Fibrous antigorite in Mount Reventino area of central Calabria

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ABSTRACT - Naturally Occurring Asbestos (NOA) can form in several types of geologic settings depending on the rock types and geologic history of an area. Calabria region has many settings that are favourable for the presence of NOA because of the variety of older metamorphic and igneous rocks and by the multiple episodes of deformation that many of these rocks have undergone. In Calabria NOA are mainly concentrated in the ophiolitic sequences belonging to the Gimigliano-Mount Reventino Unit in the southern part of the Sila massif and along the Coastal Chain. The amphibole-group asbestos, in particular tremolite, is the most common type of asbestos found in Calabria. However, serpentine minerals are widespread, especially in Mount Reventino surroundings. The purpose of this study was to detect and characterize asbestiform antigorite, one of the natural mineral fibers of the serpentine group, very abundant and commonly found associated with asbestos chrysotile in metabasites and serpentinites outcrops in the Mount Reventino area. The set of the different analytical techniques: optical microscopy, scanning and transmission electron microscopy combined with energy dispersive spectroscopy and Fourier transform infrared spectroscopy analyses allowed its complete characterization. Antigorite occurs as fibers with a length-to-width ratio around 20 and more. The toxicological studies indicate a carcinogenic potential more closely aligned to that amphibole asbestos. In absence of epidemiologic studies, further research about the degree of asbestiform antigorite hazard are necessary. The data obtained enable using the same prevention measures as for asbestos fibers in order to taken actions to avoid or diminish a possible risk although fibrous antigorite is not recognized in most asbestos regulation.

Keywords: Fibrous antigorite; Asbestos; SEM; TEM; FTIR.

1. INTRODUCTION

NOA (Naturally Occurring Asbestos) is the term applied to the natural geologic occurrence of any of the six types of asbestos minerals (chrysotile, crocidolite, amosite, tremolite, actinolite, anthophyllite) (Nichols et al., 2002). In Calabria NOA are mainly concentrated in the ophiolitic sequences cropping out in Mount Reventino area, in the southern part of the Sila massif, and along the Coastal Chain (Bloise et al., 2014, 2016). When these rocks are disturbed by human activities, as road construction, mining and agriculture, or natural events, as landslide, they can be released in the surrounding environment as primary sources of pollution (Karagüzel and Kiliç, 2000; Burragato et al., 2005; Suzuki et al., 2005; Gamble and Gibbs, 2008; Langer, 2008; Cavallo and Rimoldi, 2013; Pugnaloni et al., 2013; Bloise et al., 2016).

In Calabria the most common type of asbestos detected in ophiolitic rocks was tremolite, belonging to amphibole group. Asbestos tremolite was found in Mount Reventino area and along Coastal Chain (Campopiano et al., 2009; Bloise et al., 2014, 2016). An other asbestos mineral was detected in these areas: antigorite belonging to serpentine mineral group. Antigorite with lizardite and chrysotile are serpentine minerals with the same theoretical chemical composition but different structure. Occasionally, the antigorite occurs in a fibrous habit with morphology similar to the amphiboles (Groppo and Compagnoni, 2007; Keeling et al., 2008; Fitz Gerald et al., 2010).

Although fibrous antigorite is not regulated, it appears to satisfy many of the determinant characteristics of an asbestos mineral resulting in a potential health risk. Preliminary toxicological studies on fibrous antigorite (Wozniak et al., 1988, 1993; Cardile et al., 2007) indicated that, for the particular samples studied, the carcinogenic
potential was more closely aligned to that of amphibole asbestos.

The aim of this work is to detect and characterize fibrous antigorite within Calabrian ophiolites.

2. AREA DESCRIPTION

Ophiolitic rocks are largely present in north-western Calabria along the Catena Costiera mountain ridge and particularly at the Monte Reventino relief which is the study area of the present work. (Alvarez, 2005; Apollaro et al., 2009; Buccianti et al., 2009; Liberi and Piluso, 2009).

Three tectonic complexes, composed of distinct tectono-metamorphic units, form the geological structure of the Monte Reventino (Ogniben, 1973; Amodio-Morelli et al., 1976; Scandone, 1982; Morten and Tortorici, 1993; Piluso et al., 2000); the basal Apennine Complex, corresponding to mostly carbonate sequences Meso-Cenozoic in age (Ietto and Barillaro, 1993; Iannace et al., 2007); an intermediate Liguride Complex, composed of metavolcanic arc rocks, Upper Jurassic-Cretaceous in age, showing a complex poly-phase structural evolution (Liberi et al., 2006; Liberi and Piluso, 2009); and, a upper Calabride Complex, consisting of a metamorphic rock assemblage that can represent a Hercynian continental lithospheric section (Piluso and Morten, 2004), including a Mesozoic sedimentary cover (Santantonio and Teale, 1987).

