POTENTIALLY TOXIC ELEMENTS (PTES) IN ACTINOLITE SERPENTINITE HOST ROCKS: A CASE STUDY FROM THE BASILICATA REGION (ITALY)

Rosalda Punturo*,,✉, Claudia Ricchiuti*, Eugenia Giorno***, Carmine Apollaro°, Domenico Miriello°, Roberto Visalli*, Maria Rita Pinizzotto°°, Carmelo Cantaro°°** and **Andrea Bloise°**

* *Department of Biological, Geological and Environmental Sciences, University of Catania, Italy,*
** *IGAG-CNR Rome.*
*** *MAT-InLAB - Department of Chemistry and Chemical Technologies, University of Calabria, Arcavacata di Rende, Cosenza, Italy.*
° *Department of Biology, Ecology and Earth Sciences, University of Calabria, Rende, Cosenza, Italy.*
°° *ARPA Sicily - Regional Agency for the Protection of the Environment - Laboratory of Catania, Italy.*
✉ *Corresponding author, email: Rosalda.punturo@unict.it*

Keywords: *potentially toxic elements; actinolite Elongated Mineral Particles; serpentinite; Southern Italy.*

ABSTRACT

It is generally accepted by the scientific community that various factors such as morphometry, biodurability and chemistry contribute to the toxic potential of elongated mineral particles. As far as the chemical composition is concerned, in addition to its major structural elements, asbestos Elongated Mineral Particles (EMPs) may contain various Potentially Toxic Elements (PTEs), which could play an important role in pathological effects on human health. In this study, the concentration levels of PTEs in two actinolite elongated mineral particles and two host-serpentinite rocks, were determined by means of inductively coupled plasma spectroscopy with optical emission spectrometry (ICP-OES). The present work aims to provide a contribution to the already existent literature studies focusing on asbestos-related toxicity with new chemical data of actinolite EMPs and host-serpentinite rocks accommodating PTEs. Study samples come from the Southern Apennine thrust belt in Basilicata region (Southern Italy), where asbestos-bearing outcrops are documented in the literature and induced pathogenic effects have been reported so far.

Geochemical results of actinolite samples revealed high concentrations of toxic elements especially Cr and Ni with values ranging between 158-870 ppm and 20-103 ppm respectively. Similarly, analyzed bulk serpentinite rocks showed Cr and Ni critical concentrations.

Based on the obtained results it is possible to assert that populations living in areas with amphibole asbestos occurrences within serpentinite outcrops, such as the studied cases, are potentially exposed to health risks related to the presence of significant amounts of PTEs.

INTRODUCTION

Serpentinites have a complex origin, involving deep parts of the Earth, including the mantle. They are formed as a result of serpentinization of ultramafic rocks (i.e., lherzolite, harzburgite and dunite) in which the main minerals are pyroxenes and olivine. From the mineralogical point of view, serpentine-group minerals (i.e., chrysotile, lizardite, antigorite) are the main constituents of serpentinite rocks (Deer et al., 2009). Although serpentinite rocks often may also contain accessory minerals such as actinolite/tremolite, chlorite, brucite, magnetite, talc or carbonates and scraps of the predecessor mineralogy such as pyroxene and olivine (Deer et al., 2009). Actinolite is a monoclinic amphibole belonging to the asbestos group, together with tremolite, amosite, anthophyllite, crocidolite and chrysotile (IARC, 2012).

Actinolite may occur either in prismatic habit and in fibrous-asbestiform form; in this latter case it is part of regulated asbestos minerals (WHO, 1986; NIOSH, 2011). It is worth noting that the various existing definitions of asbestos (Campbell et al., 1977; Alleman and Mossman, 1997; Case et al., 2011; NIOSH, 2011; Gualtieri, 2012; Williams et al., 2013), result in a lack of standardized definition for fibres (Kane et al., 1996), term replaced with "elongated mineral particles" (EMPs) by NIOSH (2011). In the present paper, we considered as EMPs those potentially inhalable particles having L > 5 μm, W < 3 μm and L/W > 3 (NIOSH, 2011; Gualtieri, 2012; 2017).

The International Agency for Research on Cancer (IARC, 2012) classified asbestos as a Group 1 carcinogen, consequently, many countries banned the use and commercialization of asbestos (IBAS, 2019). However, the presence of asbestos-containing materials (ACMs) not properly preserved and the environmental exposure to the natural occurrence of asbestos (NOA), still represents an unsolved concern. In fact, the global territory is characterized by a wide occurrence of NOA outcrops (e.g., USA, India, Canada, China, Italy; Virta, 2006; Ricchiuti et al., 2020) that, due to weathering processes (e.g., erosion) or human activities (e.g., road construction, agricultural activities), may release dust containing potentially inhalable EMPs into the atmosphere (Punturo et al., 2015; Marrocchino et al., 2020). The asbestos toxicity is attributed to the physical-chemical characteristics of the EMPs such as the size, the surface area, the ability to generate reactive oxygen species (ROS), the biopersistence as well as the chemical composition (Fubini and Otero Arean, 1999; Shukla et al., 2003; Fubini and Fenoglio, 2007; Donaldson et al., 2010). The presence of trace elements, especially heavy metals, in the EMPs structure provide a contribution to their toxic potential due to the capability of these elements to induce lung cancer if released into the body once the EMP is inhaled (Dixon et al., 1970; Baumgardt et al., 1986; Nemery 1990; Bargagli et al., 2008; Wei et al., 2014; Bloise et al., 2017a; Punturo et al., 2019a; 2019b; Bloise et al., 2020). Therefore, the chemical characterization and the quantification of the amount of potentially toxic elements (PTEs) hosted in the elongated mineral particle structure, in addition to other parameters (i.e., size, biodurability), results crucial to understand their potential hazard (Bloise et al., 2017a; Gualtieri, 2018). Similarly, potentially toxic elements present in ophiolite rocks may be released into the environment by leaching of the host rocks and their respective sediments and soils thus subsequently increasing their concentrations in soil waters and groundwaters (Apollaro et al., 2011; 2019; Fuoco et al., 2020). The contamination sources of PTEs are multiple and widespread in the environment; namely, some examples are represented by contaminated soil, road dust, industrial effluents as well as particles produced by the combustion of fossil fuels. In the specific case of this study, localities have been selected as a case in point because no anthropogenic sources such as industrial activities are located in their neighborhood, but rather geogenic sources such as natural weathering of rocks have been identified as the main causes of the presence of PTEs. In the Basilicata region (Southern Apennines), both Episcopia and San Severino Lucano villages are characterized by the extensive occurrence of ophiolitic rocks that are well known to contain asbestos fibres (Dichicco et al., 2017; 2019; Punturo et al., 2018; Ricchiuti et al., 2021) and PTEs that can become bioavailable and mobilized (Mistikawy et al., 2020). Previous works carried out in the same areas (Bloise et al., 2017b; Punturo et al., 2018; 2019a) revealed the presence of asbestos minerals (i.e., tremolite asbestos and actinolite asbestos) with dimensions (i.e., width, length) matching with regulated those (length > 5 μm, width < 3 μm; WHO, 1997) and therefore classified as asbestos under European law (Directive, 2003/18/CE, 2003). As a matter of fact, serpentinite rocks that widely occur in the study area, are among the most critical lithotype from the environmental point of view due to the high contents of heavy metals such as Cr, Ni, Co and other PTEs. Indeed, the capability of asbestos EMPs to host PTEs in their structure makes them released into the body once ingested or inhaled. Nevertheless, the concentration levels of PTEs in ultramafic rocks (e.g., peridotites and serpentinites) are extremely variable due to the heterogeneities of mineralogy, mineral chemistry, structural properties of the rocks, characteristics strictly dependent on the different geological settings and geodynamic evolutions (Deschamps et al., 2013). Since contained within ultramafic rocks, PTEs can be released into water and soils by means of weathering and pedogenic processes. For instance, previous studies conducted in the ophiolite outcrops of the Gimigliano Mount-Reventino Unit area in the the Southern Apennine (GMRU; Calabria region, Southern Italy) revealed that water interacting with ophiolitic rocks is characterized by high concentrations of PTEs such as Cr, Ni, Cu, Zn, Pb, due to the dissolution of primary phases such as serpentine and amphiboles (Apollaro et al., 2011; 2019; Fuoco e al., 2020) thus highlighting the importance of the mineralogical and chemical characterization for assessing contaminated groundwater and soil in ophiolitic outcrops.

According to the literature, PTEs may have a negative impact on ecosystems and human health; for instance, in the case of ingestion, the absorption of PTEs occurs in the gastrointestinal tract (Yuswir et al., 2013), whereas in the case of inhalation they dissolve in lung fluids and may enter the blood circulation by crossing the air-blood barrier of the respiratory system (Kastury et al., 2017). Toxicological studies based on the investigation of the bronchoalveolar fluids and inhaled atmospheric particulate interactions (Censi et al., 2011a; 2011b), show how the metallic elements are released into the human body and may produce various health effects (Nordberg et al., 2007).To date, several studies showed an increased number of lung diseases in the Basilicata region, mainly related to environmental exposure to asbestos (Bernardini et al., 2003; Burragato et al., 2004; Pasetto et al., 2004; Beneduce et al., 2008; Bloise et al., 2012; Bloise 2017b; Dichicco et al., 2018; 2019, Punturo et al., 2018). As a matter of fact, epidemiological studies conducted on twelve villages of the Basilicata region, revealed a significant excess of negative health effect in NOA-correlated cases in rural areas; for instance, the exposure to asbestos minerals related to asbestos dispersion and pollution from natural sources in the Basilicata region has been recognized as the main cause of many mesothelioma cases documented in the area 20 km far away from Episcopia village (e.g., Beneduce et al., 2012) thus making the study area of great scientific interest.

