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Geochemical and mineralogical characterization of tremolite asbestos contained in the Gimigliano-Mount Reventino Unit (Calabria, south Italy)

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ABSTRACT - In the recent years, many studies have focused on rocks containing naturally occurring asbestos (NOA) with the purpose of determining the potential health risks to exposed neighboring populations. Environmental exposure to NOA has been shown to be a cause of several types of lung disease. The toxicity of asbestos fibres should also depend on the concentration of trace elements and their release in the environment. In this regard the aim of the present work was to characterize four samples of pure tremolite asbestos belonging to Gimigliano-Mount Reventino Unit (Calabria, south Italy). Through a several analytical techniques such as X-ray powder diffraction (XRPD), scanning electron microscopy combined with energy dispersive spectrometry (SEM–EDS), differential scanning calorimetry (DSC), derivative thermogravimetric (DTG) and atomic absorption spectroscopy (AAS), the size, morphology, crystallinity and chemical composition of tremolite samples were discussed to define the impact on the environment and human health.

Keywords: Tremolite asbestos; mineralogical characterization; trace elements; southern Italy.

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1. INTRODUCTION

Tremolite asbestos $Ca_2Mg_5Si_8O_{22}(OH)_2$ belongs to a calcic amphibole group and is one of the dangerous naturally occurring asbestos (NOA), a term referring to asbestos fibres as a natural constituent of rocks or soils. This mineral usually occurs with an elongated and/or bladed prismatic habit, but it may also appear acicular or fibrous. The tremolite toxicology, such as for all mineral asbestos group, has been associated with size, durability and chemical composition (Mossman et al., 2011; Pugnaloni et al., 2013). From the crystallographic point of view, the tremolite structure consists of double chains of corner-sharing T(1,2) tetrahedra occupied by Si and strips of edge-sharing M(1,2,3) octahedra occupied by Mg, both of which extend in the c-direction. Hence, there are two topologically distinct types of tetrahedra and three distinct types of octahedra. At the junction of the strip of octahedra and the double-chain of tetrahedra is the M(4) site, which is occupied by Ca (and minor Mg or Fe) (Hawthorne and Oberti, 2007; Ballirano et al., 2017).

In the recent years, several investigations have been performed on samples of fibrous tremolite collected at different localities of Italy (e.g., Gualtieri et al., 2014; Vignaroli et al., 2014; Bloise et al., 2017a). This is due to its relatively widespread diffusion in rocks that are currently subjected to excavation for numerous construction projects (railway lines, motorways etc.). In fact, the human health risks are based on the potential fibres inhalation, when they become airborne through rocks (e.g., serpentinite) weathering or human activities producing dust (Harper, 2008; Culley et al., 2010). In Calabria, recent studies dealt with monitoring of natural asbestos occurrences in ophiolite units that widely crop out in the central and northern parts of the region and consider their release into environment (Bloise et al., 2012, 2014, 2016a; Punturo et al., 2015).

The problem is not just related to the dispersion of the fibres into the air, but also to the toxic elements release. In fact, the tremolite has a high capability to host a large number of toxic elements and species, such as all asbestos minerals. The asbestos carcinogenesis effects due to the presence of trace metals is amply recorded (IARC, 1993, 2012) and tremolite asbestos could be an important source of these dangerous traces elements. In a recent work, Bloise et al. (2016b), showed that toxic metals, such as Mn, Co and Ni in tremolite asbestos from Val d'Ala (Italy) were present in a high amount (>1000 ppm, 26.92 ppm and 473 ppm respectively). This finding is in line with the results of Upreti et al. (1984), who analysed tremolite asbestos from Bhilwara (India) by X-Ray fluorescence (i.e. XRF), and concluded that it contained a considerable amount of Mn, Co and Ni.

Moreover, considering that weathering processes are the main causes of hazardous traces elements dispersion into environment (Scarciglia et al., 2008; Buccianti et al., 2009; Guagliardi et al., 2013 a,b, 2016 a,b; Perri et al., 2015, 2016) weathered NOA can be a cause of environmental and health concern. In fact, soils that developed on ophiolitic bedrocks (serpentinite/metabasite) are usually rich in asbestos minerals and/or heavy metals, which are known to have a negative impact on agricultural activity and on environmental quality (Kierczak et al., 2008; Dermatas et al., 2015). In some cases, the concentration of trace elements in the serpentinite-derivative soils (such as Cr, Ni, Co, V) was very high and exceeds the regulatory thresholds for public, private and residential green use (Apollaro et al., 2007 a,b). Moreover, several dangerous elements could be leaching of ophiolitic host rocks and their respective sediments and soils with subsequent risky increase of concentration in soil waters and groundwaters (Apollaro et al., 2009, 2011, 2012, 2013 a,b, 2015).

