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The First Occurrence of Asbestiform Magnesio-Riebeckite in Schists in the Frido Unit (Pollino Unesco Global Geopark, Southern Italy)

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Abstract: In this paper, new mineralogical and petrographical data of asbestiform Magnesio-riebeckite from ophiolite cropping out in the Pollino Unesco Global Geopark (southern Italy) are presented. Magnesio-riebeckite schists with HP-LT index mineral assemblage recorded metamorphic events in blueschist facies in the Frido Unit. Previous toxicological studies showed that asbestiform Magnesio-riebeckite species exhibited high carcinogenicity in previous intraperitoneal injection experiments with rats. The results have been obtained using different analytical techniques such as X-ray fluorescence (XRF), scanning electron microscopy with energy dispersive spectroscopy (SEM-EDS), and electron probe micro analysis (EPMA). Results show that all the samples contain fibrous Magnesio-riebeckite and/or prismatic, acicular crystals in aggregates. The concentration of elements in Magnesio-riebeckite crystals is: Na_2O (4.12–6.26 wt%), MgO (8.22–10.87 wt%), FeO (19.07–23.81 wt%), SiO_2 (52.05–56.06 wt%), CaO (1.12–4.53 wt%), Al_2O_3 (1.34–1.93 wt%), and MnO (0.10–0.34 wt%). Magnesio-riebeckite crystals are documented in the Pollino Unesco Global Geopark for the first time. For this reason, the aim of this paper is the characterization of Magnesio-riebeckite to improve the knowledge of this mineral in the studied area, because the release of fibers into the environment is dangerous for human health.

Keywords: magnesio-riebeckite; asbestos minerals; schists; blueschist facies; Pollino Unesco Gobal Geopark

1. Introduction

The problem of toxicity and carcinogenicity of asbestos minerals has long been discussed since the 20 century, because it represents a clear consequence for human health. The term asbestos represents a series of six natural asbestiform silicate minerals, which include serpentine (chrysotile), as well as amphibole minerals (tremolite, actinolite, anthophyllite, amosite, and crocidolite that represent a variety of commercial term of fibrous riebeckite) that are defined by law in Europe and in several countries worldwide [1–4] and also by Italian law (D.Lgs. 2008). Asbestos minerals are flexible, heat-resistant, and chemically inert. These minerals usually occur with an elongated, prismatic, acicular, or fibrous habit, which can be easily separable in thin fibers and can be inhaled up the respiratory tract. Asbestos fibers, when present in natural geologic outcrops, can be defined as naturally occurring asbestos (NOA) [5,6]. In Basilicata, NOA are mainly concentrated in the ophiolitic sequences cropping out in Pollino Unesco Global Geopark (southern Italy) [2,4,7]. In this area, the most common types of asbestos are serpentine and tremolite, and in a recent study, also edenite [2]. The structure of amphiboles minerals is characterized by the presence of Si^{4+} and Al^{3+} in the tetrahedral site that form double chains running parallel to c-axis, forming columnar and fibrous crystals. Magnesio-riebeckite is a monoclinic

(C2/m) sodic amphibole with ideal formula Na_2 Fe_2^{3+} $(Fe^{2+},Mg)_3$ $[SiO_8O_{22}$ $(OH)_2]$ [8,9]. The name 'riebeckite' was first used by [10] in order to describe a blackish amphibole in Socotra (Yemen) by Dr. E. Riebeck. In the schist of the Frido Unit, in addition to the prismatic variety, the crystals of Magnesio-riebeckite is very common, and shows fibrous habit comparable with size (length ≥ 5 μm and width < 3 μm with aspect ratio > 3:1), as defined by Directive 2003/18/CE. In terms of geometrical feature, morphology, and size, it belongs to the regulated asbestos minerals, together with chrysotile, tremolite, actinolite, anthophyllite, and amosite. Riebeckite also occurs in mossy aggregate or in fibrous habits. The term "blue asbestos" refers to the blue, highly fibrous variety. The crystallographic structure of riebeckite 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^{2+} Fe^{2+} and Fe^{3+}, both of which extend in the c-direction.