It is worth noting that, even though in the past previous works carried out by higher institute of health (e.g., Bernardini et al., 2003) related mesothelioma disease to exposure to asbestos tremolite, up to now there are no cases related to natural occurrences of actinolite in the Basilicata region.

In this scenario, this work focuses on the determination of PTEs amounts in selected actinolite asbestos using inductively coupled plasma spectroscopy with optical emission spectrometry (ICP-OES).

As a case study, we selected ophiolite units cropping out in the Basilicata region (Southern Italy), whose quantification of trace elements in serpentinite rocks from which actinolite elongated mineral particles have been extracted may be used to assess and compare the concentration levels and to understand their contribution in term of PTEs in similar geological contexts.

STUDY AREA

In the present study, actinolite asbestos specimens and serpentinite host rocks cropping out in the Basilicata region, Southern Italy, have been selected as a case study and have been examined by a chemical point of view. The study area (Fig, 1a), sits in the surrounding of Episcopia and San Severino Lucano villages, within the Pollino UNESCO Global Geopark (Fig. 1b). The UNESCO Global Geopark covers 1.925 km^2 and includes the administrative territories of 56 municipalities, 24 of which are in Basilicata and 32 in Calabria. The resident population consists of 150,624 inhabitants (https://en.unesco.org/global-geoparks/pollino). The ophiolite terrains, which represent remnants of oceanic lithosphere do occur oriented approximately NW-SE (Fig. 1b). They are ascribed in the literature to the so-called Liguride Complex and provide information on the processes of accretion that developed between the Late Cretaceous-Eocene and Oligocene following the closing Tethys Ocean (Knott, 1987; Monaco and Tortorici, 1995; Cirrincione et al., 2015; Vitale et al., 2019). Indeed, according to the literature, after undergoing ocean floor metamorphism (from greenschist to amphibolite facies), these rocks, where involved in a subduction event starting in late Oligocene, were incorporated in the Ligurian Accretionary Complex, underwent deformation reaching HP/LT conditions (blueschist facies testified by Na-amphibole), to be later exhumed in the Tortonian (Mazzeo et al., 2017; Monaco et al., 2020). At the scale of the outcrop, serpentinites are green-bluish in color and are locally very brittle, as indicated by the large number of fractures that are usually filled by amphibole asbestos. As it may be observed in Fig. 1c, serpentinite lithotypes entirely constitute the bedrock of the vil-

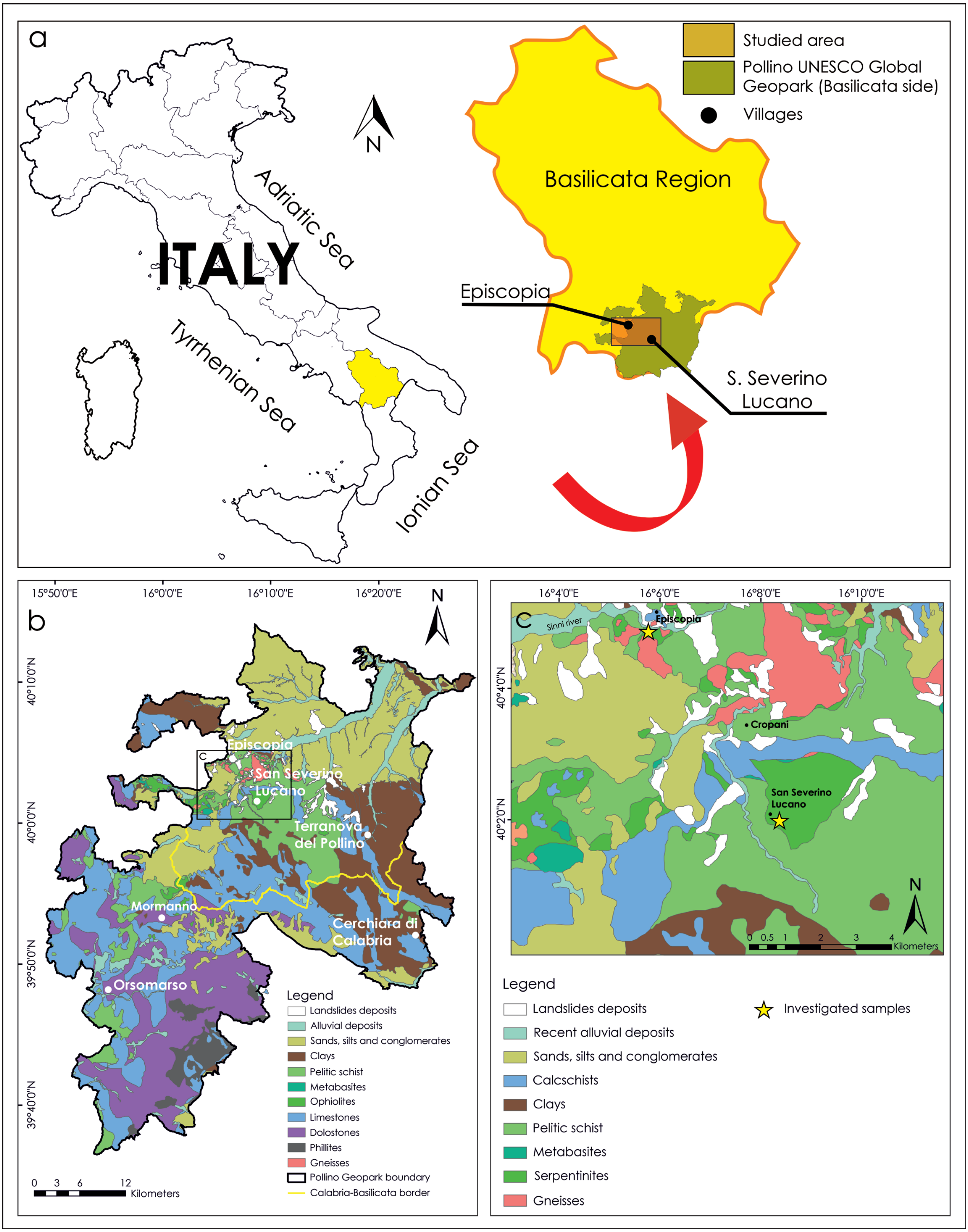

Fig. 1 - a) simplified geographical context of the study area, within the Pollino UNESCO Global Geopark, where the Episcopia (40°4'32".88 N, 16°5'56".40 E) and San Severino Lucano (40° 1' 19'' N, 16° 8' 20'' E) villages are located (Basilicata region, Italy); b) simplified geological sketch map of the Pollino UNESCO Global Geopark (modified after Apollaro et al., 2021); c) geo-lithological setting of the study area, with particular regards to the villages of Episcopia and San Severino Lucano (Bloise et al., 2019; Punturo et al., 2019a) with the location of the investigated samples.

lage of San Severino Lucano and of its surroundings. Previous detailed field survey carried out near the sampling sites highlighted that the area is characterized by sparse vegetation and by soils developed on serpentinite bedrocks (Punturo et al., 2019a). The area of San Severino Lucano is crossed by various streams, of which the Frido Stream is the main (Monaco et al., 2020). The village of Episcopia is located NW of San Severino (Fig. 1c); serpentinites are well-exposed in the village surroundings and display a vivid green colour. The overall thickness of serpentinite rocks ranges from 30-40 meters to 100-120 meters at the south, in correspondence with the orographic left and right of the Sinni River, respectively (Bloise et al., 2019; Monaco et al., 2020).

MATERIALS AND METHODS

It is worth noting that these serpentinite rocks have already been characterized by the mineralogical point of view in previous works (sample S19, Bloise et al., 2017b; sample E12, Bloise et al., 2019) with special regard to the morphological parameters (i.e., length, width) of asbestos fibres (e.g., actinolite); hence, the mineralogical features (i.e., actinolite asbestos) did prompt a further geochemical investigation. In order to avoid the elemental contribution by other minerals to compositional features of actinolite, during the selection of actinolite specimens we paid attention and exclusively collected individuals with the following requirements: a) asbestiform habit; and b) absence of any intergrowths with other occurring minerals and of any mineral inclusions. Fig. 2 shows the mesoscopic appearance of the studied samples: i) actinolite EMPs from Episcopia village (sample ACT_EPS: Fig. 2a); ii) actinolite EMPs from San Severino Lucano village (sample ACT_SSL; Fig. 2b); iii) serpentinite rock from Episcopia village (sample Serp_EPS; Fig. 2c); iv) serpentinite rock from San Severino Lucano village (sample Serp_SSL; Fig. 2d). Inductively coupled plasma spectroscopy with Optical Emission Spectrometry (ICP-OES), Agilent 710 Technology, was used to determine the trace elements concentration levels (As, Ba, Cd, Co, Cr, Cu, Li, Mo, Ni, Pb, Sb, Sn, Ti, V, Zn) on either actinolite EMPs and on serpentinite host rocks; even though before chemical analysis, actinolite EMPs were manually selected by using a binocular microscopy to avoid the possible contamination by other mineral impurities, if any, it is worth specifying that it was not possible to exclude the presence of nano-sized other species. Using a microwave Milestone MLS Mega 1200 with HPR 1000/10 vessels, 100 mg of powder of sample were dissolved in a mixture of Mer-