Shallow groundwaters interacting with ophiolitic rocks are generally characterized by high concentrations of several trace elements derived through dissolution of primary solid phases (Marini and Ottonello, 2003; Critelli et al., 2014, 2015 a,b). Specifically, Cr(VI) is one of the main traces elements which was found in different areas of the world where ophiolitic rocks crop out (Marini and Ottonello, 2003; Morrison et al., 2009, and references therein; Vasilatos et al., 2010; Wood et al., 2010). The release in the groundwaters of Cr (VI) and others heavy metals from rocks, sediments and soils is regulated by a multitude of variables which play an important role. Therefore, the mineral and geochemistry characterization of asbestos minerals is important to define the potential environmental contamination in soils and groundwaters in areas where NOA can be found.

Previous studies showed that asbestos tremolite was the main constituent of metabasites in the ophiolitic sequence of Mount Reventino (Punturo et al., 2015). In this regards 4 samples of pure asbestos tremolite belonging to the Gimigliano-Mount Reventino Unit (South Italy) were characterized from mineralogical and geochemistry point of view through different analytical techniques (XRPD, SEM/EDS, DSC/DTG, AAS).

1.1. Geological Setting

The Calabrian Peloritan Orogen (CPO) represents a fragment of the European margin, which was thrust onto the Maghrebian-Sicilian and Appennine thrust-and-fold belts during the Europe-Apulia collision in Oligocene-Early Miocene (e.g., Amodio Morelli et al., 1976; Cirrincione et al., 2015 and references therein).

The CPO has been divided into two sectors, a Northern one and a Southern one, which are separated by a strike-slip tectonic line running along the Catanzaro trough (Boccaletti et al., 1984; Tansi et al., 2007).

The study area occurs on Mt. Reventino (Fig. 1) located in the Sila Piccola in the northern sector of the Calabrian-Peloritan Orogen (Alvarez, 2005; Liberi and Piluso, 2009).

This is a nappe pile, which can be described as the superposition of three major structural elements that represent different paleogeographic domains: (i) The Apennine Units Complex made up of Mesozoic sedimentary and metasedimentary successions (Trias-Miocene) (Iannace et al., 2007; Vespasiano et al., 2012a, 2015c, 2016 a,b; Apollaro et al., 2016); (ii) The structurally intermediate allochthonous Alpine Liguride nappe (Tithonian-Neocomian) made up of a series of Alpine metamorphic units including a Cretaceous-Paleogene metapelitic-ophiolitic-carbonate assemblage (Critelli et al., 2015a; Liberi and Piluso 2009; Van Dijk et al., 2000; Vespasiano et al., 2012b, 2014, 2015a,b) (iii) The Calabride Complex formed by Hercynian and pre-Hercynian gneiss, granite and metapelite. The Calabride complex comprises three major Paleozoic tectono-metamorphic units: (a) the Bagni Unit, made up of metapelite, metarenite and metabasite; (b) the Castagna Unit, comprising paragneiss and schist; (c) the Sila Unit, represented by metamorphic and plutonic rocks and a Mesozoic cover (Van Dijk et al., 2000).

The Liguride nappe consists of HP-LT ophiolitic sequences, in which a metabasic and metaultramafic association constitutes the basis of a complex metasedimentary cover, ranging from pelagic to flyschoid types of sediments.

The ophiolitic sequence includes: (i) a serpentinized mantle of ultramafic rocks and ophicalcites, cropping out only in the Gimigliano-Mount Reventino area and in close association with overlying metabasites (Critelli et al., 2015a); (ii) metabasalts and subordinate metadolerites, with transitional MORB affinity; (iii) a metasedimentary cover including both pelagic facies and flyschoid facies, composed of alternating metapelites, metalimestones and metarenites of uncertain ages.

The geology of Mount Reventino is characterized mainly by lenses of metabasalts and serpentinites limited in contact, by low angle tectonic systems, with the metapelites and metarenites of the Frido unit (Fig. 1). The massive-banded metabasalts and serpentinites lenses constitute the summit of Mount Reventino (Alvarez, 2005). In the ophiolitic bodies, the serpentinites occupy the cores of the major tight folds and are partially or completely surrounded by isolated bodies of metabasalts (Alvarez, 2005).