The release of Magnesio-riebeckite fibers in the study area is the result of weathering processes and human activities, such as road construction, causing one or more respiratory diseases for the people that are living in proximity of a naturally occurring asbestos area. For this reason, the crystal chemical characterization of Magnesio-riebeckite in the schists of the Frido Unit is extremely relevant for environmental and health issues. Furthermore, this study may provide new information for the Italian mapping of natural sites that are characterized by the presence of the asbestos minerals in the Pollino Unesco Global Geopark.

2. Geological Outline

The study area is located in the Southern Apennines, northeast of Pollino Unesco Global Geopark (Figure 1a). The ophiolite-bearing terranes described as Liguride Complex [11,12] have been interpreted as remnants of an accretionary wedge developed between the Calabria terrane and Apulian platform involved in the orogenic wedge during the Neogene time [13]. It has been subdivided into different tectono-metamorphic units. From bottom to top, it consists of the blueschist Frido Unit, the Episcopia-San Severino Mélange, and non-metamorphic North Calabrian Unit [2,14,15] (Figure 1b). The Frido Unit represents the uppermost unit of the ophiolite-bearing terranes [16], and mainly consists of polydeformed sequence, including blocks of oceanic and continental type rocks, and metasediments [13,17–22]. The ophiolite sequence from the Frido Unit consists of basalts and tectonized serpentinites containing blocks of metabasites, and rodingites [7,17,21,23–29], foliated metabasites [30], and metapillow lava [31]. Serpentinites result from serpentinization of mantle peridotites, that show porphyroclastic texture [7,25,28]. Bodies of continental crust rocks, generally overlying slices of serpentinites [17,21] (Figure 1b), are mainly composed of altered garnet gneisses, garnet biotitic gneisses, and leucocratic gneisses and gneisses with albitic veins [17,32]. The mineral assemblages in the rocks of the Frido Unit show a polyphase HP metamorphism, overprinted by a lower pressure greenschist facies metamorphism [33]. Overprinting high-pressure metamorphism is related to early Alpine event [17]. For the blueschist facies, pressure ranged between 8 to 12 kbar and temperatures are 350 ± 50 °C [34], with a geothermal gradient of 8 °C/km [35].