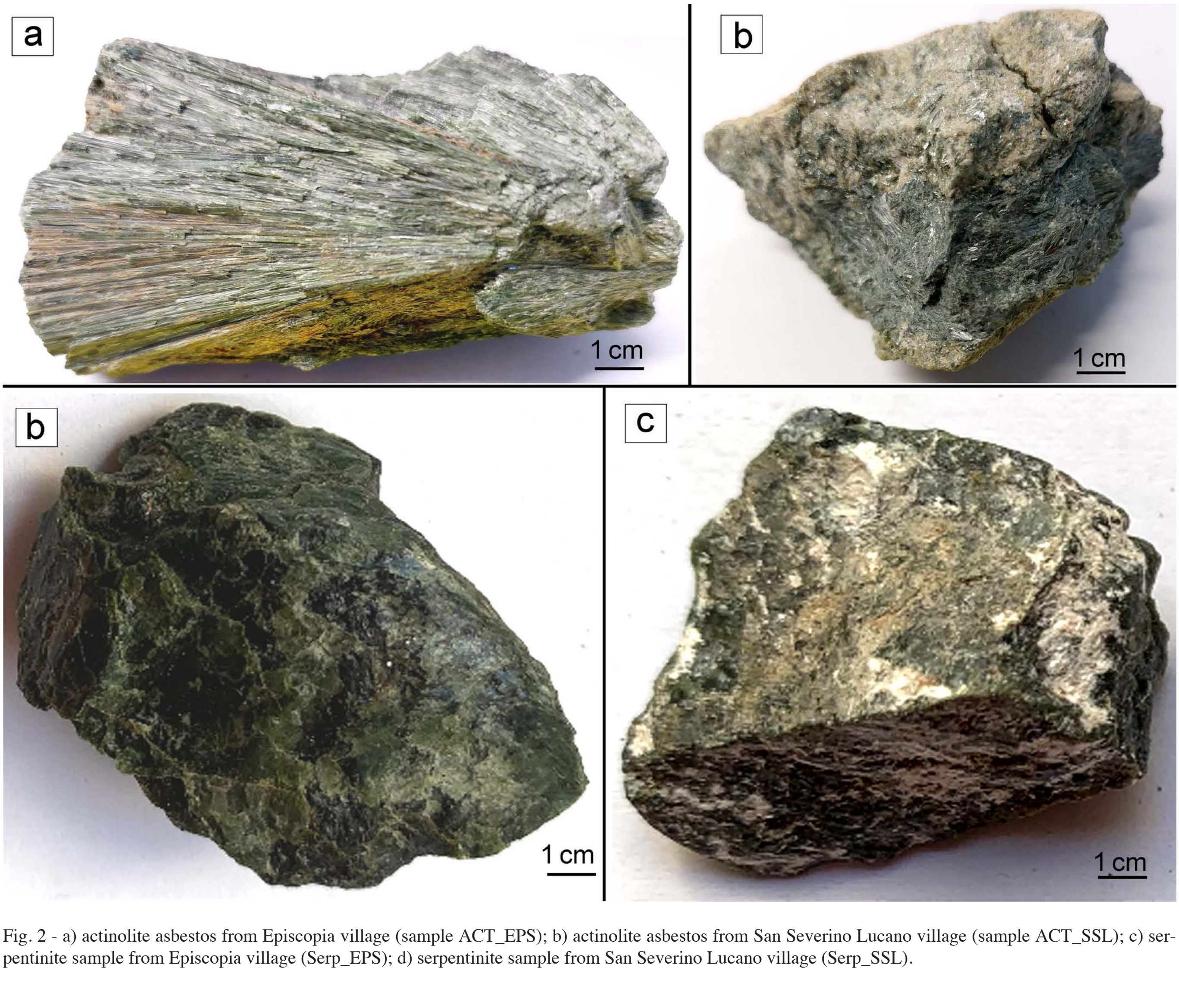

Fig. 2 - a) actinolite asbestos from Episcopia village (sample ACT_EPS); b) actinolite asbestos from San Severino Lucano village (sample ACT_SSL); c) serpentinite sample from Episcopia village (Serp_EPS); d) serpentinite sample from San Severino Lucano village (Serp_SSL).

ck ‘‘suprapur’’ quality acids, hydrofluoric acid (1.5mL), nitric acid (0.5mL), and hydrofluoric acid (1.5mL). After complete dissolution, a small amount of boric acid was added to the composition to neutralize samples before ICP-OES analysis. The calibration curves were prepared using the O2Si ® “multielement smart solutions”. The instrumental limit of quantification considered (LOQ) for each element was determined with the white method, and the values obtained correspond to those provided by the ISO-11885: Waters quality - Determination of selected elements by inductively coupled plasma optical emission spectrometry (ICP-OES). To ensure the reproducibility, all of the measurements were performed in triplicate.

RESULTS

Quantification of PTEs hosted in actinolite mineral particles

The inductively coupled plasma spectroscopy with optical emission spectrometry (ICP-OES), allowed measuring the concentration of trace elements (As, Ba, Cd, Co, Cr, Cu, Li, Mo, Ni, Pb, Sb, Sn, Ti, V, Zn) in actinolite elongated mineral particle samples. Results revealed different contents in the analyzed samples, as shown in Table 1. Due to the well-known negative effects caused by some heavy metals on human health (IARC, 2012), special regard has been paid to Cr, Ni, As, Co, Cu, Zn, V, and Pb. The obtained data highlighted that Cr and Ni are the most abundant elements in the studied actinolite samples (Fig. 3a) with values of about 158 ppm (ACT_EPS), 870 ppm (ACT_SSL), and about 103 ppm (ACT_EPS) and 19.7 ppm (ACT_SSL) respectively (Table 1). It is worth noting that As (54.3 ppm), Co (25 ppm), Zn (56 ppm) and V (9.7 ppm) are abundant in ACT_EPS, whereas ACT_SSL is enriched in Cu (61.9 ppm) and Pb (22.4 ppm). The concentration levels of the other trace elements detected in the investigated specimens (Ba, Cd, Li, Mo, Sb, Sn, Ti), are quite similar in both actinolite samples (Table 1), except for Sn, and Ti. Results revealed a concentration of 6 ppm versus 4.8 ppm (Ba), 4.9 ppm versus 2.5 ppm (Cd), 1.1 ppm versus 3.8 (Li), 6.9 ppm versus 7.5 (Mo), 13.4 ppm versus 8.8 (Sb), in ACT_EPS and ACT_SSL respectively. Other metals such as Sn and Ti result much higher in ACT_SSL with values of 150 ppm (Sn) and 26.5 ppm (Ti), versus 24.3 ppm (Sn) and 11.9 ppm (Ti) in ACT_EPS.

Quantification of PTEs in serpentinite host rocks

The concentration of trace elements (As, Ba, Be, Cd, Co, Cr, Cu, Mo, Ni, Pb, Sb, Sn, Ti, V, Zn) was also measured in serpentinite host rock samples from Episcopia (Serp_EPS) and San Severino Lucano (Serp_SSL) villages (Table 1). Also in this case, due to the potential impact of some trace elements on human health (IARC, 2012) special attention has been paid to some heavy metals such as Cr, Ni, Co, V, Cu and Zn (Fig. 3b). Chemical results revealed that Cr and Ni are the most abundant among the trace elements investigated, showing concentration levels of 1424.07 ppm (Cr) and 2092.50 ppm (Ni) in serpentinite from Episcopia village (Serp_EPS), and of 1591.92 ppm (Cr) and 1945.84 ppm (Ni) in serpentinite from San Severino Lucano (Serp_SSL) village. As for the other trace elements considered, Co (91.94 ppm) and Cu (37.48 ppm) were more abundant in serpentinite from Episcopia (Serp_EPS), whereas serpentinite from San Severino Lucano (Serp_SSL) is enriched in V (48.33 ppm) and Zn (31.21 ppm). Trace elements such as As, Be, Cd, Mo, Sb, Sn, and Ti have been detected in very low amounts (e.g., < 1 ppm; Table 1).

DISCUSSIONS

PTEs in actinolite EMPs and in serpentinite host rocks

In the present study, a geochemical investigation showed that both the analyzed actinolite samples (i.e., ACT_EPS and ACT_SSL) are enriched in Cr, Ni, As, Co, Cu, Zn, V and Pb. Specifically, Cr and Ni are the most abundant trace elements detected and suggest the potential toxicity of the EMPs since several studies showed their impact on human health, if present in excessive amounts (e.g., stomach and lung cancer;

Table 1 - Trace element contents (ppm) in the investigated actinolite samples (ACT_EPS, ACT_SSL) and serpentinite rocks (Serp_EPS; Serp_SSL) from Episcopia and San Severino Lucano villages obtained by ICP-OES.

ppm	ACT_EPS	ACT_SSL	Serp_EPS	Serp_SSL
As	54.3	7.1	60.23	9.76
Ba	6.1	4.8	14.59	6.53
Cd	4.9	2.5	0.03	0.02
Co	25	n.d.	91.94	76
Cr	158.1	870	1424.07	1591.92
Cu	23.7	61.9	37.48	25.74
Li	1.1	3.8	n.d.	n.d.
Mo	6.9	7.5	0.12	0.16
Ni	102.8	19.7	2092.5	1945.84
Pb	15.2	22.4	0.57	23.01
Sb	13.4	8.8	0.05	0.03
Sn	24.3	150	0.06	0.09
Ti	11.9	26.5	520.23	440.02
V	9.7	7.5	45.78	48.33
Zn	56	38.9	19.33	31.21