2. SAMPLING AND ANALYTICAL METHODS

A total of 4 pure asbestos tremolite samples were collected within and in the surrounding of Mount

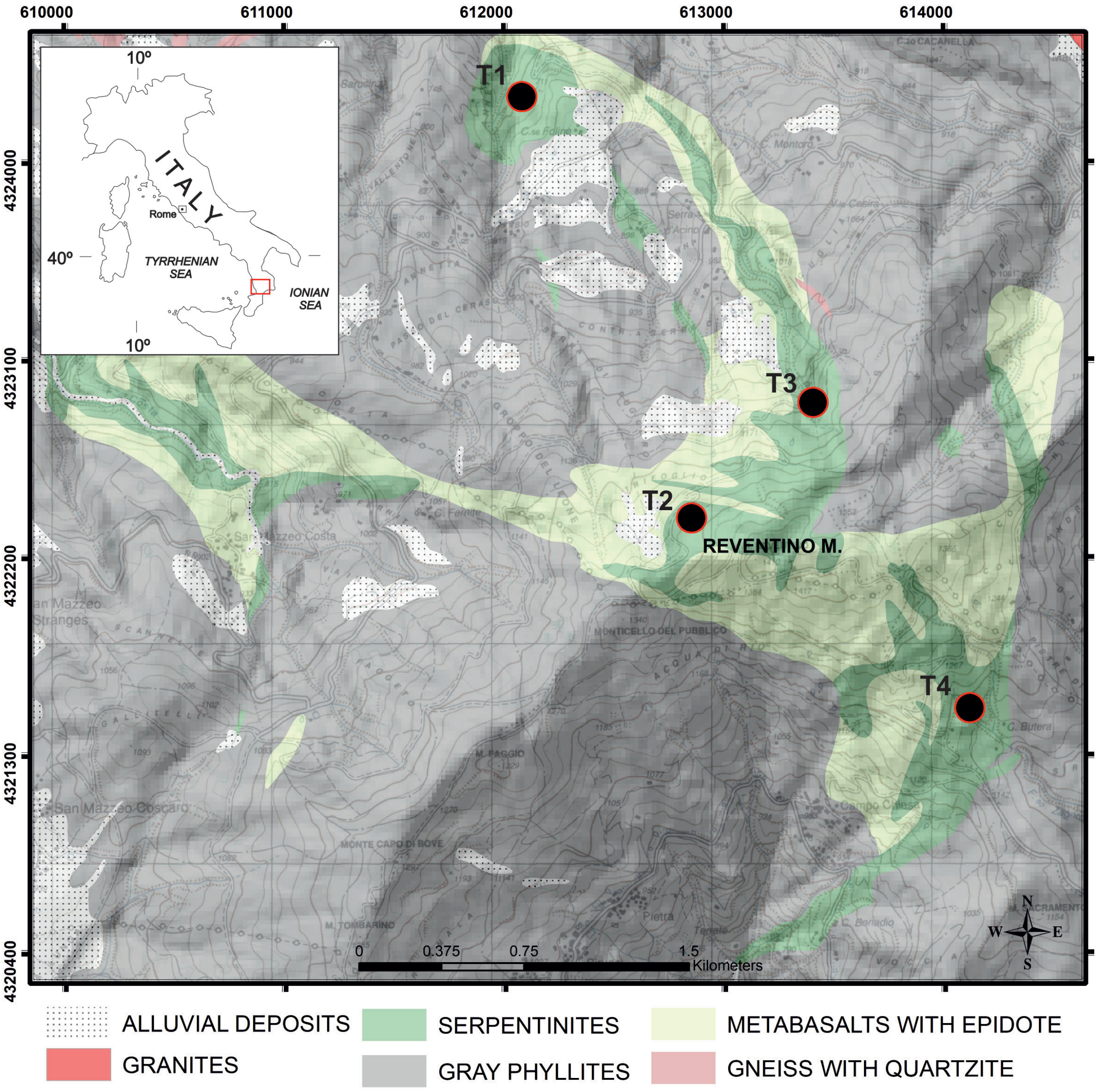

Fig. 1 - Simplified geological map of the investigated area with the location of collected sample sites.

