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ORIGINAL ARTICLE

Amphibole in vermiculite mined in Argentina. Morphology, quantitative and chemical studies on the different phases of production and their environmental impact

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Abstract Vermiculites with impurities of amphibole, a dry fine residue and calcined materials from three deposits in the province of Córdoba, Argentina, were studied. From a commercial perspective, amphiboles are considered as "asbestos", a group of silicate minerals with strong and flexible fibres that are heat resistant and chemically inert, and thus well suited for heat insulation. These fibrous particles have provoked controversies about the toxicity impact on human health and the development of diseases such as mesothelioma, asbestosis or lung cancer. Their commercialization and exploitation are currently prohibited. The sampled minerals were identified with a petrographic microscope, chemical analyses, SEM and XRD. It was concluded that amphibole minerals are present in all the deposits studied and in every phase of plant production, but not all of them have asbestiform characteristics.

Keywords Vermiculite · Amphibole · Asbestos

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Introduction

Vermiculites are phyllosilicate minerals derived from weathering or hydrothermalism of micas. Their distinctive characteristics are prominent accordion-like unfolding and expansion when heated to 800–1,000 °C, depending on the composition and content of the vermiculite-bearing material. After processing (heat expansion), the material is very lightweight and exhibits fire and sound-insulating properties. Thus, it is well suited for many commercial applications (Van Gosen et al. 2002).

All vermiculite ores contain variable amounts of other minerals that were formed along with the vermiculite in the rock (Addison and Davies 1990). They occur as major components such as feldspars, pyroxenes, amphiboles, carbonates and quartz, as well as minor components such as phosphates, iron oxides, titanium oxides and zircon (Atkinson et al. 1982).

In the province of Córdoba, Argentina, there are vermiculite deposits in production, which have similar mineralogy with impurities such as quartz, iron oxides and amphibole: tremolite ($Ca_2Mg_5Si_8O_{22}[OH]_2$)–ferroactinolite ($Ca_2Fe_5Si_8O_{22}[OH]_2$) series.

In previous work, asbestiform amphibole minerals showing a parallel arrangement of long fibres were recognized (Lescano et al. 2011). These amphibole minerals occur in nature mostly as prismatic crystals or as cleavage fragments broken off the original crystals, but a few can also occur in the fine fibrous forms typical of asbestos (Addison and Davies 1990).

These fibrous particles have provoked controversies about the toxicity impact on human health and the development of diseases such as mesothelioma, asbestosis or lung cancer.

The association of amphibole asbestos with mined vermiculite has received significant nationwide attention since

November 1999, when the *Seattle Post-Intelligencer* newspaper reported that unusually high incidences of asbestos-related mortality and respiratory disease occur in the small, vermiculite-mining town of Libby, Montana, United States of America (Van Gosen et al. 2002).

From a commercial perspective, asbestos are a group of silicate minerals that will easily separate into strands of thin, strong fibres that are flexible, heat resistant and chemically inert, and thus well suitable for heat insulation (Cossette 1984; Ross 1981; Ross et al. 1984; Skinner et al. 1988; Zoltai 1981). Although not commonly viewed this way, there are two basic definitions of asbestos: one is physical and the other is chemical. The first deals with its morphology or shape, and the second, used by USA regulatory agencies such as EPA (Environmental Protection Agency) and OSHA (Occupational Safety and Health Administration), includes six minerals species: chrysotile, crocidolite, amosite, tremolite, actinolite and anthophyllite (Ross 1981; Gunter 1994; Wylie 1988).

It is worth noting that there are numerous studies on amphibole toxicity due to its morphology. Davis et al. (1991) reported that the different morphologic forms of tremolite produce dusts with very different carcinogenic potentials. Oyarzun et al. (2009) stated that in the tailings