n.d.= not detected

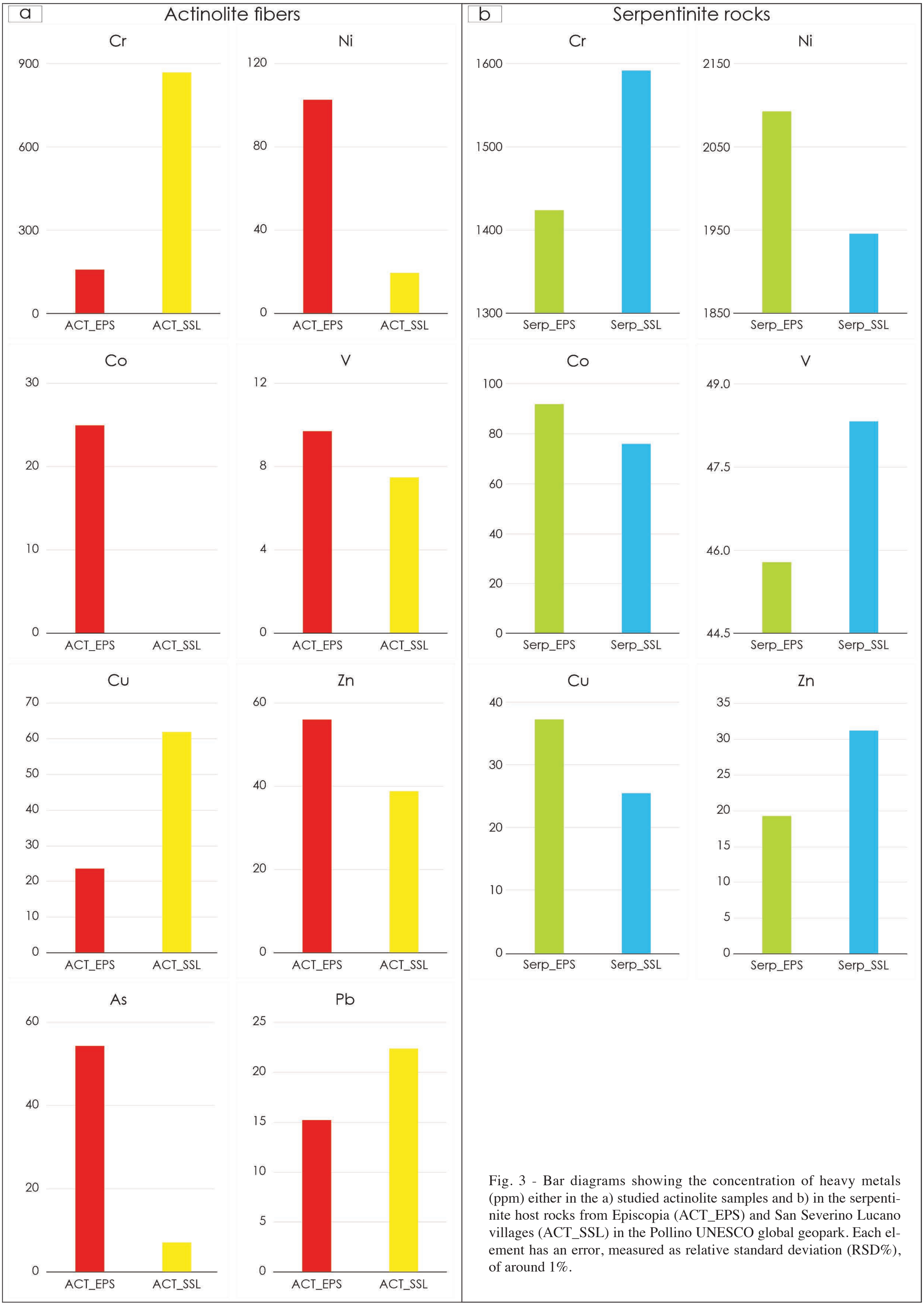

Fig. 3 - Bar diagrams showing the concentration of heavy metals (ppm) either in the a) studied actinolite samples and b) in the serpentinite host rocks from Episcopia (ACT_EPS) and San Severino Lucano villages (ACT_SSL) in the Pollino UNESCO global geopark. Each element has an error, measured as relative standard deviation (RSD%), of around 1%.

Shekhawat et al., 2015). In fact, Cr in the hexavalent redox state is the most dangerous form of chromium and may cause health problems as well as the main human health effects associated with Ni exposure consist of respiratory carcinogenicity. (Buxton et al., 2019). It has been documented that, in minerals occurring within serpentinite rocks Cr is mainly present in the trivalent redox state; however, oxidation of Cr(III) from Cr-spinels is considered to be a potential source of Cr(VI) identified in serpentine soil solutions (Oze et al., 2004). *In vivo*, it has been documented since long time that chromium readily dissolves from intrapleurally administered chrysotile in rats, and is leached at much higher rates than iron (Holmes et al., 1967; Morgan et al., 1971). Chromium is a metal existing in oxidation states of 0, +2, +3, and +6. Among them, hexavalent chromium (Cr^{6+}) have been shown to be the most carcinogenic (e.g., Bridgewater et al., 1994). However, also Cr(III) has been suggested that causes DNA damage in in vitro test systems (e.g., Plaper et al., 2002). As for the other trace elements, the high concentration levels of heavy metals such as As, Co, Cu, Zn, V and Pb contribute to the toxic potential of the samples since their impact on human health is well known. Among them, for instance, arsenicum is an ubiquitous metalloid present in rocks, soil and natural water; it can be found in natural matrices both as inorganic forms As(III), As(V) or organic forms (Fuoco et al., 2022). Many studies on the illness- inducing effects of human exposure to As have shown that both forms of As are potentially harmful to human health and therefore considered it a cytotoxic element (e.g., Hughes et al. 2011). Moreoverr, several studies have examined the relationship between arsenic exposure and intake and increased lung cancer mortality (Nackerdien et al., 1991; Salnikow et al., 2000; Kawanishi et al., 2001; Chen et al., 2003; IARC, 2012, Miriello et al., 2013). Indeed, the International Agency for Research on Cancer (IARC) classified the As compounds as carcinogenic to humans (Group 1) based on sufficient evidence of carcinogenicity in humans. The most important sources for the human to exposure to As are represented by alimentary products alimentary and drinking water (Kapaj et al., 2006). Significant contamination of groundwater from several regions of the world (Ulery et al., 2006) results from either erosion and leaching from geological formations. Furthermore, it is worth noting that the anthropic component should not be neglected relative to uses of As for industrial purposes, mining activities and metal processing, and applying pesticides and fertilizers based on As. Prolonged exposure to As increases the risk of developing a number of serious health effects, such as skin lesions and cancer of the liver, lung, bladder, kidney, and skin, and neurological, respiratory, cardiovascular, and developmental effects (Clair-Caliot et al., 2021). In our study, the actinolite specimen from the village of Episcopia resulted in being enriched in arsenicum (54.3 ppm), thus suggesting further investigations to be carried out to assess its bio-availability in the environment.

In summary, the quantification of PTEs in the investigated samples revealed the highest amounts of Ni, As, Co, Zn and V in actinolite from Episcopia village (ACT_EPS) while actinolite from San Severino Lucano village (ACT_SSL) is enriched in Cr, Cu and Pb.

For the purposes of the present study, the total balance of PTEs (i.e., ΣAs, Ba, Cd, Co, Cr, Cu, Li, Mo, Ni, Pb, Sb, Sn, Ti, V, Zn) hosted in the mineral particle structure, may be useful to define which one among the two actinolite specimens analyzed, can be considered the most hazardous based on the PTEs amounts. It is worth mentioning, that there are numerous different factors able to influence the degree of poisoning caused by PTEs such as their concentration, the toxicity of the chemical, the duration and frequency of the exposure, but commonly the poisonous effect of heavy metals is attributed to the dose. Therefore, if we wanted to suppose which actinolite sample is more potentially hazardous based on the PTEs total amount (other conditions being equal), we would assume that actinolite from the village of San Severino Lucano (ACT_SSL) is the sample with the highest amount of PTEs and therefore presumably more toxic than actinolite from the village of Episcopia (ACT_EPS). As a matter of fact, the sum of the PTEs investigated in ACT_SSL is 1231.4 pm vs 513.4 ppm of ACT_EPS (Fig. 4c, Table 2).

In general, the occurrence of PTEs in the elongated mineral particle may be explained by either the presence of contamination from other species such as chromite and magnetite (Kumar and Maiti, 2015; Bloise et al., 2020), or by isomorphic substitutions (Morgan and Cralley, 1973; Ballirano et al., 2017). In fact, amphiboles show high capability for hosting trace elements in octahedral sites (i.e., M1, M2, M3) thus justifying the great amount of PTEs detected in the studied samples. Moreover, a previous study conducted by Ricchiuti et al., (2021) revealed significant amounts of PTEs in tremolite asbestos (Table 2, TR_EPS, TR_SSL) extracted from serpentinite rocks cropping out in the Basilicata region - Pollino Massif, thus testifying the presence of toxic elements in the study area and specifically in elongated mineral particles, that affect the whole composition of the host serpentinite rock. For instance, as far as Cr, it is worth noting the relatively low amount in actinolite vs high amount in tremolite noticed in specimens from Episcopia, that would suggest a larger contribution to bulk rock by tremolite; differently, actinolite collected at San Severino Lucano seems to contribute, together with tremolite, to the Cr content within serpentinite (see also Table 2). On the whole, as shown by chemical results, Cr and Ni are the most abundant heavy metals detected in the studied serpentinite samples. A limit value for some toxic elements (e.g., Cr, Ni) in soil and stream water has been established by the Italian Government (Legislative Decree N° 152 of 03//04/2006) but no limit exists for rocks and minerals in general. With the aim of proving the potential hazard due to the high amounts of some heavy metals in the investigated serpentinites, the same thresholds have been considered for rocks. Results revealed that Cr and Ni exceed the maximum admissible contents (Fig, 5) for the public, private, and residential green use (Limit A, Cr = 150 ppm; Ni = 120 ppm) and commercial and industrial use (Limit B, Cr = 800 ppm; Ni = 500 ppm). The high levels of heavy metals emphasize the potentially risk related to the natural exposure to serpentinites cropping out in the study area which are enriched in toxic elements that could contaminate soils and groundwater due to weathering processes and human activities even far away from the area where ophiolite crops out. Indeed, it is worth noting that some Authors (Beneduce et al., 2008; 2012) pointed out that the wide dispersion of the asbestos minerals by running water in the Pollino National Park area is a consequence of the cataclastic conditions of the serpentinite outcrops and, according to these authors, a crucial role in the dispersion of such minerals far from their source rock is to be found in the peculiar geomorphological features of each drainage basin in which the ophiolite-bearing rocks crop out.