Reventino (Fig. 1) where people routinely conduct outdoor activities such as agricultural activities. Serpentinite outcrops were rarely covered by vegetation (Fig. 2a) and thus, highly exposed to weathering. Field observations showed that the asbestos tremolite samples were white coloured and present mainly two varieties: fibrous and massive (Fig. 2b).

In the laboratory, the samples were preliminarily studied in reflected light using a Zeiss Axioskop 40 microscope. Tremolite samples showed a fibrous morphology under the microscope. The fibrous samples were disaggregated with a needle in order to choose fibres free from alteration or impurities to be studied by XRPD and DSC/DTG.

For XRPD and DSC/DTG investigations, samples were mechanical milled using Bleuler Rotary Mill (container and ring set are made out of tungsten carbide alloy), with a capacity of 100 mL, for 30 seconds at a speed of 900 revolutions per minute (rpm). Further samples were quartered to obtain about 10 g of homogeneous representative material.

X-ray Powder diffraction patterns were obtained on a Bruker D8 Advance X-ray diffractometer with CuKα radiation, monochromated with a graphite sample monochromator at 40 kV and 40 mA. Scans were collected in the range of 3-66° 2θ, with a step interval of 0.02° 2θ and step-counting time of 3 seconds. EVA software (DIFFRACplus EVA) was used to identify the mineral phases in each X-ray powder spectrum, experimental peaks being compared with 2005 PDF2 reference patterns.

Derivative thermogravimetric and differential scanning calorimetry (DTG/DSC) was performed in an

Fig. 2 - a) Serpentinite outcrops of Mount Reventino; b) zoom of asbestos tremolite in outcrop.

alumina crucible under a constant nitrogen flow of 30 cm^3min^{-1} with a Netzsch STA 449 C Jupiter in 25-910 °C temperature range, and a heating rate of 10 °C/min. DTG-DSC were obtained using Netzsch proteus thermal analysis software. Instrumental precision was checked by repeated collections on a kaolinite reference sample (five collections), revealing good reproducibility (instrumental theoretical T precision of ±1.2 °C) and theoretical weight sensitivity of 0.10 µg.

Secondary electron SEM imaging was performed on a FEI Quanta 200 equipped with a field emission gun (FEG) equipped with an energy dispersive spectrometer (EDS). EDS microanalysis, were achieved by the standardless quantification using ZAF correction method. For SEM investigations, a fragment of each sample was fixed on SEM stub using double-sided conductive adhesive tape and subsequently coated by graphite.

Determination of As, Cr, Cu, Pb, Ni, Fe, Mn, Sr, Ba and V were executed by AAS, with a contrAA300 equipped with Air/Acetylene-Acetylene nitrogen protosside burner and an hydride vapor generator system. Cu, Pb, Ni, Fe, Mn, Sr analysis were performed in Air/Acetylene Flame while Cr, Ba, and V were carried out in Flame Protossido/Acetilene. As analysis was performed using the hydride vapour generator technique.

Samples were digested in 3:1:1 ratio of Hydrochloric (3), Nitric (1) and Hydrofluoric (1) acid mixture in microwave Milestone MLS Mega 1200 with HPR 1000/10 vessels.

3. RESULTS AND DISCUSSION

3.1. XRPD and DTG/DSC characterization

The XRPD patterns of the four samples collected in areas of Mount Reventino (Fig. 1) have similar trends. Results of XRPD patterns showed that samples were mainly composed of tremolite coexisting with a small amount of serpentine minerals (e.g., Fig. 3; Tab. 1).

DSC curve of tremolite asbestos sample (T2) exhibits a number of both endothermic and exothermic peaks in the range 300-700 °C (Fig. 4) that can be explained by the presence of impurities in the sample. Thermal analysis enabled us to identify the serpentine minerals that are otherwise indistinguishable by XRPD. In this regard, the wide peak at 601.2 °C is due to the chrysotile dehydroxylation (Bloise et al., 2017a). The peak at 372.6 °C is due to the dehydroxylation of brucite while the very weak peak at 535.0 °C is generated by the dehydroxylation of chlorite (Földvári, 2011) present as very minor impurity. DSC proved to be a very effective tools for identifying small amounts of minerals like brucite and siderite undetectable. by XRPD analysis (Bloise et al. 2016c). In the sample (T2), the wide endothermic peak at 725.9 °C on DSC curve (Fig. 4) was ascribed to tremolite breakdown although its decomposition started at 690 °C and ended at about 790 °C in agreement with the literature data (Bloise et al., 2008, 2017b). The presence of tremolite in sample (T2) was also clearly confirmed by the maximum loss rate peak at 736.9 °C on DTG curve