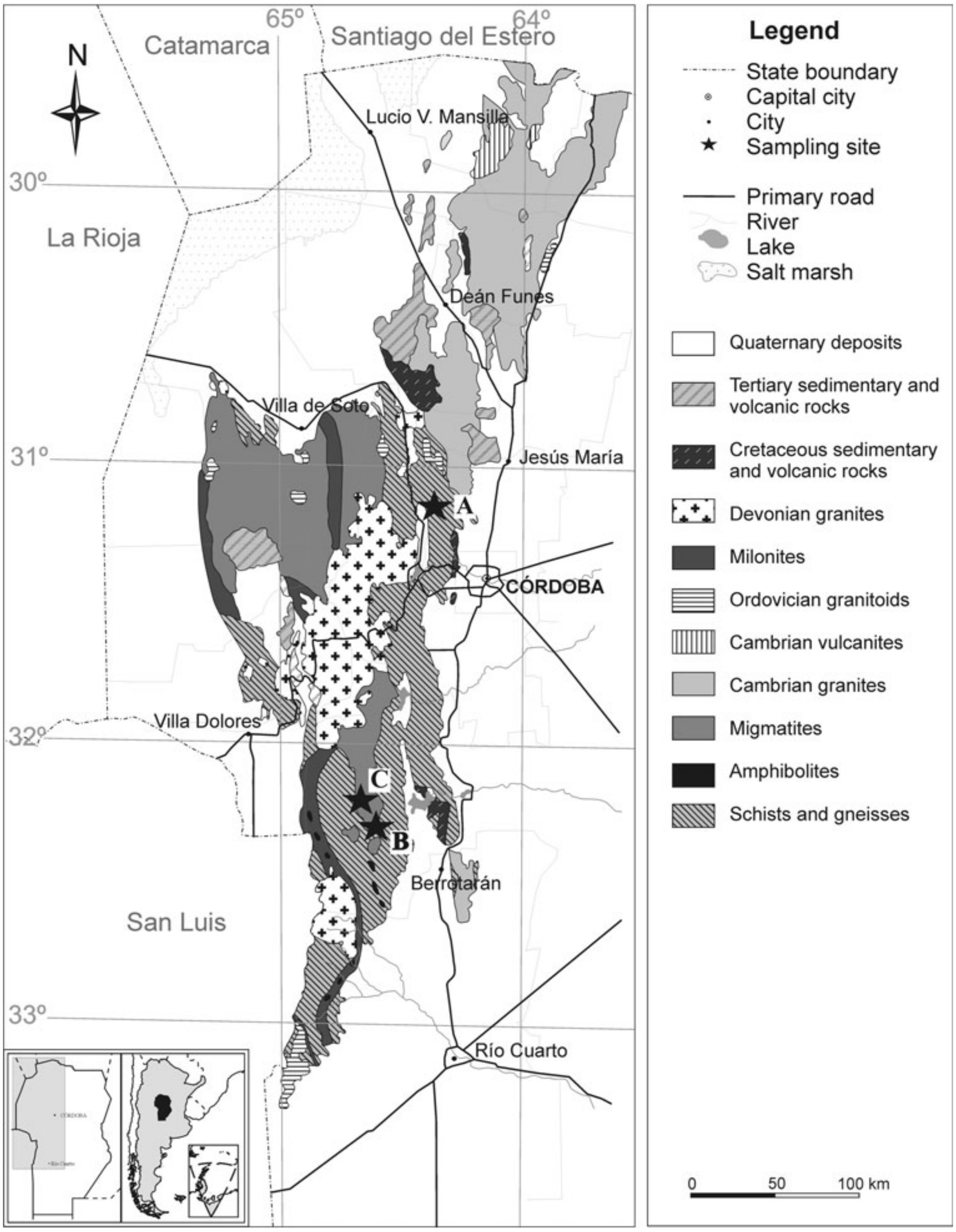

Fig. 1 Location of vermiculite deposits, province of Córdoba, Argentina

of a Chilean mine, amphiboles present an advanced stage of partition of the greatest crystals into fine acicular crystals, many of which are in the range of a few 100 nm and have the typical asbestiform width-length ratio and morphology in a strict sense.

The objective of this work is to characterise minerals with potential adverse effects on human health that occur as vermiculite impurities in three deposits of the province of Córdoba, Argentina, and to study the mineralogical and morphological characteristics of amphiboles in different production stages.

Location and geological setting

Three vermiculite deposits of the province of Córdoba, Argentina, hereinafter, referred to as A, B and C, were studied (Fig. 1). Deposit A is located in the Sierra Chica of Córdoba. The host rock belongs to the La Falda metamorphic complex (Lyons et al. 1997), which is composed of biotitic and sillimanitic gneisses, amphibolites and scarce marbles and ultramafic rocks. The ultramafic rocks are talc-rich and crosscut by dykes of granites and tonalites that form a biotite-rich reaction halo in the contact zone. Vermiculite deposits B and C are located in the south of the province of Córdoba, on the eastern slope of the Sierra de Comechingones. The area is composed of high-grade metamorphic rocks that belong to the Atos Pampa-Cerro Pelado anatectic complex. It is formed by cordieritic diatexites and stromatites within which amphibolites, serpentinized harzburgites and pyroxenites occur (Bonalumi and Gigena 1987). Ultramafic bodies have been intruded by pegmatites rich in quartz and plagioclase, which generate a biotite-rich reaction halo in contact with serpentinite rocks.

Materials and methods

Representative natural samples from three deposits of vermiculite (A, B and C) were taken in veins. Two different materials from treatment plants were also collected. The fine dry residue that correspond to the exfoliated mineral from the oven and the fireplace fine calcined residue collected in the filters.

The dry fine residue and calcined materials from the different production stages were analysed.

The sampled minerals were identified with an Olympus SZ-Pt trinocular stereomicroscope and an Olympus B2-UMA trinocular petrographic microscope, both equipped with a built-in SONY video camera with a digital capture system, a JEOL JSM 35 CP scanning electron microscope, DX4 with an ultrathin window with a range of analysis from $Z = 5$ (B) to $Z = 92$ (U) and a X Rigaku D-Max III—C X-ray diffractometer with Cu Kα radiation and a