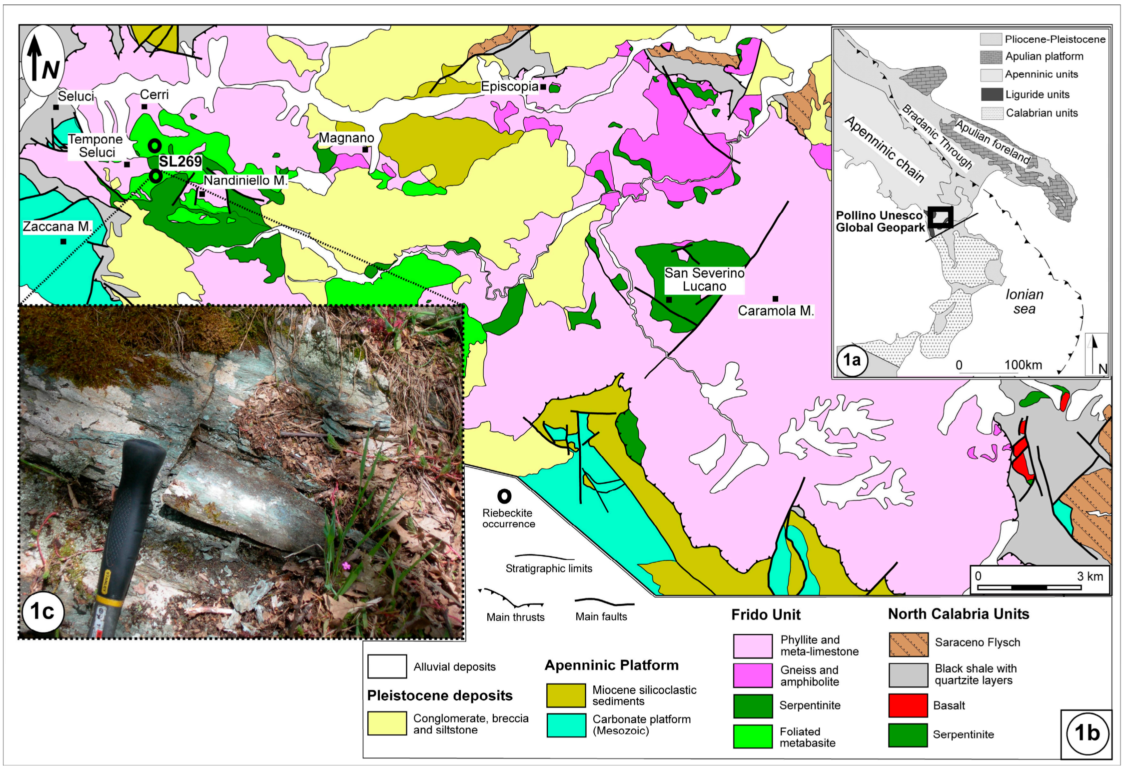

Figure 1. (**a**) Simplified tectonic sketch of the southern Apennines; (**b**) geological map of the northeast area of Pollino Unesco Global Geopark with samples site; (**c**) outcrop of mylonitic green Mg-riebeckite schists associated to foliated metabasites.

3. Sampling and Analytical Methods

Twelve riebeckite schist specimens associated with foliated metabasites were collected in the Mount Nandiniello area in the Pollino Unesco Global Geopark (Figure 1b). Three representative samples were georeferenced with GPS system and were selected for X-ray Fluorescence, SEM-EDS, and EPMA (SL269a, SL269b, and SL269c). Samples SL269a (N 40°03′33.2″–E 15°58′43.3″), SL269b (N 40°03′12.3″–E 15°45′33.3″), and SL269c (N 40°02′42.9″–E 15°20′8.8″), are fine-grained, strongly foliated, and with mylonitic texture (Figure 1c). Petrographic observation was carried out by optical polarizing microscopy (OM), using a ZEISS microscopy, on thin sections of rocks. The chemical characterization of whole-rock was performed using an X-ray fluorescence (XRF BRUKER S8-TIGER) at the Department of Biology, Ecology, and Earth Sciences (DiBEST), University of Calabria (Arcavacata di Rende, Cosenza, Italy). Elemental analyses for major (wt%: SiO_2, TiO_2, Al_2O_3, Fe_2O_3, MnO, MgO, CaO, Na_2O, K_2O, and P_2O_5) and some trace elements (ppm: Ni, Co, Cr, V, Sc, Zn, Cu, Rb, Sr, Y, Zr, Nb, Ba, La Ce, Th, and Pb) concentrations were obtained at the Department of Biology, Ecology, and Earth Science, University of Calabria (Arcavacata di Rende-Cosenza, Italy) using XRF PHILIPS PW-1480 and following the matrix correction methods by [36,37]. The structural water was removed from sample powders by heating at 1030 °C for 1 h. Loss on ignition (LOI) was determined from the total weight change. SEM-EDS analyses were performed on the polished thin sections at the Istituto di Metodologie per l'Analisi Ambientale (CNR-Tito scalo, Potenza, Italy), using a FESEM ZEISS SUPRRA 40 Oxford INCA scanning microscope with detector X ACT SSD; analytical conditions were 3 to 20 kV accelerating voltage and WD from 3 to 8.5. Electron probe micro analysis were performed on Magnesio-riebeckite crystals, using a JEOL JXA-8200 probe, in wavelength-dispersive mode with 15 kV acceleration potential, 20 nA beam current, and a counting time of 20 s at the Freie Universität of Berlin. Natural and synthetic minerals were used for standardization.