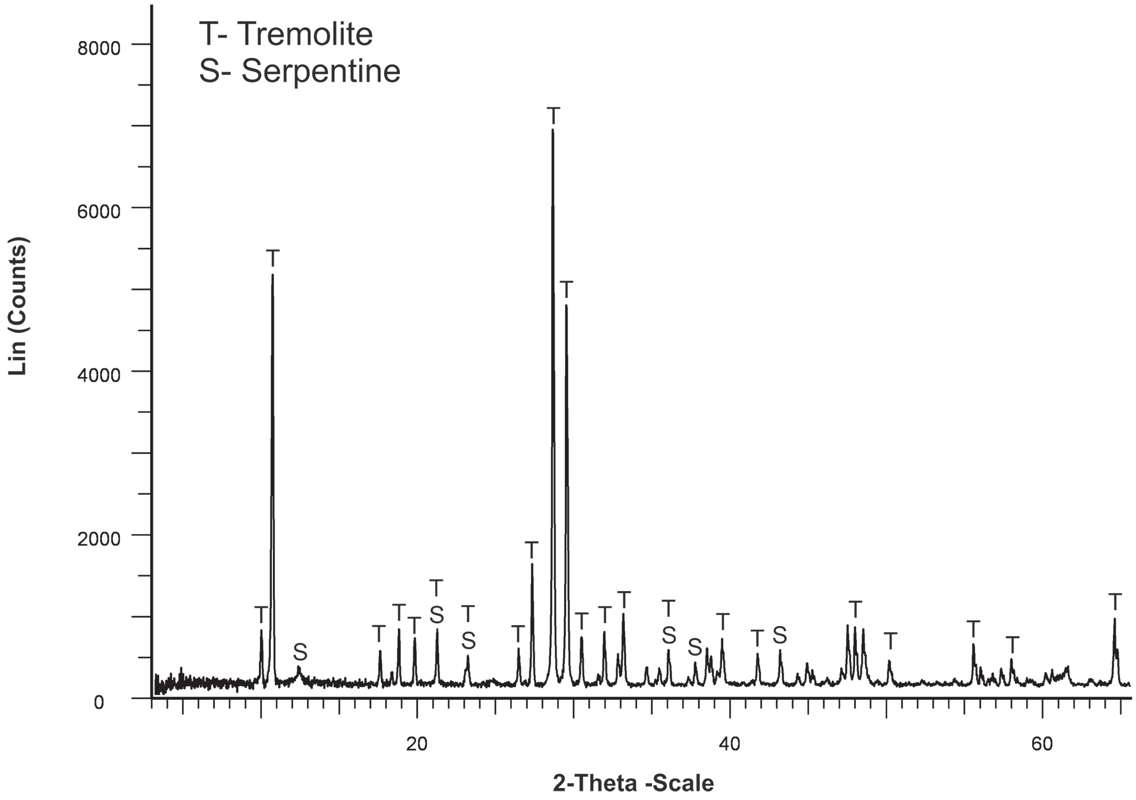

Fig. 3 - XRPD pattern of asbestos tremolite (sample T2).

Samples	Phases detected
T1	Tr>>Chr>Chl
T2	Tr>>Chr>Chl>Mag
T3	Tr>>Chr>Mag>Chl
T4	Tr>> Atg>Chr>>Chl

Tab. 1 - Mineralogical assemblage detected by XRPD, SEM/EDS, DSC/DTG. Tr tremolite, Atg antigorite, Chr chrysotile, Mag magnetite, Chl chlorite.

(Fig. 4). Finally, the exothermic DSC signal at 828.2 °C was related to a complete recrystallization of asbestos tremolite and minor serpentine into diopside and forsterite (Bloise et al., 2009, 2016c). By cross-checking all of the data obtained by XRPD and DSC/DTG, tremolite proved to be the most abundant mineral found in the area of Mount Reventino even if chrysotile and small amounts of other minerals were also present (Tab. 1).