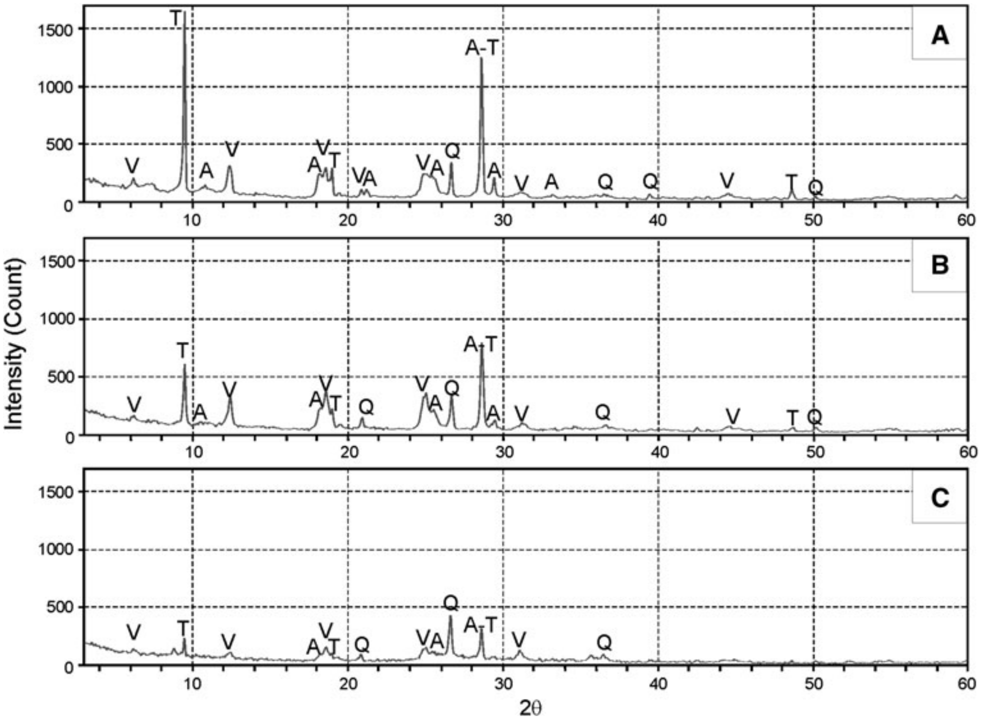

Fig. 2 **a** XRD patterns from the natural sample. **b** Fine residue from the dryer. **c** Fine residue generated in the heating furnace (*V* vermiculite, *T* talc, *A* amphibole, *Q* quartz)

graphite monochromator operated at 35 kV and 15 mA, respectively. The major elements were analysed by ICP at Activation Laboratories Ltd. (Actlabs, Canada).

Results

X-ray diffraction

Material from deposit A

XRD patterns from the natural sample (Fig. 2a) suggested vermiculite, due to peaks of 7.15 and 3.57 Å. Talc, quartz and less intense reflections attributed to amphibole and chlorite were also recognized. The mineralogy of the fine residue from the dryer (Fig. 2b) is similar to that of the natural material, showing a decrease in the intensity of peaks of vermiculite, quartz, talc and actinolite. Figure 2c depicts the fine residue generated in the heating furnace. The reflections decrease in intensity because the temperature affects the crystallinity.

Material from deposit B

Figure 3a, corresponding to the natural sample, shows the presence of vermiculite with maximum reflections at 7.15 and 3.58 Å and phlogopite in subordinate amounts. Minerals of the tremolite–ferroactinolite series, with their peaks at 8.4 and 3.12 Å, were recognized. Talc (t), quartz (q) and chlorite (cl) were also identified.

After the drying process of vermiculite, the fine residue has the same mineralogy as the untreated rock; although the reflection intensity decreases for chlorite, quartz, amphibole and vermiculite, and increases for talc and phlogopite (Fig. 3b). In Fig. 3c, corresponding to heated fine residue, the mineralogy is the same as in the untreated rock. Reflection intensities are lower than that of the residue from the drying stage.

Material from deposit C

In the natural material, phlogopite, with its maximum reflections at 3.35, 2.014 and 9.99 Å, and subordinate vermiculite with very good crystallinity were identified.

In the exfoliated material, such as the fine material and the residue from the plant fireplace, the same minerals as in the natural sample were identified. In both cases, the relationship of vermiculite/phlogopite increases and considerably reduces the intensity of the reflection as a result of the heat treatment.

Amphibole was not identified in any material from deposit C.