More in detail, the Monte Reventino ophiolitic complex is mostly characterized by large lensoid bodies of metabasalts and serpentinites separated from metapelites and metarenites (belonging to the Frido unit) by low angle tectonic surfaces. Metabasalts and serpentinites bodies outcrop along the peak of Monte Reventino forming large-scale tight folds in which the serpentinites occupy the nuclei of the folds, partially to completely surrounded by metabasalts (Alvarez, 2005).

3. METHODS AND MATERIAL STUDIED

Over 100 samplings were carried out in a study area located around Mount Reventino in Calabria (Southern Italy), covering the villages of Conflenti, Platania, San Mango D’Aquino, Martirano Lombardo and Gimigliano (Fig. 1).

The samples were studied by a stereomicroscope (Leica M250C) for the initial search for fibers and a polarized light microscope (PLM, Leica DM 2500P) for their identification. The microscope was equipped with phase contrast objectives and using the dispersion staining the identification of fibers was possible. Fibrous part of the samples was observed using also scanning electron microscope (SEM, LEO 440) combined with energy dispersive spectroscopy (EDS, Oxford Instrument INCA), Fourier transform infrared spectrometer (FTIR, Spectrum One, Perkin Elmer) and transmission electron microscope (TEM, Fei Tecnai 12 G2).

SEM and EDS analysis allowed the observation of the morphology and the chemical characterization of fibers.

FTIR spectra were obtained using diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) with the following instrument operative parameters: acquisition range 4000-400 cm\(^{-1}\), resolution 4 cm\(^{-1}\) and 32 scans.

After dispersion of the samples in isopropyl alcohol, TEM grids were prepared placing a drop (20 mL) of suspension on a 300 mesh copper grid coated with an amorphous carbon film.

TEM analysis was conducted at an accelerating voltage of 120 kV, equipped with an electron energy filter (Gatan, model Biofilter) and a Peltier cooled charge-coupled device-based slow scan camera (Gatan, model 794 IF). The micrographs were acquired at low magnifications and at high resolution. Nanoarea electron diffraction (NED) patterns were obtained using a nanometre-sized coherent parallel beam of electrons.

4. RESULTS

In addition to asbestos tremolite described in other works (Campopiano et al., 2009; Bloise et al., 2012, 2014), in the Mount Reventino area an important presence of fibrous antigorite was detected. Antigorite is present as cross-fiber veins and irregular patches in the metabasites, although becomes more abundant in serpentinitic outcrops. Optical properties, color and chemical composition do not allow distinguishing between antigorite and chrysotile. The fibrous phases detected in the samples were observed by PLM. The detection of chrysotile and fibrous antigorite in ophiolitic rocks was not simple. Under polarized light conditions the morphology and color in relation to the orientation of the polarized light was observed.

For a liquid with n=1.550 and high dispersion index of refraction, both chrysotile and antigorite showed blue and magenta color. The antigorite fibers under polarization have a behavior slightly different from that of chrysotile fibers. A careful observation of the samples under PLM was of primary importance to decide which analytical technique to use in succession to confirm and improve the PLM results.

The fibers separated from massive samples were observed under the SEM and TEM. Both techniques confirmed in all samples the abundant antigorite with fibrous habit and presence of chrysotile. Antigorite fibers morphology was similar to the amphiboles but with lamellar fibers (Fig. 2), while the chrysotile showed its classical soft form wave (Fig. 3). The different morphology is best seen in figure 4. EDS spectra are shown in figure 5. The peak of iron in the antigorite EDS spectrum was always present while on average it was missing in the chrysotile EDS spectrum.

A rapid discrimination between chrysotile and antigorite was done with TEM screening analysis. The absence of an empty core running along the fiber represents a tool to distinguish antigorite fibers from
chrysotile (Belluso et al., 2017). A more careful check with NED has clearly identified the two minerals.

Figure 6 shows NED antigorite pattern, in the form of a hexagonal array of clusters of spots and a fiber of antigorite with l/d ratio greater than 20. The typical wavy layer structure of antigorite was defined at high resolution (Fig. 7). The cylindrical lattice of chrysotile develops a typical tubular form seen by TEM (Fig. 8). Its diffraction pattern shows the characteristic lines of streaking.

FTIR analysis confirmed antigorite in many samples. An example of spectrum of antigorite is shown in figure 9. In the region of OH stretching vibration, the 3674
cm⁻¹ peak is very clear (Heller-Kallai et al., 1975; Uehara and Shirozu, 1985; Mellini et al., 2002; Della Ventura, 2017). In antigorite, the Fe content is generally higher than chrysotile so this peak shifts to lower frequencies compared to the peak of chrysotile. The progressive substitution of Mg by Fe²⁺ moves the OH stretching frequency to lower wavenumber (Mellini et al., 2002; Keeling et al., 2008). In the region of tetrahedral sheet stretching vibration, the most evident band is found around 980-970 cm⁻¹ and a second one at higher energy, near to 1086-1080 cm⁻¹ (Heller-Kallai et al., 1975; Mellini et al., 2002; Groppo and Compagnoni, 2007). This band is ascribed to Si-O vibrations. The region to the right-hand side of the spectrum (from about 1500 to 400 cm⁻¹) is called the fingerprint region. The importance of the fingerprint region is that each different compound produces its own unique pattern of peaks.