3.2. SEM–EDS characterization

SEM morphological observations showed asbestos tremolite fibres which appeared to be straight, poorly flexible and were approximately 100 μm in length. However, the length of a single fibre, separated as best as possible by sonication and measured under optical microscope, may reach 1 mm. EDS chemical analysis reported in figure 5 showed the presence of a substantial amount of Fe. Nevertheless, Si vs. $Mg/(Mg + Fe^{2+})$ diagram (Leake et al., 1997; Hawthorne and Oberti, 2007) allowed to classify all the analysed samples as tremolite (Fig. 6). However, Fe and other trace elements concentrations were further investigated by AAS technique to define the amount of potentially harmful elements that can be released into environment.

3.3. AAS characterization

Through AAS analytical technique, the following trace elements were measured: As, Ba, Cr, Cu, Fe, Mn, Ni, Pb, Sr and V. Tab. 2 showed the content of the trace elements for each sample. Fe and Mn were the most abundant metals in all the tremolite samples and the highest values were observed for sample T1 (28088.24 ppm and 867.65 ppm respectively). These results were in line with the concentrations of Fe which was detected by EDS analyses (Fig. 5). Fe was present in very high amount and could be considerate as a minor element that may substitute Mg in M(1), M(2), M(3), M(4) sites (Oberti et al., 2007).

Concentration levels of V were high related to others detected elements and were similar in the studied samples whereas Ni concentrations (Tab. 2) were variable but in the same order of magnitude. However, the highest level of nickel was detected in the sample T4 (458.01 ppm). These results are in line with previous study which reported that Ni can occupy the specific crystallographic M(1) and M(3) sites in synthetic calcic amphibole (Della Ventura et al., 1997). The concentrations of Cr in the studied samples, albeit high, were less abundant than Ni and others elements concentrations (Fe, Mn, V). The

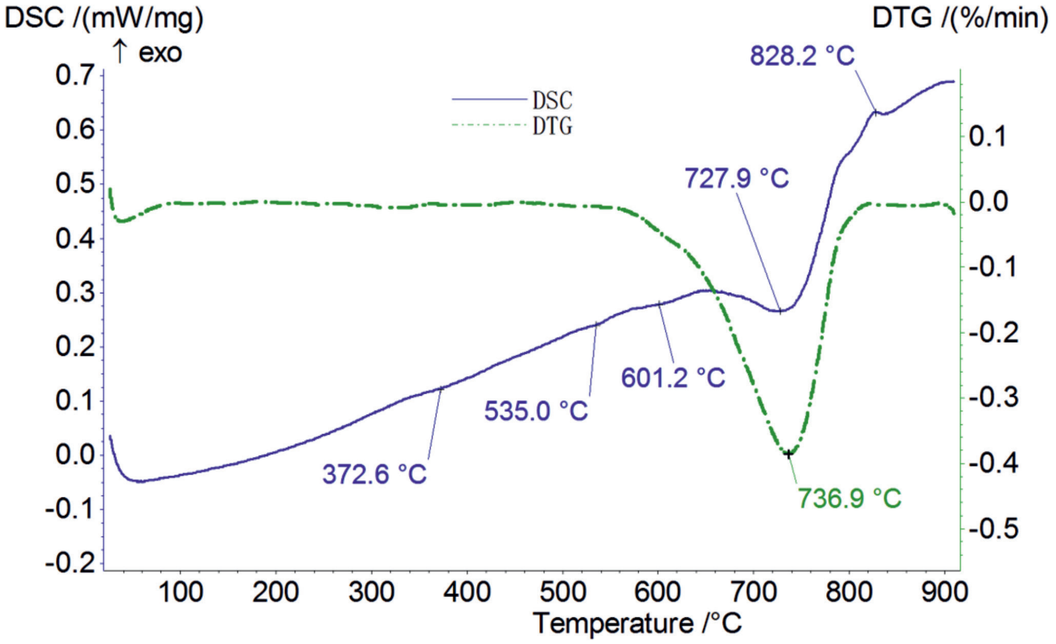

Fig. 4 - Thermal analysis of asbestos tremolite (sample T2).