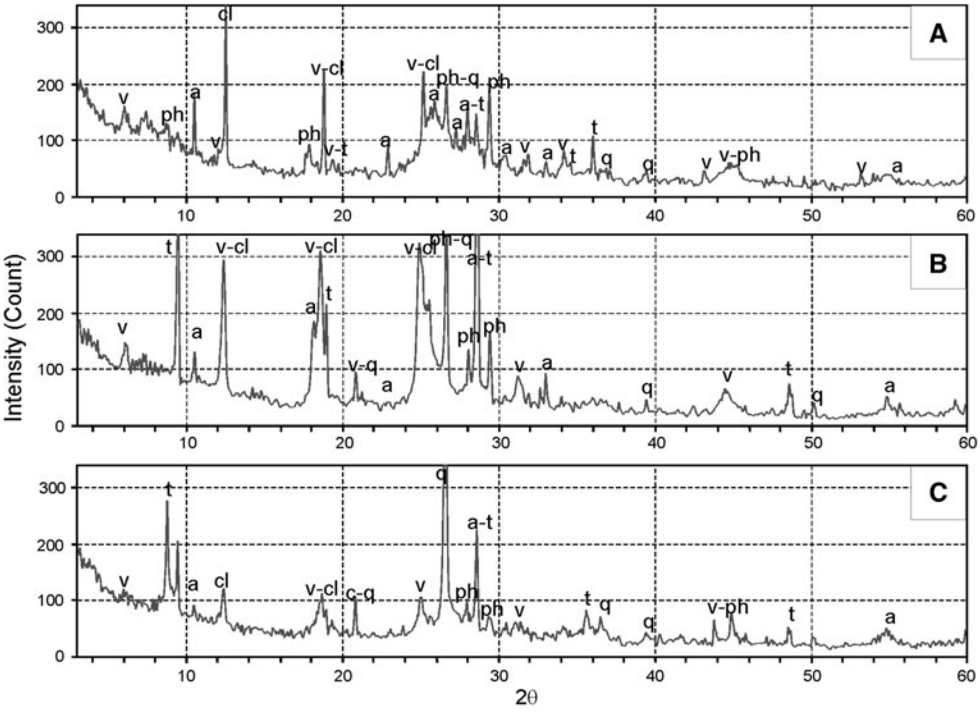

Fig. 3 **a** XRD patterns from the natural sample. **b** Fine residue from the dryer. **c** Fine residue generated in the heating furnace (*v* vermiculite, *ph* phlogopite, *t* talc, *a* amphibole, *cl* chlorite, *q* quartz)

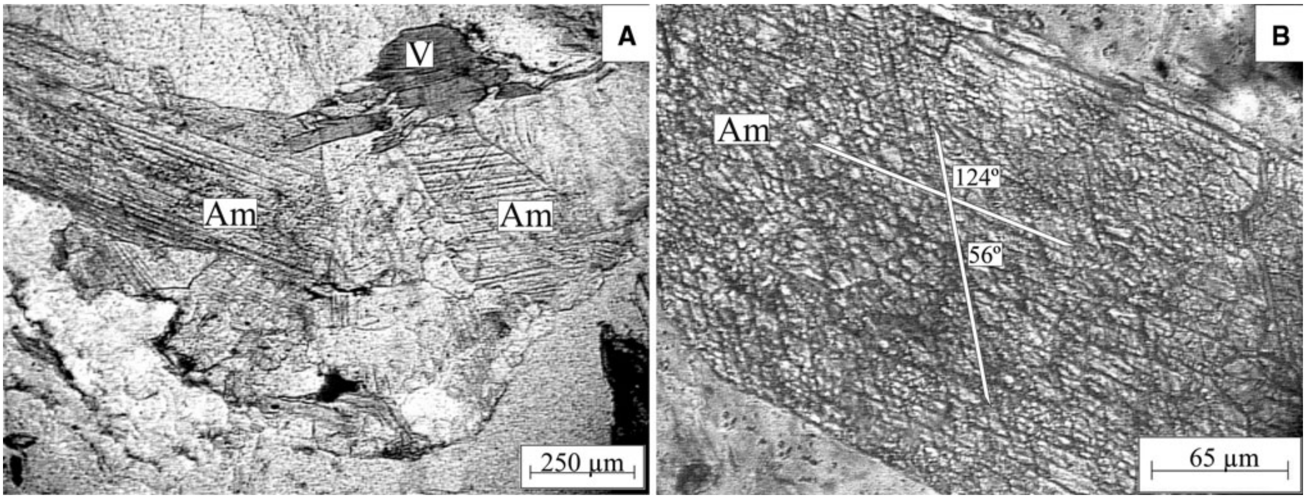

Fig. 4 **a** Basal and long prismatic amphibole. **b** Basal section of amphibole, cleavage in two sets, 56° and 124° (*Am* amphibole; *V* vermiculite)

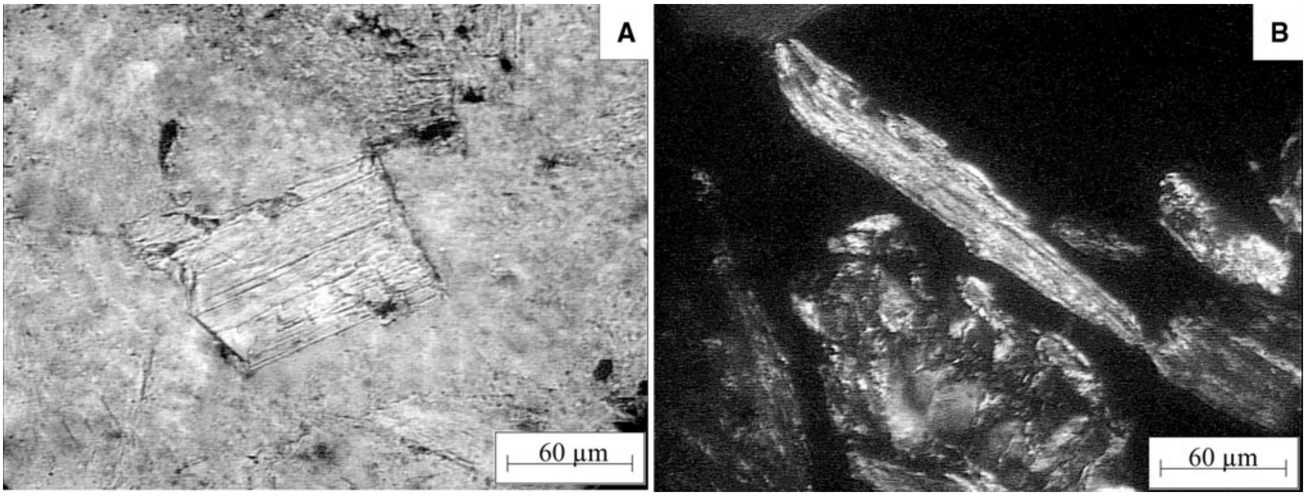

Fig. 5 **a** Amphibole, tabular habit (fine residue from the dryer). **b** Fibrous habit (residue from the oven)

Polarizing microscopy

Material from deposit A

The natural material mainly composed of dark brown micaceous minerals, with marked pleochroism and almost parallel extinction, was determined as vermiculite. It varies in size, has irregular shapes and a platy habit. The presence of veins of cryptocrystalline silica (chalcedony), abundant anhedral quartz crystals with undulose extinction and minor phlogopite with colourless and platy habit were observed. In contact with quartz, talc has crystallized as fibrous aggregates.