4. Previous Studies of Asbestos Minerals in the Pollino Unesco Global Geopark

The presence of NOA in ophiolite rocks had been documented in the Pollino Unesco Global Geopark [4,7]. Previous studies on serpentinite rocks highlighted that they are made up of fibrous minerals accounting for 55% of the total mineral composition [2]. The serpentinites have been characterized using different analytical techniques μ-Raman spectroscopy, FT-IR spectroscopy, SEM-EDS, and EPMA (electron probe micro analysis), and confirmed the presence of serpentine and amphibole group minerals (lizardite, chrysotile, antigorite, and tremolite-actinolite) [7]. In addition, [2] revealed for the first time the occurrence of edenite in the serpentinite rocks of the Frido Unit. Bloise et al. (2019) showed that in the geographic area near Episcopia (Pollino Unesco Global Geopark), significant health problems are NOA-correlated.

5. Results and Discussion

In addition to asbestos serpentine, tremolite, and edenite described in other works [2,4,7,28], in ophiolite rocks from the Frido Unit (Pollino Unesco Global Geopark), a presence of fibrous Magnesio-riebeckite has been detected in schists. Samples analyzed by optical microscopy shows that the schists cropping out close to the Mount Nandiniello area in the Pollino Unesco Global Geopark are fine-grain foliated rocks and mainly consist of Magnesio-riebeckite, glaucophane, epidote, stilpnomelane, quartz, and chlorite. The schists exhibit evidence of a very pervasive deformation, as indicated by the preferred orientation of Magnesio-riebeckite, glaucophane, chlorite, and stilpnomelane. Magnesio-riebeckite occurs as elongated prismatic fibrous or radial fibrous aggregates (Figure 2a,b) with dark green-blue color and vitreous luster. Glaucophane is light blue to deep bluish violet with strong pleochroism and occur as prismatic crystals in the matrix. Epidote crystals have a subidioblastic habit and are found in matrix. Subidioblastic stilpnomelane crystals are present along the main schistosity and are associated with the other crystals along the main foliation (Figure 2a). Quartz grains commonly show undulose extinction and recrystallization to smaller new grain aggregate. Chlorite crystals occur as fibrous-radiated aggregates and form the schistosity (Figure 2b). Two generations of chlorite are observed, one coarse-grained and the latter are oriented parallel to the foliation with the main assemblage and are also a product of the breakdown of Na-amphiboles.

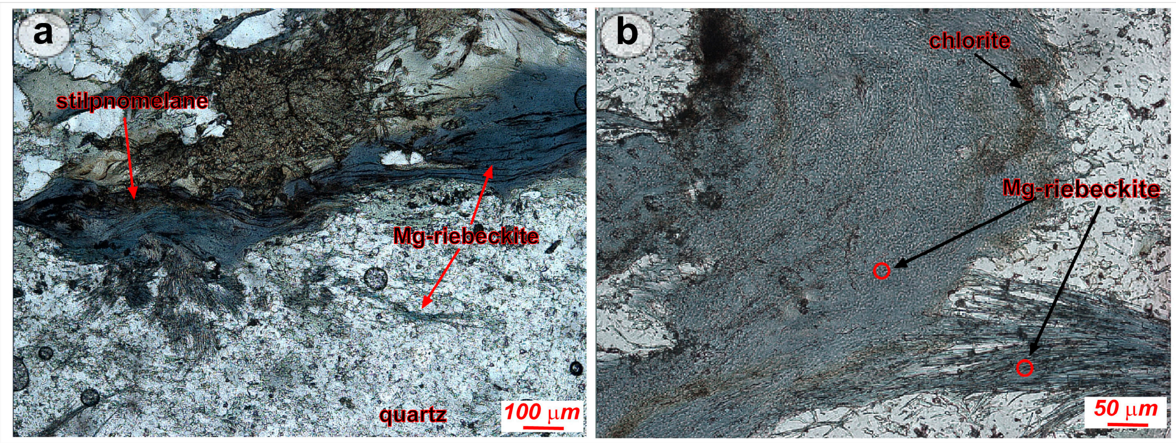

Figure 2. Photomicrographs of Mg-riebeckite schists (crossed polars); (**a**) Magnesio-riebeckite and stilpnomelane crystals along the main schistosity; (**b**) chlorite crystals occur as fibrous-radiated aggregates along the schistosity. (The small red circles indicate the position of point analysis with electron probe micro analysis (EPMA)).