In the present work, we documented and showed by chemical data of actinolite mineral particles (see Tables 1-2), that actinolite specimens investigated from both sites (i.e., Episcopia and San Severino Lucano villages) are particularly

Table 2 - Cr, Ni and sum (Σ) of elements concentration (ppm) of ACT_EPS (actinolite from Episcopia); ACT_SSL (actinolite from San Severino Lucano); ACT_GMRU (actinolite from Gimigliano-Mount Reventino Unit; TR_EPS (tremolite from Episcopia); TR_SSL (tremolite from San Severio Lucano).

Type	ppm	Cr	Ni	∑(As, Ba, Cd, Co, Cr, Cu, Li, Mo, Ni, Pb, Sb, Sn, Ti, V, Zn)	∑(As, Ba, Co, Cr, Cu, Ni, Pb, Sb, V, Zn)
Elongated Mineral Particles	ACT_EPS	158.1	102.8	513.40	464.30
	ACT_SSL	870	19.70	1231	1041
	ACT_GMRU	14.86	14.50	-	150.55
	TR_EPS	1120	1830	3551	-
	TR_SSL	550	480	1318	-
Serpentinite rocks	Serp_EPS	1424	2093	4307	3787
	Serp_SSL	1592	1946	4199	3758
	Serp_GMRU	2691	1982		

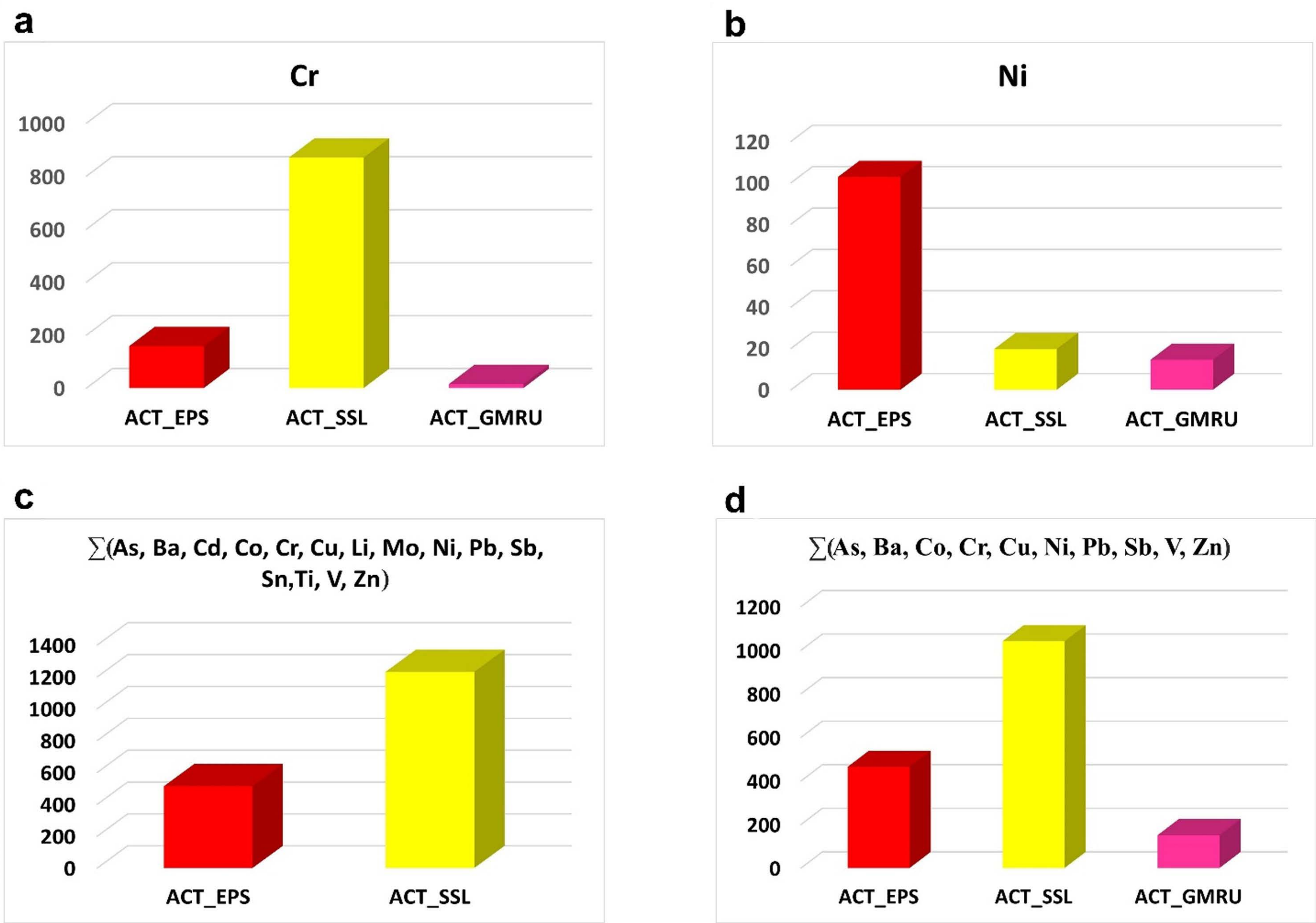

Fig. 4 - Concentration of Cr (a) and Ni (b) and sum of PTEs concentrations (ppm) in the investigated actinolite samples; the actinolite sample studied by Bloise et al., (2020) shown for comparison. ACT_EPS = actinolite from Episcopia village (Basilicata region); ACT_SSL = actinolite from San Severino Lucano village (Basilicata region); ACT_GMRU = actinolite from Gimigliano-Mount Reventino Unit (Calabria region).

enriched in Cr and Ni, thus suggesting a significant contribution by this mineral species to the total amounts of such trace elements within the serpentinite host rock.

Cross-country comparison of actinolite samples

Moreover, the comparison of Cr and Ni amounts detected in the studied actinolite samples with those ones of actinolite asbestos (i.e., ACT_GMRU) coming from similar ophiolite sequences cropping out in the Gimigliano-Mount Reventino Unit, southwards in the Calabria region studied by Bloise et al., (2020), emphasized how these samples are enriched in such heavy metals. Indeed, as shown in Fig. 4a and b, there is a clear difference in Cr and Ni contents among the three actinolite samples. Specifically, actinolite from San Severino Lucano (ACT_SSL) proved to be the most enriched in Cr

(Fig. 4a) followed by actinolite from Episcopia (ACT_EPS) and actinolite from GMRU (ACT_GMRU) which shows very low Cr amounts (14.86 ppm), while the highest concentrations of Ni (Fig. 4b) were found in ACT_EPS followed by ACT_SSL and lastly ACT_GMRU (14.5 ppm).

In addition, by comparing our data set with those of actinolite asbestos from the Gimigliano-Mount Reventino Unit studied by Bloise et al., (2020), actinolite from San Severino Lucano village (ACT_SSL) proved to be once again the sample with the highest total amount of toxic metals (As, Ba, Co, Cr, Cu, Ni, Pb, Sb, V, Zn; Fig. 4d) followed by actinolite from Episcopia village (ACT_EPS) and actinolite from GMRU outcrops (ACT_GMRU). The reason why we found these differences in PTEs concentrations among the compared samples may be explained by the various geochemical/petrological processes involved during the genesis of the mineral particles (Tiepolo et al., 2007; Bloise et al., 2017a).

Moreover, the comparison of our data with those one obtained by Bloise et al., (2020) was useful for assessing the differences in contents for Cr and Ni elements (Table 2), if any. As shown in Fig. 6a and b, all of the three compared rocks are characterized by significant amounts of these heavy metals, with the highest concentration levels of Cr (2691 ppm), detected in serpentinite rocks from GMRU (Serp_GMRU, Bloise et al., 2020) followed by Serp_SSL and Serp_EPS, whereas serpentinite from Episcopia is the most enriched in Ni, followed by serpentinite from GMRU and serpentinite from San Severino Lucano which show comparable values (1982 ppm and 1945.84 ppm respectively). These data suggest a different contribution from the mineral phases constituting serpentinite rocks from the study area (Episcopia and San Severino Lucano villages, Basilicata region) and those of serpentinite from Gimigliano-mount Reventino Unit (GMRU; Calabria region) in terms of Cr and Ni contents.

Unlike actinolite samples from the Basilicata region, actinolite asbestos from GMRU (Calabria region) showed very low amounts of Cr and Ni thus suggesting a greater influence of other mineral phases such as spinel, magnetite and pyroxene present in the serpentinite host-rock.

CONCLUSIONS

The chemical investigation conducted on two actinolite EMPs and two serpentinite host rocks cropping out in the Basilicata region allowed making significant considerations related to the presence of potentially toxic elements (PTEs) having a potential negative impact on human health. As a matter of fact, the quantification of PTEs in the selected actinolite samples revealed high concentrations of toxic elements (i.e., Cr, Ni, As, Co, Cu, Zn, V, Pb) especially Cr (870 ppm maximum value) and Ni (103 ppm maximum value), that in addition to the intrinsic toxicity of actinolite elongated mineral particles, results in an enormously dangerous combination for humans. Chemical results also suggest that, in addition to other mineral phases (e.g., spinel, magnetite, pyroxene), a significant contribution is provided by actinolite species to the total amounts of heavy metals such as Cr and Ni of serpentinite host-rock. As a matter of fact, analyzed bulk serpentinite host rocks showed concentrations of Cr and Ni exceeding the maximum admissible contents established by the Italian law (Italian Legislative Decree No. 152/2006) for public, private, and residential green use (Limit A) as for industrial commercial use (Limit B).