Amphibole minerals of the tremolite–ferroactinolite series were identified by their optical properties. The crystals are colourless or pale to dark green and have weak pleochroism. The change of colour is intimately linked to compositional variation and the oxidation of iron. They are present as long prismatic and tabular crystals (Fig. 4a) or as fibrous aggregates. Basal crystals with perfect basal cleavage in two sets, 56° and 124°, are recognized (Fig. 4b). Cleavage traces parallel to the crystal length are observed in longitudinal sections. The birefringence is moderate to strong and the extinction of the longitudinal sections is between 10° and 18°. The fibre size varies from 80 to 100 μm in length and the average width is 90 μm. The modal content of amphibole in the sample is greater than 10 %.

The fine dry residue generated in the first production stage shows the same mineralogy as the natural material, but the size of the crystals decreases significantly. Vermiculite, laminar and secondary quartz are still present in the sample. Some crystals of the tremolite–ferroactinolite series have a fibrous habit exceeding 500 μm in length and

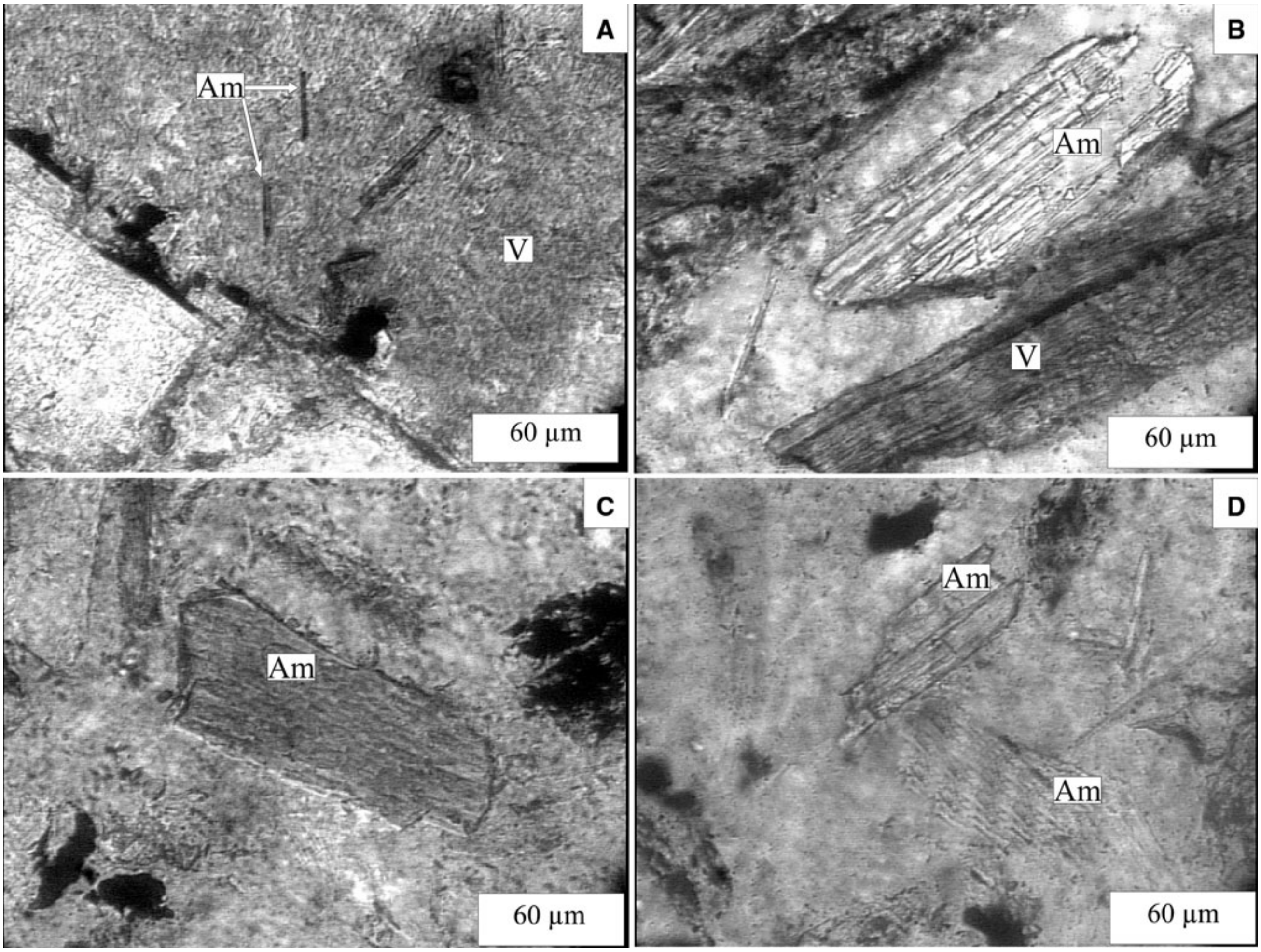

Fig. 6 **a** Amphiboles in the natural material, pre-production. They are scattered among thin flakes of vermiculite. **b** Amphiboles are present as prismatic aggregates. **c** Fine residue from the dryer. Amphibole with tabular habit. **d** Amphibole in the residue from the oven