Whole-rock chemical analyses for investigated samples are reported in Table 1. X-ray fluorescence analyses suggest relatively homogeneous compositions between the three samples. Major element data show that SiO_2 is the dominant oxide (55.00 to 56.87 wt%), followed by Al_2O_3 (16.66 to 17.03 wt%), Fe_2O_3 (8.26 to 9.20 wt%), MgO (6.47 to 7.00 wt%), and Na_2O (7.66 to 8.01 wt%). Concentrations of the other major elements are low. In order to testify the occurrence of Magnesio-riebeckite fibrous crystals, we made morphological investigation with scanning electron microscope and microanalytical investigation (EDS analyses) on single crystals of amphiboles. Results showed that the crystals have Magnesio-riebeckite composition.

Table 1. Major and minor elements abundances of schists of the Frido Unit in the Pollino Unesco Global Geopark. (n.d. = not detected).

Sample	SL269a	SL269b	SL269c
Oxides (wt%)			
SiO_2	56.87	55.00	55.34
TiO_2	0.75	0.82	0.80
Al_2O_3	16.66	17.00	17.03
Fe_2O_3tot	8.26	9.00	9.20
MnO	0.12	0.10	0.13
MgO	6.47	7.00	6.90
CaO	0.9	0.82	0.93
Na_2O	7.66	8.01	7.90
K_2O	n.d.	0.2	0.4
P_2O_5	0.06	0.09	0.07
LOI	2.25	1.96	1.3
Sum	100	100	100
ppb			
Ni	0.203	0.210	0.204
Co	0.107	0.110	0.109
Cr	0.118	0.130	0.120
V	0.117	0.120	0.119
Sc	0.028	0.025	0.030
Zn	0.315	0.29	0.30
Cu	0.239	0.241	0.237
Rb	0.216	0.220	0.218
Sr	0.039	0.037	0.040
Y	0.132	0.133	0.132
Zr	0.985	0.985	0.987
Nb	0.076	0.08	0.078
Ba	0.0004	0.0002	0.0003
La	0.0081	0.009	0.008
Ce	0.0151	0.014	0.015
Th	0.013	0.014	0.011
Pb	0.0051	0.005	0.0053

SEM images of the Magnesio-riebeckite evidence the presence of fibrous minerals with acicular and also lamellar habit. Fiber sizes are approximately between 5–20 µm in length and have diameters of about 1 µm. Representative images of Magnesio-riebeckite fibers are reported in Figure 3a–c. EDS chemical analysis (Figure 3) showed the presence of a substantial amount of Fe; in fact, crocidolite is among amphibole asbestos, one of the richest in iron [38]. Fe catalyze generation of reactive oxygen species (ROS) [39–41], and therefore is important for asbestos toxicity.

