla showed a $Fe_{tot}$ content between *ca.* 0.59 and *ca.* 0.71 apfu, except for sample 3 which displayed $Fe_{tot}$ content of *ca.* 0.42 apfu. The fibrous richterite from Libby revealed an intermediate $Fe_{tot}$ content of *ca.* 0.46 apfu. For comparison, the UICC crocidolite used in this work as the reference compound in the reactivity tests displayed a $Fe_{tot}$ of *ca.* 4.0 apfu, almost an order of magnitude higher than the other samples.

The Fe oxidation states, obtained by Mössbauer analysis on the various fibrous amphiboles, was heterogeneous. In fact, the tremolite samples showed a $Fe^{3+}/Fe_{tot}$ ratio very low, the maximum value reaching 0.24. The $Fe^{3+}/Fe_{tot}$ ratios obtained for the fibrous amphiboles from Biancavilla were higher, clustering around 0.6 and 0.9. Finally, both the fibrous richterite from Libby and the UICC crocidolite showed similar, intermediate Fe oxidation state ($Fe^{3+}/Fe_{tot}$ of 0.65). By combining the chemical, spectroscopic and Rietveld refinement data, $Fe^{2+}$ was assigned to the octhaedral layer [M(1) + M(2) + M(3)]. In particular, for all fibrous tremolites a substantial $Fe^{2+}$ equidistribution was observed over M(1), M(2) and M(3) octahedral sites. Only for the samples 1 and 2 from Biancavilla part of $Fe^{2+}$ was also found to be ordered at M(4) site. $Fe^{3+}$ was mainly located at M(2) site, being disordered over the different octahedra only in the sample 3 and 4 from Biancavilla (Table 1).

Table 1 - Site scattering (s.s.) values in electrons per formula unit for the investigated fibrous amphiboles, obtained from the structure refinement (left) and calculated from the possible site occupancy (right). Possible site occupancy (at centre) was derived from combining chemical and structural data. Data from San Mango tremolite, sample 1 and sample 3 from Biancavilla are reported as an example.

| **San Mango** | s.s. from refinement | Possible site occupancy | s.s. from site occupancy |
|---|---|---|---|
| M(4) | 38.92(12) | $Ca_{1.97}$; $Na_{0.02}$; $Mn_{0.01}$ | 39.87 |
| Sum *B* sites | **38.92(12)** | | **39.87** |
| M(1) | 25.01(12) | $Mg_{1.87}$; $Fe^{2+}_{0.13}$ | 25.82 |
| M(2) | 24.48(12) | $Mg_{1.84}$; $Fe^{3+}_{0.02}$; $Fe^{2+}_{0.13}$ $Al_{0.01}$ | 26.11 |
| M(3) | 12.70(8) | $Mg_{0.94}$; $Fe^{2+}_{0.06}$ | 12.84 |
| Sum *C* sites | **62.19(19)** | | **64.31** |

| **San Mango** | s.s. from refinement | Possible site occupancy | s.s. from site occupancy |
|---|---|---|---|
| A | 4.6(2) | $K_{0.10}Na_{0.37}$ | 6.0 |
| A*(m)* | – | – | – |
| Sum *A* sites | **4.6(2)** | | **6.0** |
| M(4) | 37.6(4) | $Ca_{1.29}Na_{0.48}Mn^{2+}_{0.07}Fe^{2+}_{0.16}$ | 37.0 |
| Sum *B* sites | **37.6(4)** | | **37.0** |
| M(1) | 25.0(3) | $Mg_{1.90}Fe^{2+}_{0.10}$ | 25.3 |
| M(2) | 28.0(3) | $Mg_{1.61}Fe^{2+}_{0.04}Fe^{3+}_{0.35}$ | 29.5 |
| M(3) | 11.8(2) | $Mg_{1.00}$ | 12.0 |
| Sum *C* sites | **64.8(5)** | | **66.8** |

| **sample 3** | s.s. from refinement | Possible site-occupancy | s.s. from site occupancy |
|---|---|---|---|
| A | 3.3(3) | $K_{0.10}$ | 1.9 |
| A*(m)* | 4.4(3) | $Na_{0.47}$ | 5.2 |
| Sum *A* sites | **7.7(4)** | | **7.1** |
| M(4) | 34.1(1) | $Ca_{1.39}Na_{0.37}Mn^{2+}_{0.06}Mg_{0.18}$ | 35.5 |
| Sum *B* sites | **34.1(1)** | | **35.5** |
| M(1) | 25.3(1) | $Mg_{1.87}Fe^{3+}_{0.12}$ | 25.6 |
| M(2) | 27.7(1) | $Mg_{1.70}Fe^{2+}_{0.03}Fe^{3+}_{0.27}$ | 28.2 |
| M(3) | 11.8(1) | $Mg_{1.00}$ | 12.0 |
| Sum *C* sites | **64.8(2)** | | **65.8** |