others have an equidimensional tabular habit and broken ends (Fig. 5a). In this production stage, the amount of amphibole decreases significantly. The residue from the oven has exfoliated mica, quartz and abundant iron oxides. Actinolite–tremolite is recognized as isolated fibres that vary from 90 μm up to 360 μm in length. Some crystals have acicular, fibrous habit and pointed ends, while others are elongated tabular (Fig. 5b). The modal content of fibres within the sample decreases by 50 % compared to the natural material.

Material from deposit B

It is composed mainly of dark to light brown vermiculite, with pleochroism and straight extinction. The size varies with the platy habit. Also, abundant quartz and talc are present as alteration products.

Amphiboles (tremolite–ferroactinolite) have weak green to pale green pleochroism, scattered among thin flakes of vermiculite, with variable size (<45 μm long) (Fig. 6a). They are present as tabular and prismatic aggregates (Fig. 6b). Basal crystals with perfect cleavage in two sets, 56° and 124°, were identified.

The mineralogy in thin sections of the dry fine residue processed by the production plant is similar to that of the natural material. Vermiculite shows platy habit and anhedral secondary quartz. There is also abundant oxidized iron. Amphiboles are present, but there is a clear decrease in number and size. In some cases, the habit of these minerals is fibrous, but tabular forms prevail with a length/width ratio smaller than 3, as in the natural material (Fig. 6c).

In thin sections, the progress in the exfoliation of vermiculite with its expanded sheets was identified in the last treatment stage. Quartz with undulose extinction and oxidized iron were also identified. Although in the minerals of the tremolite–ferroactinolite series crystals with fibrous habit were recognized, isometric forms generally prevail (Fig. 6d). The modal content of amphibole in the sample decreased significantly.

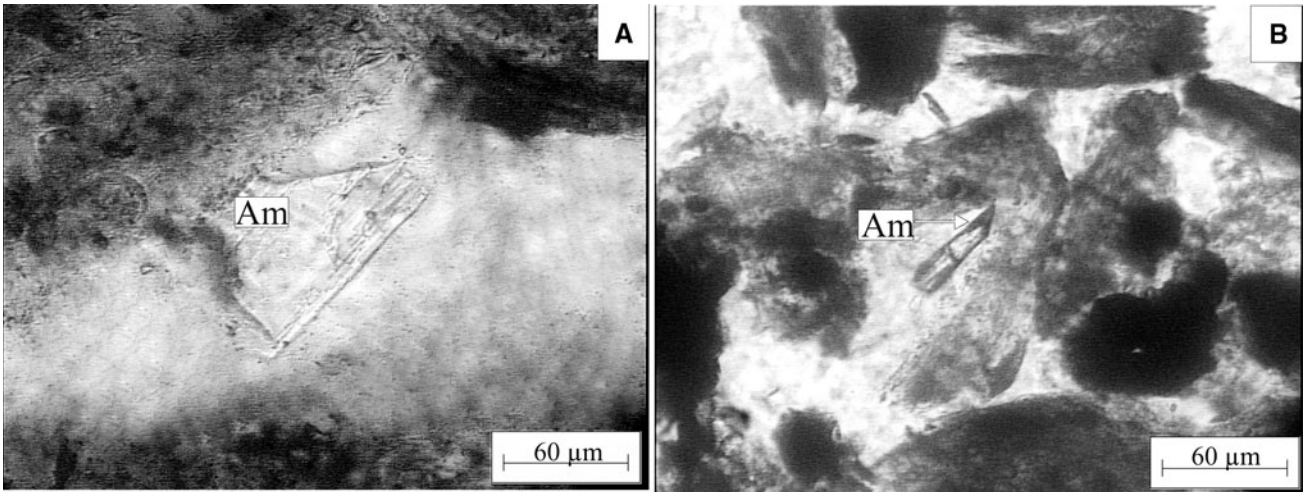

Fig. 7 **a** Natural sample. Amphibole in vermiculite. **b** Fine amphibole in the residue from the chimney (*Am* amphibole)