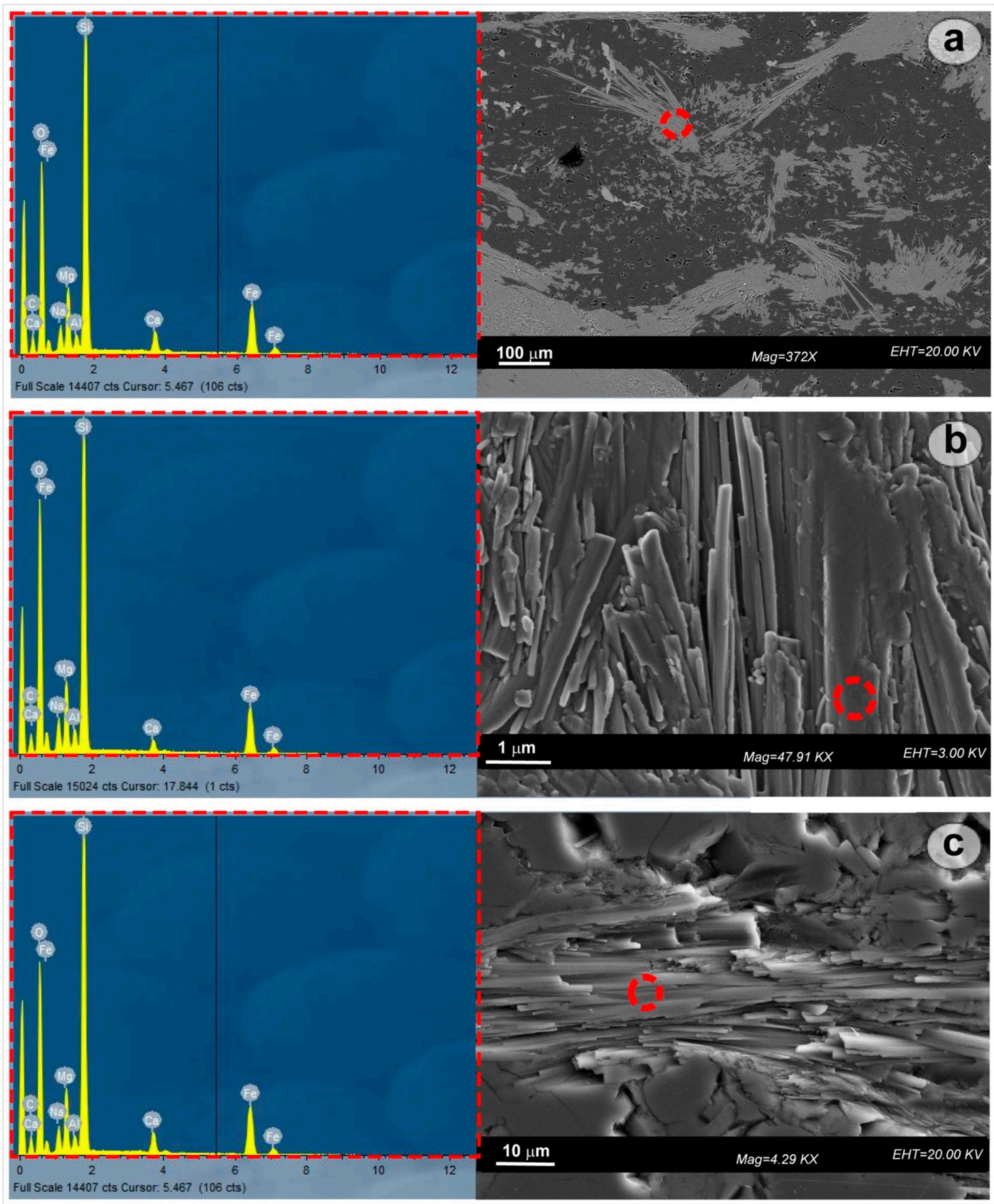

Figure 3. SEM images and relative point analysis of asbestos (**a**) and acicular/lamellar (**b**,**c**) Magnesio-riebeckite.

Crystals of sodium amphibole don't show zoning and compositional variation. Microprobe analysis of amphibole crystals are reported in Table 2.

Table 2. Representative EPMA analyses of selected fibrous Magnesio-riebeckite crystals in the schists from the Frido Unit in the Pollino Unesco Global Geopark. (n.d. = not detected).