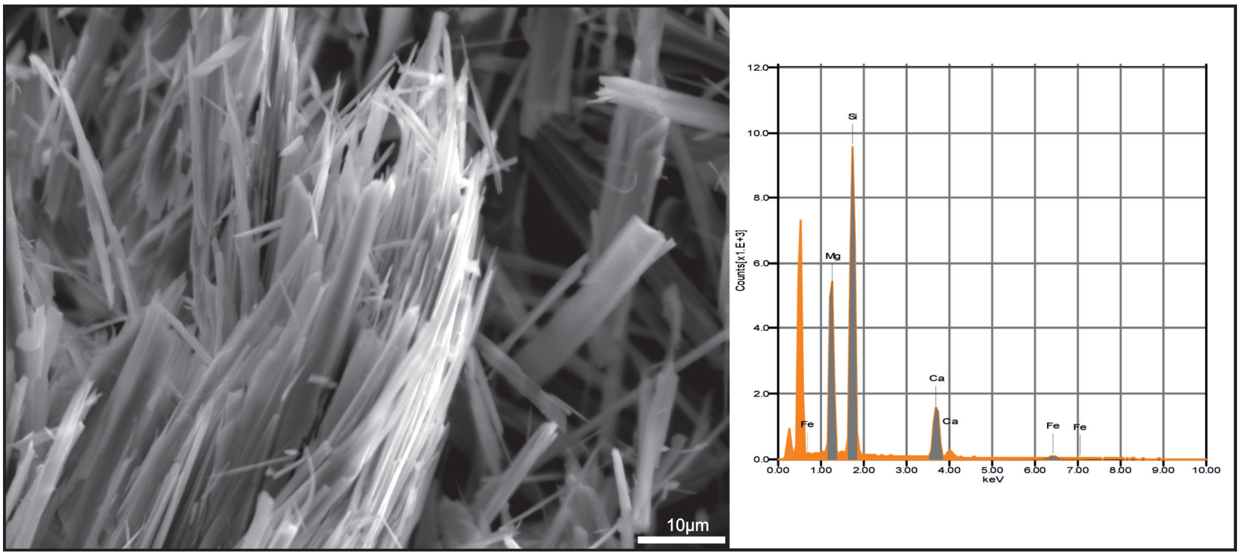

Fig. 5 - SEM/EDS analysis of asbestos tremolite (sample T2).

concentrations of Cr observed in order of abundance are as follows: 172.4 ppm (sample T2), 145.2 ppm (sample T3), 126.47 ppm (sample T1) and 123.5 ppm (sample T4). Literature data showed that Cr can be a major component in calcic, sodic-calcic and sodic amphiboles occupying mainly M(2) sites (Oberti et al., 2007). The concentrations of Cu and Sr were similar in all the samples (Tab. 2). Even the concentration of As, Pb and Ba were similar but the amounts were very low in each analysed samples (Tab. 2). Minerals impurity (e.g., chrysotile, chlorite) discriminated by X-Ray and DTG/DSC analyses are also source of trace elements but unfortunately AAS cannot discriminate the trace elements present in asbestos tremolite samples and the contribute of impurities one. Nevertheless, traces elements levels detected in the four samples in this work are in line with literature data obtained using different analytical techniques (Holmes et al., 1971; Morgan and Cralley, 1973; Bowes and Farrow, 1997; Bloise et al., 2016a). The Italian government, given Legislative Decree N°.152 of 03/04/2006, has established a limit values for some toxic elements in soil and stream water, but not for mineral samples. Adopting the same thresholds for minerals some elements exceeds the regulatory limits. Specifically, all the samples exceed the thresholds for public, private and residential green use (Limit A) and commercial and industrial use (Limit B) for