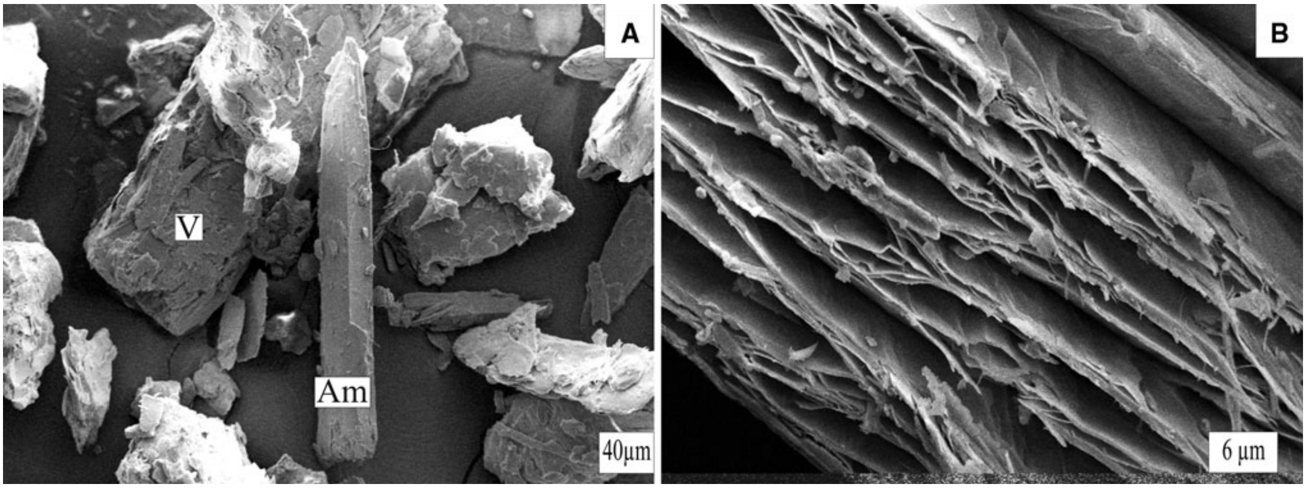

Fig. 8 **a** Natural material: elongated amphibole crystal with splintery fracture. **b** Exfoliated vermiculite (*V* vermiculite; *Am* amphibole)

Material from deposit C

The natural material consists of brown crystals, with strong pleochroism and straight extinction, which was determined as a mineral of the mica group. Intercrystalline spaces are filled with anhedral quartz with undulose extinction and abundant iron oxides. In the contact zone between mica and quartz, talc crystallizes. Amphiboles of the tremolite–actinolite series are associated with these minerals. The fibre length varies from 50 to 100 μm (Fig. 7a). The exfoliated coarse material shows the optical characteristics of the expanded vermiculite with a significant increase in volume. They are dark brown crystals with straight extinction. Inside the vermiculite, there are fibres of the amphibole group of different sizes. The length/width ratio is the same as in the natural sample, but the total number of fibres is significantly lower. The modal content of amphibole in the sample was estimated at 1 %. The habit is fibrous, but equidimensional tabular fragments are also observed.

In the fine residue from the oven, exfoliated mica minerals with a substantially open structure and a less variable size of minerals of the ferroactinolite–tremolite series occur (see Fig. 7b).

Scanning electron microscopy (SEM)

Material from deposit A

Vermiculite is present as packages of stacked and oriented sheets. Amphiboles are elongated fibrous forms and long prismatic crystals (Fig. 8a) that occur in the intercrystalline spaces of micas and as isolated crystals. Some ends of the crystals are irregular and others have a splintery tip. No