Number of Analyses	269-5	269-4	269-4a	269-3	269-3a	269-2a8	269-4b	269-1	269-1a	269-11
SiO_2	54.1	54.97	54.81	55.60	55.39	54.48	54.90	54.83	54.74	52.52
TiO_2	0.12	0.10	0.06	0.04	0.04	0.08	0.08	0.23	0.11	0.18
Al_2O_3	1.34	1.43	1.55	1.39	1.58	1.31	1.52	2.26	1.52	1.93
FeO	22.08	22.57	22.90	22.14	22.78	21.41	22.18	21.39	22.49	23.81
MnO	0.34	0.10	0.20	0.28	0.32	0.33	0.22	0.13	0.15	0.20
MgO	9.75	9.24	8.87	9.79	9.01	10.08	9.14	8.33	9.08	8.79
CaO	3.93	3.03	2.07	3.98	2.25	4.32	3.07	1.12	2.41	2.90
Na_2O	4.66	5.01	5.62	4.70	5.47	4.60	5.09	6.02	5.29	4.61
K_2O	0.07	0.06	0.03	0.05	0.05	0.05	0.02	0.08	0.10	0.05
Cr_2O_3	n.d.	0.04	0.09	n.d.	n.d.	n.d.	0.03	n.d.	0.02	0.02
Sum	96.40	96.56	96.21	97.96	96.90	96.66	96.24	97.13	96.64	95.00
Si	7.90	7.99	7.99	7.98	8.00	7.93	8.01	8.09	7.99	7.75
Ti	0.01	0.01	0.01	0.00	0.00	0.01	0.01	0.03	0.01	0.02
Al	0.23	0.24	0.27	0,23	0.27	0.23	0.26	0.39	0.26	0.33
Fe^{3+}	1.39	1.39	1.51	1.26	1.49	1.24	1.30	1.28	1.47	1.88
Fe^{2+}	1.31	1.35	1.28	1.39	1.26	1.37	1.41	1.36	1.27	1.05
Mn	0.04	0.01	0.02	0.03	0.04	0.04	0.03	0.02	0.02	0.02
Mg	2.12	2.00	1.93	2.09	1.94	2.19	1.99	1.83	1.98	1.93
Ca	0.61	0.47	0.32	0.61	0.35	0.67	0.48	0.18	0.38	0.46
Na	1.32	1.41	1.59	1.31	1.53	1.30	1.44	1.72	1.50	1.32
K	0.01	0.01	0.01	0.01	0.01	0.01	0.00	0.01	0.02	0.01
XMg	0.62	0.60	0.60	0.60	0.61	0.62	0.59	0.57	0.61	0.65
XFe^{3+}	0.91	0.85	0.85	0.85	0.85	0.88	0.83	0.76	0.85	0.95
XFe^{2+}	0.38	0.40	0.40	0.40	0.39	0.38	0.41	0.42	0.39	0.35

The amphibole structural formula in samples is recalculated on the grounds of 23 oxygens. Cations per formula obtained by electron microprobe of these amphibole range from: Si = 7.75–8.09, Na = 1.32–1.72, CaO = 0.32–0.67, Mg = 1.83–2.19, Al = 0.23–0.39, and Fe^{3+} = 1.26–1.88. Low amounts of several trace element (Mn and Cr) are also present in the crystals. Magnesio-riebeckite is grouped as sodic types amphiboles according to [42,43]. The diagram [44] allowed us to classify all the analyzed samples as Magnesio-riebeckite (Figure 4).