It is well known that, in addition to "bulk" chemical and structural factors (*e.g.*, Fe content, its oxidation state and site distribution), the toxicity of asbestos is also strictly related to the surface properties. In fact, it is at the surface of the fibers that the interactions with the biological environment occur. In the present case, investigation of the fibrous amphiboles by XPS revealed that for all samples, except sample 1 from Biancavilla (whose surface resulted unoxidized), the Fe oxidation state at the surface is always higher than that of the bulk. The highest difference between surface and bulk oxidation state is displayed by San Mango tremolite, which is 10 times more oxidized on the surface (Fig. 1). In addition, for all fibrous amphiboles most of $Fe^{3+}$ on the surface (from 70 to 100%) was revealed to be hosted in $Fe^{3+}$-hydroxide. The information obtained by the crystal chemical characterization of the fibrous amphiboles was therefore taken into account in the subsequent analysis of their reactivity.

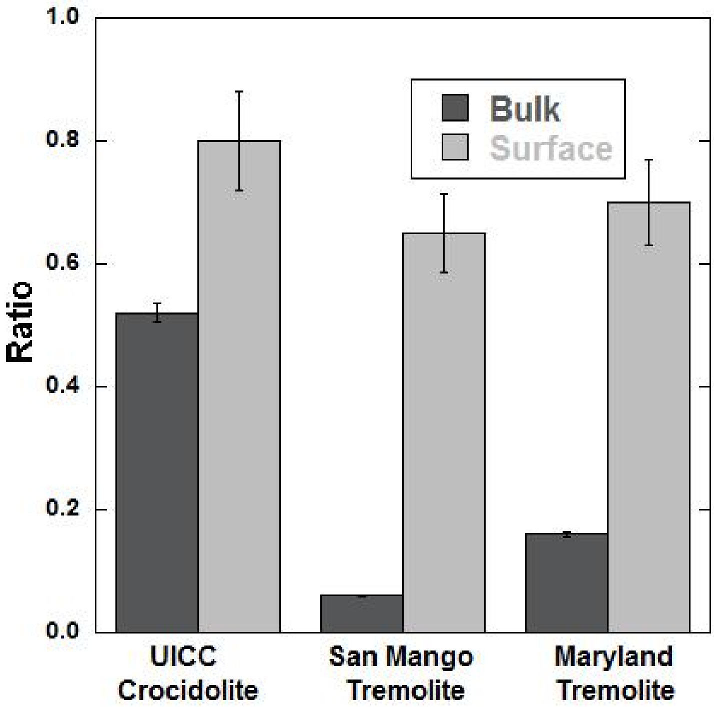


Fig. 1 - Comparison of $Fe^{3+}/Fe_{tot}$ atomic ratios between bulk (Mössbauer results) and surfaces (XPS results) of asbestos samples.

Test of reactivity performed on the fibrous amphiboles revealed that the UICC crocidolite is the most active in both the HO° radical production and the linolenic acid peroxidation. In addition, the concentration of HO° radicals produced by the fibrous amphiboles is related to their $Fe_{tot}$ content, in agreement with the Fenton and Haber-Weiss reactions. On the contrary, no relationship between fiber $Fe_{tot}$ content and lipidic peroxidation was observed.

Results of MTT tests showed that cell mortality induced by the fibers is not always correlated with their chemical reactivity. However, a correlation between cytoxicity and reactivity was found between UICC crocidolite and Mt. Rufeno tremolite, which displayed comparable activity in the production of monoaldehydes. Finally, attempts to correlate the response of the treated cells to the fiber physico-chemical features confirmed the importance of their surface properties. A significant delay of cell mortality was observed for San Mango tremolite, which showed the highest content of oxidized Fe at the surface with respect to that in the bulk.

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