The obtained results represent considerable findings related to the presence of PTEs in potentially inhalable elongated mineral particles as well as in the environment since heavy metals may be mobilized and discharged into other environmental matrixes (e.g., water, soils) thus expanding the contamination source and the potential interaction with the human body. Finally, the present study provides novel chemical details on actinolite EMPs within the two serpentinite host rocks present in the studied areas, making it possible to assess that the health risk for the population leaving nearby the two villages and even at a distance from the source serpentinite rock might be attributed not only to the presence of NOA but also to the high amounts of PTEs. Moreover, provided that serpentinite-bearing outcrops are widespread worldwide, the obtained results may be set up as a pilot research for assessing asbestos-related pollution in similar geological contexts.

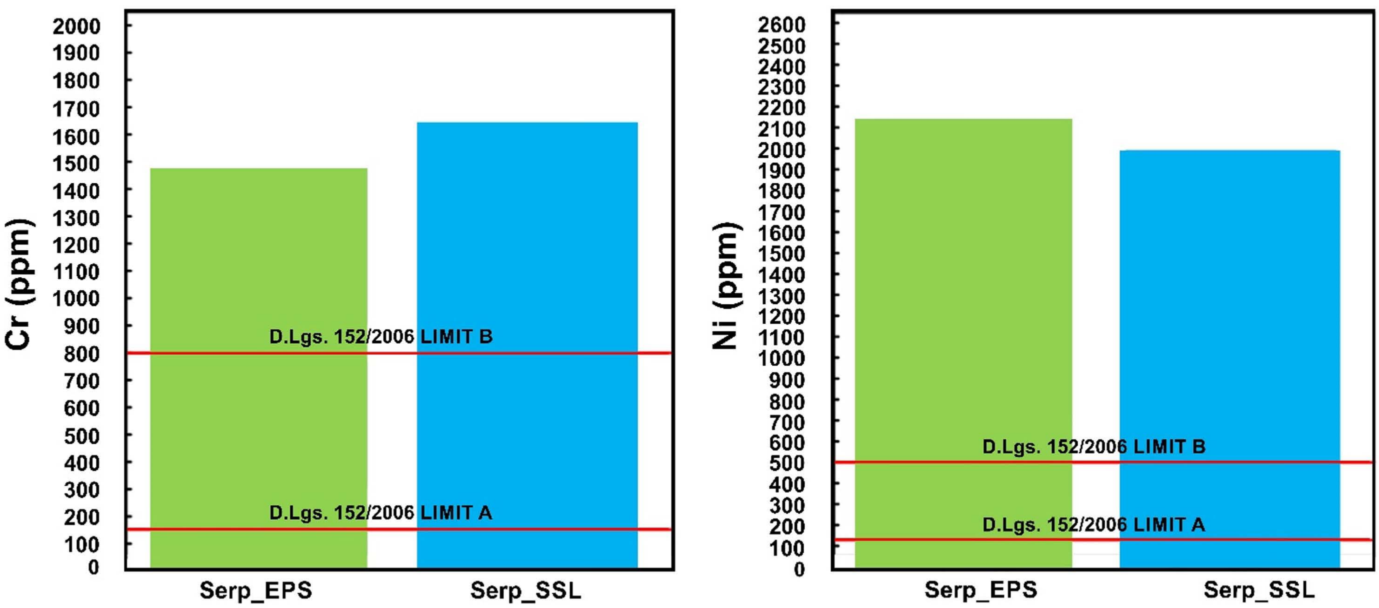

Fig. 5 - Cr and Ni concentrations of serpentinite samples of the study area (Episcopia, sample Serp_EPS; San Severino Lucano, sample Serp_SSL). Thresholds values (red lines) regulated by Italian Law (Legislative Decree N°.152 of 03/04/2006) are also indicated. Limit A = limit value for public, private, and residential green use; Limit B = limit value for commercial and industrial use.

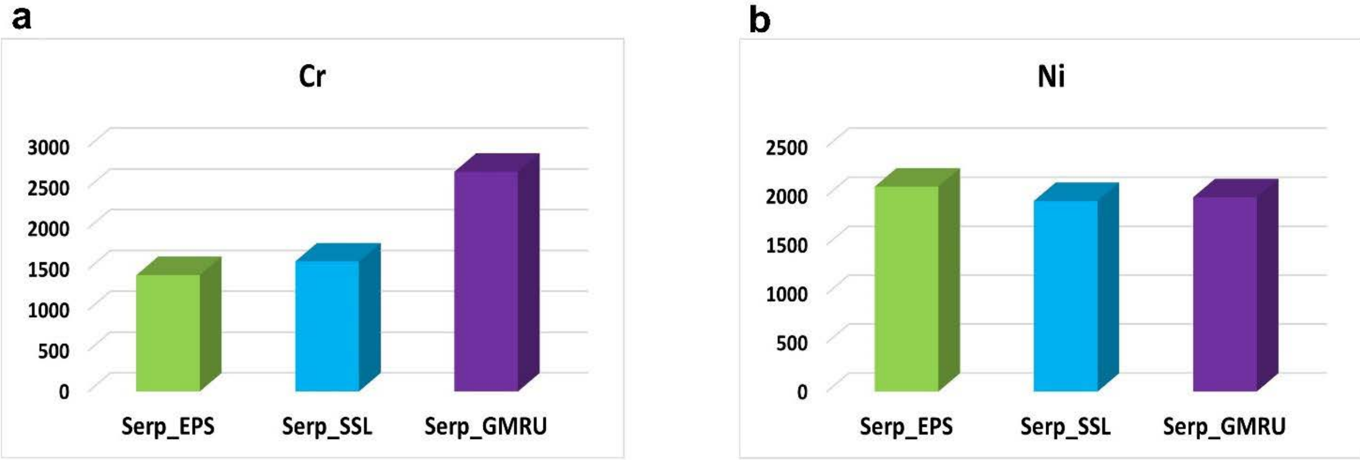

Fig. 6 - concentration levels of Cr (a) and Ni (b) in serpentinite rocks from Episcopia (Serp_EPS), San Severino Lucano (Serp_SSL) and Gimigliano-Mount Reventino Unit (Serp_GMRU; Bloise et al., 2020).

ACKNOWLEDGMENTS

The Authors are grateful to reviewers' comments and suggestions, that improved the first version of the manuscript. Editorial handling by Alessandra Montanini is acknowledged. Part of this research was funded by University of Catania, in the frame of PIACERI 2020-2022 funding program [responsible of the project: Gaetano Ortolano Grant Number 22722132153, within the project: "Combined geomatic and petromatic applications: The new frontier of geoscience investigations from field- to micro- scale-(GeoPetroMat)"], and by PIACERI 2020-2022 funding program (Linea 1 chance, grant number 22722132173; responsible Rosalda Punturo).

Availability of data and materials

All the raw data and materials used for this research are available at the University of Calabria and at the University of Catania upon request.

REFERENCES

Alleman J.E. and Mossman B.T., 1997. Asbestos revisited. Sci. Am., 277: 70-75.

Apollaro C., Fuoco I., Bloise L., Calabrese E., Marini L., Vespasiano G. and Muto F., 2021. Geochemical modeling of water-rock interaction processes in the Pollino National Park. Geofluids, 6655711. https://doi.org/10.1155/2021/6655711.

Apollaro C., Fuoco I., Brozzo G. and De Rosa R., 2019. Release and fate of Cr (VI) in the ophiolitic aquifers of Italy: the role of Fe (III) as a potential oxidant of Cr (III) supported by reaction path modelling. Sci. Total Environ., 660: 1459-1471, https://doi.org/10.1016/j.scitotenv.2019.01.103.

Apollaro C., Marini L., Critelli T., Barca D., Bloise A., De Rosa R., Liberi F. and Miriello D., 2011. Investigation of rock-to-water release and fate of major, minor, and trace elements in the metabasalt eserpentinite shallow aquifer of Mt. Reventino (CZ, Italy) by reaction path modelling. Appl. Geochem., 26: 1722-1740. https://doi.org/10.1016/j.apgeochem.2011.04.028.

Ballirano P., Bloise A., Gualtieri A.F., Lezzerini M., Pacella A., Perchiazzi N., Dogan M. and Dogan A.U., 2017. The crystal structure of mineral fibres. In: A.F. Gualtieri (Ed.), Mineral Fibres: crystal chemistry, chemical-physical properties, biological interaction and toxicity, Eur. Miner. Union, London, p. 17-53. https://doi.org/10.1180/EMU-notes.18.2.

Bargagli E., Monaci F., Bianchi N., Bucci C. and Rottoli P., 2008. Analysis of trace elements in bronchoalveolar lavage of patients with diffuse lung diseases. Biol. Trace Elem. Res., 124: 225-235. https://doi.org/10.1007/s12011-008-8143-6.

Baumgardt B., Jackwerth E., Otto H. and Tölg G., 1986. Trace analysis to determine heavy metal load in lung tissue. Int. Arch. Occup. Environ. Health, 58: 27-34. https://doi.org/10.1007/BF00378537.

Bernardini P., Schettino B., Sperduto B., Giannadrea F., Burragato F. and Castellino N., 2003. Tre casi di mesotelioma pleurico ed inquinamento ambientale da rocce affioranti di tremolite in Lucania. Giorn. It. Medicina Lavoro ed Ergonomia, 25: 8-411.

Beneduce P., Di Leo P., Filizzola C., Giano S.I. and Schiattarella M., 2008. Valutazione della pericolosità da rilascio di amianto da materiali naturali: un esempio dal Parco Nazionale del Pollino (Italia meridionale). Mem. Descr. Carta Geol. It., 78: 13-30.