The fingerprint of antigorite spectrum is shown in Fig. 10. The study of fingerprint (1150-400 cm⁻¹ region with structural features of the serpentines) is very important to rule out the presence of lizardite. (Yariv and Heller-Kallai, 1975; Mellini et al., 2002). The band around 568-564 cm⁻¹, corresponding to Si-O bending, is well evident in the antigorite spectra (in our sample 567 cm⁻¹) whereas is systematically absent in lizardite (Mellini et al., 2002). The difference is due to the different symmetry of the two minerals. Another important peak of antigorite fingerprint is the peak assigned to bending vibrations of Mg-OH bond around 619-617 cm⁻¹. These features are absent in the spectra of lizardite and of chrysotile; so antigorite could be always univocally recognized studying this spectral region (Mellini et al., 2002; Viti and Mellini, 1996; Keeling et al., 2008).

5. DISCUSSION

Ophiolites are known sources of NOA. In Calabria, southern of Italy, the ophiolites of the Mount Reventino have a considerable importance as they are a significant mineralogical and economical resource. They spread along the left side of the Savuto valley, in the province of Catanzaro, and extend as far as the Tyrrhenian Sea over a vast territory embracing numerous villages. Previous studies (Campopiano et al., 2009; Bloise et al., 2012, 2014) showed that the amphibole-group asbestos minerals, in particular tremolite, are the most common type of asbestos found in ophiolites of the Mount Reventino. The outcrops with a light green colour are rich in amphiboles, brittle, and easily broken into blocks, for this reason they are used for concrete production and in building stones. The rocks with a dark green colour contain fewer amphiboles and they are more durable. They are used in pavings, indoor flooring and lapidary production. The presence of asbestos, as known, causes significant environmental implications. When a deposit is classified as a ophiolitic mining site, the asbestos content within the deposit must be preliminary assessed, as defined in the Ministerial Decree of 14 May 1996. Finally, the exposure assessment of workers during extraction and processing of ophiolitic rocks becomes necessary in order to establish the best working conditions and to reduce risk for human health.

At present there are inactive quarries that could lead to uncontrolled exploitation of crushed stone, determining the release of large amount of fibers in the surrounding environment.

Our results indicate an important presence of antigorite with asbestiform habit and minor chrysotile in all samples of the ophiolitic rocks cropping out in the neighbouring of villages of Conflenti, Platania, San Mango D'Aquino, Martirano Lombardo and Gimigliano in the Mount Reventino area. The distinction between fibrous antigorite and chrysotile is a complex task which involved different analytical approaches. The coupling of more analytical techniques is the key for a good analysis mostly when the sample is from a natural environment. The microscopic techniques allow the discrimination between asbestiform particles and non-asbestiform particles, and among these, TEM coupled with electron diffraction allows reliable identification between the two minerals.

We want to pay attention to the presence of fibrous antigorite besides asbestos tremolite. Several authors...
Fig. 5 - Representative EDS spectra of antigorite (a) and chrysotile (b) fibers.

Fig. 6 - Transmission electron micrograph of antigorite fiber with NED pattern; sample from Mount Reventino surroundings.
already described the detection of fibrous antigorite in other areas (Groppo and Compagnoni, 2007; Keeling et al., 2008; Fitz Gerald et al., 2010) and discussed about its potential hazard (Stanton et al., 1981; Wozniak et al., 1988, Bernstein et al., 2005; Cardile et al., 2007).

The question of the carcinogenic potential of asbestiform antigorite and its significance as possible health hazards is not at all resolved. Antigorite from the area of Mount Reventino showed fibers with a length-to-width ratio around 20 and more, depending on the variability in fibrous form of the mineral from different villages within the study area. The toxicological studies indicate a carcinogenic potential more closely aligned to that amphibole asbestos (Keeling et al., 2008). In absence of epidemiologic studies, further research on the degree of asbestiform antigorite hazard are necessary and actions shall be taken to avoid or diminish a possible risk using the same prevention measures as for asbestos fibers.

6. CONCLUSIONS

On the bases of the analytical data and the above discussion, it is possible conclude that:

- the wholly serpentinized mantle ultramafic rocks outcropping in Mount Reventino area (Central Calabria) have fibrous antigorite, the most common asbestiform species belonging to the group of serpentines was fibrous antigorite. A minor amount of chrysotile was also found;
- fibrous antigorite and chrysotile can be distinguished using different analytical method such as optical microscopy, scanning electron microscopy combined with energy dispersive spectroscopy, transmission electron microscopy and Fourier transform infra-red spectrometry; the only use of optical microscopy fails in discriminating between the two minerals;
- although fibrous antigorite is not recognized in most asbestos regulation, it could represent a potential hazard for human health; therefore a precautionary approach by local public health authorities is recommended in order to reduce the possible exposure to this mineral;
- further studies are necessary to state correlations between a possible exposure to fibrous antigorite and health effects.
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