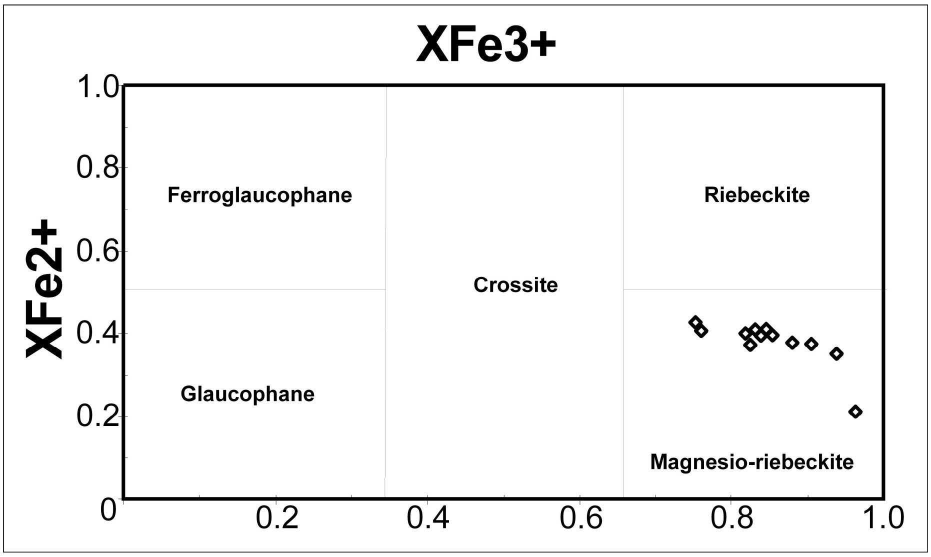

Figure 4. Amphibole classification diagram [42,43].

The chlorite structural formula was recalculated on the basis of 14 oxygens. The chlorite is associated with the epidote crystals and occurs along amphibole. Chlorite shows high contents in

FeO ranging between 24.05 to 26.50 wt% and MgO ranging between 16.08 to 18.10 wt%; consequently, chlorite is classified as Fe-Mg chlorite. The composition of epidote crystals corresponds to epidote s.s. The epidote structural formula was recalculated on the basis of 12.5 oxygens and are recalculated to the formula $X_2Y_3(Si,Al)_3O_{12}$ (OH), assuming all the iron is ferric. Epidote crystals occur as inclusions in Magnesio-riebeckite crystals.

6. Conclusions

In the schists cropping out in the Mount Nandiniello area in the Pollino Unesco Global Geopark, fibrous minerals such as Magnesio-riebeckite, for the first time, were identified by cross-checking the data obtained through several analytical techniques. In this area, the ophiolitic rocks contain asbestos minerals. The most common are fibrous serpentine and amphiboles such as tremolite and edenite [2]. Schists of Mount Nandiniello showed that the samples have a high amount of fibrous Magnesio-riebeckite and is almost associated with other phases (glaucophane, chlorite, epidote, quartz, and stilpnomelane). Under optical microscope, Magnesio-riebeckite appears as needle-shaped crystals with dark green-black and bluish-green color. SEM observation allowed us to characterize the habit of Magnesio-riebeckite. Crystals appears with fibrous habit and size between 5–20 μm in length and diameter about 1 μm, respectively, comparable to regulated asbestos minerals with aspect ratio (length:diameter) major of 3:1.

EPMA and EDS analyses proved that FeO is abundant in the Magnesio-riebeckite crystals as compared with riebeckite from Alinci (Republic of Macedonia) [45]. In the Pollino Unesco Global Geopark, serpentinites and Magnesio-riebeckite schists are employed as civil constructions and building stones and this could lead to release of fibers in the air, of which the effects may be not negligible. It would be important to take into consideration the degree of risk of the presence of these minerals in the study area, as it could represent a potential hazard for human health, although Magnesio-riebeckite is currently not regulated as asbestos by either the European Parliament or the European Council of 27 March 2003. Further studies are able to establish the correlation between exposure and health effects. The identification by different analytical techniques in this area of fibrous minerals such as serpentine, tremolite, edenite, and now also Magnesio-riebeckite is important for public health and environmental protection [46]. In conclusion, we think that the mapping of these minerals and detailed field and laboratory analysis [47] are compulsory to improve our knowledge on the mode of occurrence of minerals, with size regulated by international normative definitions, in the rocks of the Pollino Unesco Global Geopark.

Author Contributions: Conceptualization, G.R. and S.L.; methodology (EPMA and SEM measurements on riebeckite crystals), S.L.; resources, G.R.; data curation, G.R., and S.L.; writing—original draft preparation, S.L. and G.R.; supervision, G.R.

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