Beneduce P., Di Leo P., Giano S. I. and Schiattarella M., 2012. Quantitative geomorphic analysis of asbestos dispersion and pollution from natural sources: the case-history of the Pollino National Park, Suthern Italy. Geogr. Fis. Dinam. Quat., 35 (1): 3-12.

Bloise A., Belluso E., Critelli T., Catalano M., Apollaro C., Miriello D. and Barrese E., 2012. Amphibole asbestos and other fibrous minerals in the meta-basalt of the Gimigliano-Mount Reventino Unit (Calabria, south-Italy). Rend. online Soc. Geol. It., p. 847-848.

Bloise A., Catalano M., Critelli T., Apollaro C. and Miriello D., 2017b. Naturally occurring asbestos: potential for human exposure, San Severino Lucano (Basilicata, Southern Italy). Environ. Earth Sci., 76: 648-661. https://doi.org/10.1007/s12665-017-6995-9.

Bloise A., Kusiorowski R., Lassinantti Gualtieri M. and Gualtieri A.F., 2017a. Thermal behaviour of mineral fibres. In: A.F. Gualtieri (Ed), Mineral fibres: crystal chemistry, chemical-physical properties, biological interaction and toxicity. Eur. Miner. Union, London, 18: 215-252. https://doi.org/10.1180/EMU-notes.18.7.

Bloise A., Ricchiuti C., Giorno E., Fuoco I., Zumpano P., Miriello D. and Punturo R., 2019. Assessment of naturally occurring asbestos in the area of Episcopia (Lucania, Southern Italy). Fibers, 7(5): 45. https://doi.org/10.3390/fib7050045.

Bloise A., Ricchiuti C., Punturo R. and Pereira D., 2020. Potentially toxic elements (PTEs) associated with asbestos chrysotile, tremolite and actinolite in the Calabria region (Italy). Chem. Geol., 558: 119896. https://doi.org/10.1016/j.chemgeo.2020.119896.

Bridgewater L.C., Manning F.C.R. Woo E.S. and Patierno S.R., 1994. DNA polymerase arrest by adducted trivalent chromium. Mol. Carcinog., 9: 122-33. https://doi.org/10.1002/mc.2940090304.

Burragato F., Mastacchi R., Papacchini L., Rossini F. and Sperduto B., 2004. Mapping of risks due to particulates of natural origin containing fibrous tremolite: the case of Seluci di Lauria (Basilicata, Italy). Nat. Hazard Abstr. Poster session NH 11.01. In: Eur. Geosci. Union, 1st General Assembly, Nice France. April 2004.

Campbell W.J., Blake R.L., Brown L.L., Cather E.E. and Sjoberg J.J., 1977. Selected silicate minerals and their asbestiform varieties: Mineralogical definitions and identification-characterization. Bureau of Mines Inform. Circular IC-8751.

Case B.W., Abraham J.L., Meeker G., Pooley F.D. and Pinkerton K.E., 2011. Applying definitions of ‘‘asbestos’’ to environmental and ‘‘low dose’’ exposure levels and health effects, particularly malignant mesothelioma. J. Toxicol. Environ. Health, Part B, 14: 3-39. https://doi.org/10.1080/10937404.2011.556045.

Censi P., Tamburo E., Speziale S., Zuddas P., Randazzo L.A., Punturo R., Cuttitta A. and Aricò P., 2011a. Yttrium and lanthanides in human lung fluids, probing the exposure to atmospheric fallout. J. Hazard. Mater., 186: 1103-1110. https://doi.org/10.1007/978-94-007-4372-4_1.

Censi P., Zuddas P., Randazzo L.A., Tamburo E., Speziale S., Cuttitta A., Punturo R., Aricò P. and Santagata R., 2011b. Source and nature of inhaled atmospheric dust from trace element analyses of human bronchial fluids. Environ. Sci. Technol., 45: 6262-6267. https://doi.org/10.1021/es200539p.

Chen L., Yang X., Jiao H., Zhao B., 2003. Tea catechins protect against lead-induced ROS formation, mitochondrial dysfunction, and calcium dysregulation in PC12 cells. Chem. Res. Toxicol., 16: 1155-1161.

Cirrincione R., Fazio E., Fiannacca P., Ortolano G., Pezzino A. and Punturo R., 2015. The Calabria-Peloritani Orogen, a composite terrane in Central Mediterranean; its overall architecture and geodynamic significance for a pre-Alpine scenario around the Tethyan basin. Per. Miner., 84 (3B): 701-749. https://doi.org/10.2451/2015PM0446 .

Deer W.A., Howie R.A., Zussman J., 2009. Rock-forming minerals. Vol. 3B, Layered silicates excluding micas and clay minerals. Geol. Soc. London, 320 pp.

Deschamps F., Godard M., Guillot S. and Hattori K., 2013. Geochemistry of subduction zone serpentinites: A review. Lithos, 178: 96-127. https://doi.org/10.1016/j.lithos.2013.05.019.

Dichicco M.C., De Bonis A., Mongelli G., Rizzo G. and Sinisi R., 2017. μ-Raman spectroscopy and X-ray diffraction of asbestos' minerals for geo-environmental monitoring: The case of the Southern Apennines natural sources. Appl. Clay Sci., 141: 292-299. https://doi.org/10.1016/j.clay.2017.02.024.

Dichicco M.C., Laurita S., Sinisi R., Battiloro R and Rizzo G., 2018. Environmental and health: The importance of tremolite occurence in the Pollino Geopark (Southern Italy). Geosci., 8 (3), 98. https://doi.org/10.3390/geosciences8030098.

Dichicco M.C., Paternoster M., Rizzo G. and Sinisi R., 2019. Mineralogical asbestos assessment in the Southern Apennines (Italy): A review. Fibers, 7: 24-27. https://doi.org/10.3390/fib7030024.

Dixon J.R., Lowe D.B., Richards D.E., Cralley L.J. and Stokinger H.E., 1970. The role of trace metals in chemical carcinogenesis: asbestos cancers. Cancer Res., 30: 1068-1074.

Donaldson K., Murphy F., Duffin R. and Poland C.A., 2010. Asbestos, carbon nanotubes and the pleural mesothelium: a review of the hypothesis regarding the role of long fibre retention in the parietal pleura, inflammation and mesothelioma. Particle and Fibre Toxicol., 7: 5-22. https://doi.org/10.1186/1743-8977-7-5.

Fubini B. and Fenoglio I., 2007. Toxic potential of mineral dusts. Elements, 3: 407-414. https://doi.org/10.2113/GSELEMENTS.3.6.407.

Fubini B. and Otero Arean C., 1999. Chemical aspects of the toxicity of inhaled mineral dusts. Chem. Soc. Rev., 28: 373-381. https://doi.org/10.1039/A805639K.

Fuoco I., De Rosa R., Barca D., Figoli A., Gabriele B. and Apollaro C., 2022. Arsenic polluted waters: application of geochemical modelling as a tool to understand the release and fate of the pollutant in crystalline aquifers. J. Environ. Manag., 301: 113796. https://doi.org/10.1016/j.jenvman.2021.113796.

Fuoco I., Figoli A., Criscuoli A., Brozzo G., De Rosa R., Gabriele B. and Apollaro C., 2020. Geochemical modeling of chromium release in natural waters and treatment by RO/NF membrane processes. Chemosph., 254: 126696. https://doi.org/10.1016/j.chemosphere.2020.126696.

Clair-Caliot G., Marks S., Hug S. J., Bretzler A., N'guessan N.D., Franck S., Tihe K. and Lalanne F., 2021. Uptake of arsenic by irrigated vegetables and cooked food products in Burkina Faso. Front. Water, 3: 667308. https://doi.org/10.3389/frwa.2021.667308.

Gualtieri A.F., 2012. Mineral fibre-based building materials and their health hazards. In: F. Pacheco-Torgal, S. Jalali and A. Fucic (Eds.), Toxicity of building materials. Woodhead Publ., Cambridge, UK, p. 166-195. https://doi.org/10.1533/9780857096357.166.

Gualtieri A.F., 2017. Mineral fibres: Crystal chemistry, chemical-physical properties, biological interaction and toxicity (Eur. Miner. Union). Ed. Gualtieri, A.F. https://doi.org/10.1180/EMU-notes.18.

Gualtieri A.F., 2018. Towards a quantitative model to predict the toxicity/pathogenicity potential of mineral fibers. Toxicol. Appl. Pharmacol., 361: 89-98.

IARC (International Agency for Research on Cancer), 2012. Arsenic, metals, fibres, and dusts. A review of human carcinogens. In: IARC Monographs on the evaluation of carcinogenic risks to humans, 100C, p. 501. Lyon, France.

Kane A.B., Boffetta P., Saracci R. and Wilbourn J.D., 1996. Mechanisms of fibre carcinogenesis. IARC Sci. Publ., 140. Lyon.

Kapaj S., Peterson H., Liber K. and Bhattacharya P., 2006. Human health effects from chronic arsenic poisoning; a review. J. Environ Sci. Health. Part A. 41 (10): 2399-2428. https://doi.org/10.1080/10934520600873571.

Kastury F., Smith E. and Juhasz A.L.A., 2017. A critical review of approaches and limitations of inhalation bioavailability and bioaccessibility of metal(loid)s from ambient particulate matter or dust. Sci. Total Environ., 574: 1054-1074. https://doi.org/10.1016/j.scitotenv.2016.09.056.

Kawanishi S., Hiraku Y., Oikawa S., 2001. Mechanism of guanine-specific DNA damage by oxidative stress and its role in carcinogenesis and aging. Mutat. Res. Rev. Mutat. Res., 488 : 65-76.

Knott S.D., 1987. The Liguride Complex of Southern Ital; a Cretaceous to Paleogene accretionary wedge. Tectonophysics,: 142 (2-4): 217-226. https://doi.org/10.1016/0040-1951(87)90124-7.