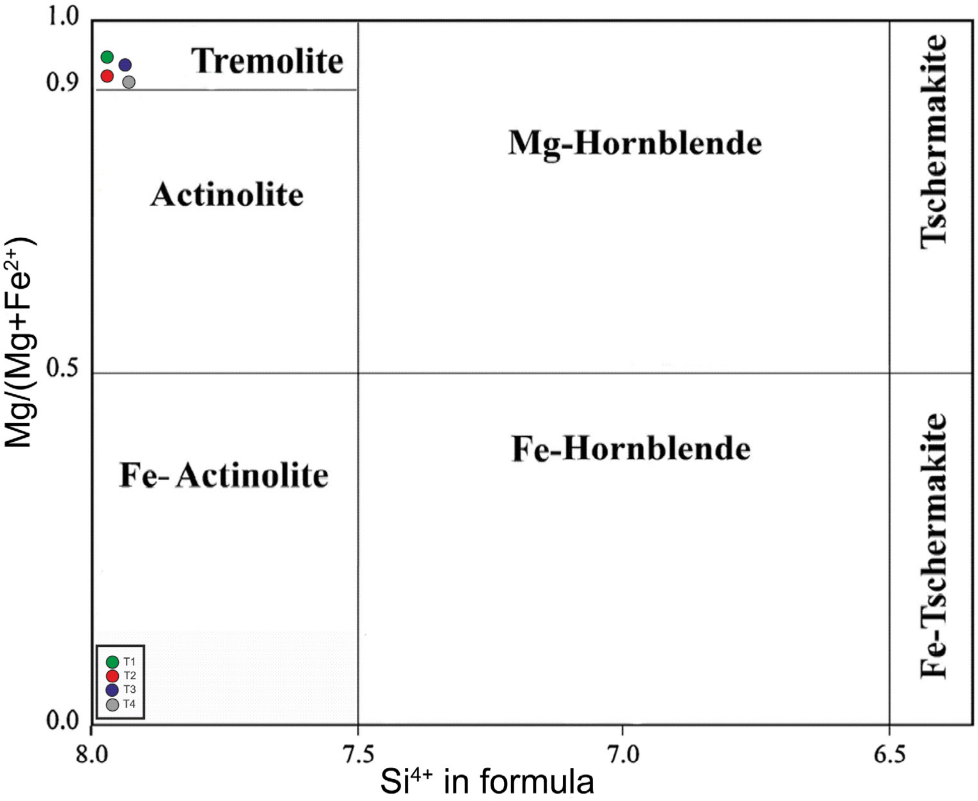

Fig. 6 - Amphibole diagram classification (after Leake et al., 1997).

Samples	As	Ba	Cr	Cu	Fe	Mn	Ni	Pb	Sr	V
	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
T1	0,12	1,33	126,47	15,58	28088,24	867,65	259,52	0,95	7,21	338,24
T2	0,15	0,96	172,40	6,46	2356,31	658,23	458,01	0,68	7,12	256,45
T3	0,13	0,74	145,20	4,42	2265,27	590,45	352,15	0,75	4,26	312,25
T4	0,11	1,45	123,50	12,11	10903,27	705,44	429,00	0,59	5,89	380,56
Thresholds Italian Law D.Lgs. 152/2006 LIMIT A	20	-	150	120	-	-	120	100	-	90
Thresholds Italian Law D.Lgs. 152/2006 LIMIT B	50	-	800	600	-	-	500	1000	-	250

Tab. 2 - Trace elements concentrations of tremolite samples and thresholds for some toxic elements for public, private and residential green use (Limit A) and commercial and industrial use (Limit B) established by Italian government given Legislative Decree N°.152 of 03/04/2006.

V. Ni concentrations exceeds the limit A in each samples whereas the Cr level exceeds this limits only in the sample T2. For example, excessive amounts of vanadium in the human body can cause asthma, rhinitis, and general anemia and even increase the possibility of uremia and lung cancer occurrence (WHO, 1990, 2001; ATSDR, 2002; Crans et al., 2004). Contact with nickel compounds can cause a variety of adverse effects on human health, such as nickel allergy in the form of contact dermatitis, lung fibrosis, cardiovascular and kidney diseases and cancer of the respiratory tract (Oller et al., 1997; McGregor et al., 2000; Seilkop and Oller, 2003). Even chromium could be a cause of several human health problems such as mouth ulcers, indigestion, acute tubular necrosis, vomiting, abdominal pain, kidney failure, stomach and lung cancer (O' Flaherty, 1996; Beaumont et al., 2008; Shekhawat et al., 2015). In this regard and considering the results of this study we can assert that the populations that lives surrounding the studied area are potentially exposed to serious health risks.

4. CONCLUSIONS

Through a several analytical techniques four samples of pure asbestos tremolite belonging to from the Gimigliano-Mount Reventino Unit (South Italy) were investigated. The XRPD and DSC/DTG analysis showed a highly amount of asbestos tremolite with others minor impurities (chrysotile, chlorite, brucite). AAS analyses proving that Fe was the most abundant among investigated elements (As, Ba, Cr, Cu, Fe, Mn, Ni, Pb, Sr and V). In fact, Fe could be considerate a minor element. Mn, V, and Cr were detected in high amounts in all the asbestos tremolite samples whereas the others trace elements as Sr, Cu, As, Pb and Ba were present in very low concentrations. Generally, the levels of traces elements were similar in all the studied samples and data obtained in this work are in agreement with literature data. These high levels of trace elements detected in the tremolite samples are potentially harmful and could contaminated soils and groundwaters as a result of weathering and human activities. Previous studies showed that the expositions of these trace elements could cause a several problems to the human health. Due to the health risks associated with NOA dispersion rates, an asbestos exposure control plan must be established.

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