Kumar A. and Maiti S.K., 2015. Assessment of potentially toxic heavy metal contamination in agricultural fields, sediment, and water from an abandoned chromite-asbestos mine waste of Roro hill, Chaibasa, India. Environ. Earth Sci., 74 (3): 2617-2633. https://doi.org/10.1007/s12665-015-4282-1.

Holmes A. and Morgan A., 1967. Leaching of constituents of chrysotile asbestos *in vivo*. Nature, 215: 441-442. https://doi.org/10.1038/215441b0.

Hughes M.F., Beck B.D., Chen Y., Lewis A.S. and Thomas D.J., 2011. Arsenic exposure and toxicology: a historical perspective. Toxicol. Sci., 123 (2): 305-32. https://doi.org/10.1093/toxsci/kfr184.

IBAS - International Ban Asbestos Secretariat, 2019. http://www.ibasecretariat.org/alpha_ban_list.php.

Marrocchino E., Telloli C., Faccia F., Rizzo A. and Volpe L., 2020. Morphological and chemical analysis of tremolite related to natural asbestos in the road paving. Episodes J. Intern. Geosci., 43 (3): 869-879. https://doi.org/10.18814/epiiugs/2020/0200s05.

Mazzeo F.C., Zanetti A., Aulinas M., Petrosino P., Arienzo I. and D'Antonio M., 2017. Evidence for an intra-oceanic affinity of the serpentinized peridotites from the Mt. Pollino ophiolites (Southern Ligurian Tethys): Insights into the peculiar tectonic evolution of the Southern Apennines. Lithos, 284-285: 367-380. https://doi.org/10.1016/j.lithos.2017.04.019.

Miriello D., Lezzerini M., Chiaravalloti F., Bloise A., Apollaro C. and Crisci G.M., 2013. Replicating the chemical composition of the binder for restoration of historic mortars as an optimization problem. Comput. Concr., 12 (4): 553-563. https://doi.org/10.12989/cac.2013.12.4.553.

Mistikawy J.A., Mackowiak T.J., Butler M.J., Mischenko I.C., Cernak R.S., Richardson J.B., 2020. Chromium, manganese, nickel, and cobalt mobility and bioavailability from mafic-to-ultramafic mine spoil weathering in western Massachusetts. USA. Environ. Geochem. Health, 1–17. https://doi.org/10.1007/s10653-020-00566-7.

Monaco C. and Tortorici L., 1995. Tettonica estensionale quaternaria nell'Arco Calabro e in Sicilia orientale. Studi Geol. Camerti, 2: 351-362.

Monaco C., Rizzo G., Punturo R. and Cirrincione R., 2020. Il Massiccio del Pollino e le ofioliti del confine calabro-lucano. In: M. Tropeano, L. Sabato e M. Schiattarella (Eds.), Guide Geologiche Regionali, Basilicata. Soc. Geol. It., p. 271-286.

Morgan A. and Cralley L., 1973. Chemical characteristics of asbestos and associated trace elements. In: P. Bogovski, J.C. Gilson, V. Timbrell and J.C. Wagner (Eds.), Biological effects of asbestos. IARC Sci. Publ, Lyon, France, p. 113-131.

Morgan A., Holmes A. and Gold C., 1971. Studies of the solubility of constituents of chrysotile asbestos in vivo using radioactive tracer techniques. Environ. Res., 4: 558-570. https://doi.org/10.1016/0013-9351(71)90016-8.

Ulery, A.L., Jobe, T. and Nemmers, S., 2006. Managing arsenic in the environment: from soil to human health. In: Naidu R., Smith E., Owens G., Bhattacharya P. and Nadebaum P. (Eds.), CSIRO Publ., Melbourne, p. 331-354. https://doi.org/10.1111/j.1365-2389.2007.00898_5.x.

Nackerdien Z., Kasprzak K.S., Rao G., Halliwell B., Dizdaroglu M., 1991. Nickel (II)-and cobalt (II)-dependent damage by hydrogen peroxide to the DNA bases in isolated human chromatin. Cancer Res., 51: 5837–5842.

Nemery B., 1990. Metal toxicity and the respiratory tract. Eur. Resp. J., 3: 202-219.

NIOSH (National Institute for Occupational Safety and Health), 2011. Asbestos fibers and other elongate mineral particles: state of the science and roadmap for research. Current Intelligence Bull., 62, Cincinnati, USA.

Nordberg G.F., Nogawa K., Nordberg M. and Friberg L.T., 2007. Handbook on the toxicology of metals, 3rd Ed. Acad. Press/Elsevier: London, Chapter 23: 446-486.

Oze C., Fendorf S., Bird D.K. and Coleman R.G., 2004. Chromium geochemistry of serpentine soils. Int. Geol. Rev., 46: 97-126. https://doi.org/10.2747/0020-6814.46.2.97.

Pasetto R., Bruni B., Bruno C., Cauzillo G., Cavone D., Convertini L., De Mei B., Marconi A., Montagano G., Musti M., Paoletti L. and Comba P., 2004. Mesotelioma pleurico ed esposizione ambientale a fibre minerali: il caso di un'area rurale in Basilicata. Ann. Ist. Sup. Sanità, 40: 251-265.

Plaper A., Jenko-Brinovec Š., Premzl A., Kos J. and Raspor P., 2002. Genotoxicity of trivalent chromium in bacterial cells possible effects on DNA topology. Chem. Res. Toxicol., 15: 943-949. https://doi.org/10.1021/tx010096q.

Punturo R., Bloise A., Critelli T., Catalano M., Fazio E. and Apollaro C., 2015. Environmental implications related to natural asbestos occurrences in the ophiolites of the Gimigliano-Mount Reventino Unit (Calabria, Southern Italy). Int. J. Environ., 9: 405-418.

Punturo R., Ricchiuti C. and Bloise A., 2019a. Assessment of serpentine group minerals in soils: A case study from the Village of San Severino Lucano (Basilicata, Southern Italy). Fibers, 7 (2): 18. https://doi.org/10.3390/fib7020018.

Punturo R., Ricchiuti C., Mengel K., Apollaro C., De Rosa, R. and Bloise A., 2018. Serpentinite derived soils in southern Italy: potential for hazardous exposure. J. Mediterr. Earth Sci., 10. https://doi.org/10.3304/JMES.2018.015.

Punturo R., Ricchiuti C., Rizzo M. and Marrocchino E., 2019b. Mineralogical and microstructural features of Namibia marbles: insights about tremolite related to natural asbestos occurrences. Fibers, (4): 31. https://doi.org/10.3390/fib7040031.

Ricchiuti C., Bloise A. and Punturo R., 2020. Occurrence of asbestos in soils: State of the Art. Episodes, 43 (3): 881-891. https://doi.org/10.18814/epiiugs/2020/0200s06.

Ricchiuti C., Pereira D., Punturo R., Giorno E., Miriello M. and Bloise A., 2021. hazardous elements in asbestos tremolite from the Basilicata Region, Southern Italy: A first step. Fibers, 9 (8): 47. https://doi.org/10.3390/fib9080047.

Salnikow K., Su W., Blagosklonny M.V., Costa M., 2000. Carcinogenic metals induce hypoxia-inducible factor-stimulated transcription by reactive oxygen species-independent mechanism. Cancer Res., 60: 3375–3378.

Shekhawat K., Chatterjee S. and Joshi B., 2015. Chromium toxicity and its health hazards. Intern. J. Advanc. Res., 3: 167-172.

Shukla A., Gulumian M., Hei T.K., Kamp D., Rahman Q. and Mossman B.T., 2003. Multiple roles of oxidants in the pathogenesis of asbestos-induced diseases. Free Radical Biol. Med., 34: 1117-1129. https://doi.org/10.1016/s0891-5849(03)00060-1.

Tiepolo M., Oberti R. Zanetti A. Vannucci R. and Foley S.F., 2007. Trace-element partitioning between amphibole and silicate melt. In: F.C. Hawthorne, R. Oberti, G. Della Ventura and A. Mottana (Eds), Amphiboles: crystal chemistry, occurrence, and health issues Rev. Miner. Geochem., 67: 417-452. https://doi.org/10.2138/rmg.2007.67.11.

Virta R., 2006. Worldwide asbestos supply and consumption trends from 1900 through 2003. U.S. Geol. Surv., 80 pp.

Vitale S., Ciarcia S., Fedele L. and D'Assisi Tramparulo F. , 2019. The Ligurian oceanic successions in Southern Italy: The key to decrypting the first orogenic stages of the Southern Apennines-Calabria chain system. Tectonophysics, 750: 243-261. https://doi.org/10.1016/j.tecto.2018.11.010.

Wei B., Yang L., Zhu O., Yu J. and Jia X., 2014. Multivariate analysis of trace elements distribution in hair of pleural plaques patients and health group in a rural area from China. Hair Ther. Transpl., 4: 2167-3118.

Williams C., Dell L., Adams R., Rose T. and Van Orden D., 2013. State-of-the-science assessment of non-asbestos amphibole exposure: Is there a cancer risk? Environ. Geochem. Health, 35: 357-377. https://doi.org/10.1007/s10653-012-9500-0.who

WHO (World Health Organization), 1986. Asbestos and other natural mineral fibres. Environ. Health Criteria, Geneva.

WHO (World Health Organization), 1997. Determination of airborne fibre number concentrations; a recommended method, by phase contrast optical microscopy (membrane filter method). https://apps.who.int/iris/bitstream/handle/10665/41904/9241544961.pdf

Yuswir N.S., Praveena S.M., Aris A.Z. and Hashim Z., 2013. Bioavailability of heavy metals using in vitro digestion model: a state of present knowledge. Rev. Environ. Health., (4): 181-187. https://doi.org/10.1515/reveh-2013-0012.

Received, December 20, 2022
Accepted, May 14, 2023
First published online, June 30, 2023