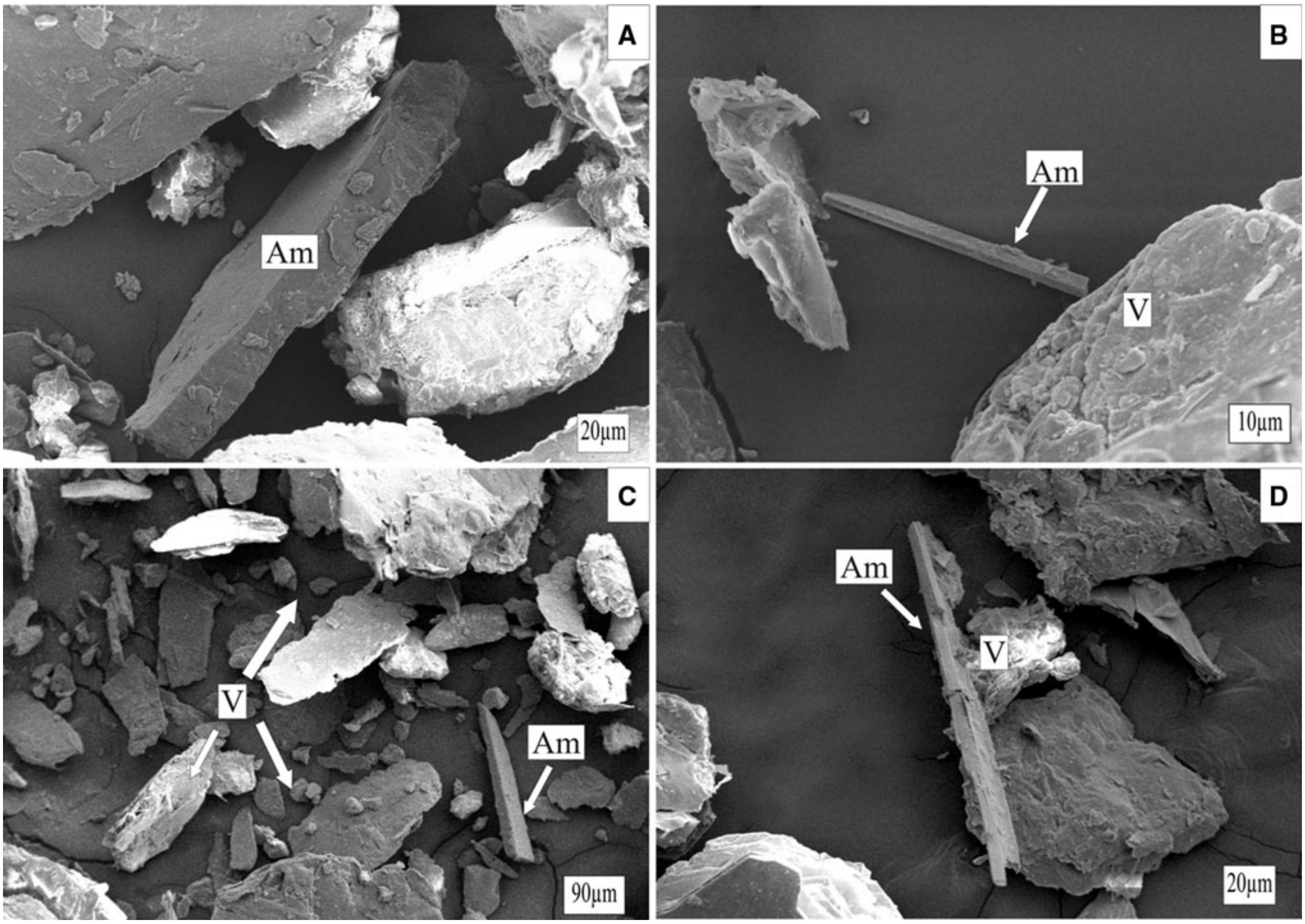

Fig. 9 Material from deposit B. **a** Elongated prismatic crystal of amphibole. **b** Amphiboles in the fine residue from the dryer. **c** After calcinations, fibrous habit of amphibole. **d** Natural material from deposit C. Fibres in contact with vermiculite

fibrous crystals with acicular habit were observed. The size varies; the crystals that fill the intercrystalline spaces of mica do not exceed 15 μm in length, while loose fibres are over 400 μm long.

The crystals of the tremolite–ferroactinolite series of the dry residue from the production plant appear in tabular elongated forms with prismatic and irregular fracture. Fibrous and acicular habits are less common. The crystal size varies and elongated forms are the largest (over 200 μm). The modal content of amphiboles decreases by 40 % compared to the natural sample. Vermiculite is completely exfoliated (Fig. 8b).

In the residue from the oven, the amphiboles are recognized as elongated strips and fibrous crystals. The ends of crystals are irregular. Amphibole is still present, but in a smaller amount than in the fine residue from the dryer. The fibre length ranges from 135 to about 500 μm and the average width is 15 μm.

Material from deposit B

In the natural sample, there was vermiculite in bundles of sheets in parallel to the basal plane, with subordinate amounts of talc. In some cases, the amphiboles were observed as elongated forms, but most of them are tabular, long prismatic crystals (Fig. 9a). The ends are pointed and sometimes irregular and splintery. There were no acicular fibrous habits.

In the fine dry residue, micaceous minerals appear as oriented sheets with platy habit and sometimes intertwined, identified as vermiculite. Amphiboles are scattered among the crystals of mica minerals. The habit is fibrous and acicular, although elongated prismatic crystals prevail as in the natural sample (see Fig. 9b). The crystal ends have an angle break typical of amphiboles, controlled by cleavage. Elongated fibres have a length/width ratio >7, with an average elongation of 200 and 25 μm width. The acicular

Table 1 Morphological studies, size and length/width ratio of 10 crystals of natural and treated samples of deposits A, B and C

Deposit A						Deposit B					Deposit C				
Natural	Particle	l (µm)	w (µm)	l/w	Type	Particle	l (µm)	w (µm)	l/w	Type	Particle	l (µm)	w (µm)	l/w	Type
	1	100	28	3.57	Fr	1	195	84	2.32	Fr	1	34.5	6	5.75	Fr
	2	300	150	2	Fr	2	210	98	2.14	Fr	2	58.6	7.9	7.42	F
	3	730	260	2.81	Fr	3	30	6	5.00	F	3	70	9	7.78	F
	4	210	30	7	F	4	62	10	6.20	F	4	59	11.7	5.04	F
	5	320	38	8.42	F	5	24	6	4.00	F	5	41	7.5	5.47	Fr
	6	810	180	4.50	F	6	45	8	5.63	F	6	30	3	10.00	F
	7	510	180	2.83	Fr	7	158	67	2.36	Fr	7	33	3	11.00	Fr
	8	113	15	7.53	F	8	165	74	2.23	Fr	8	60	7.5	8.00	Fr
	9	120	20	6.00	Fr	9	69	10	6.90	F	9	105	15	7.00	Fr
	10	315	42	7.50	Fr	10	184	85	2.16	Fr	10	30	7	4.29	F
	Average	352.8	94.3	5.22		Average	114.2	44.8	3.89		Average	52.1	7.76	7.17	
Fine dry residue	1	220	35	6.29	Fr	1	265	151	1.75	Fr	1	48	7.9	6.08	Fr
	2	139	28	4.96	F	2	625	209	2.99	Fr	2	97	7.8	12.44	F
	3	250	38	6.58	F	3	172	60	2.87	Fr	3	60	7.9	7.59	F
	4	524	124	4.23	Fr	4	105	30	3.50	F	4	58	45	1.29	Fr
	5	122	24	5.08	F	5	48	10	4.80	F	5	50	15	3.33	Fr
	6	286	36	7.94	F	6	55	15	3.67	F	6	82	10	8.20	F
	7	185	55	3.36	Fr	7	227	162	1.40	Fr	7	47	7	6.71	Fr
	8	100	26	3.85	Fr	8	115	38	3.03	F	8	68	8.2	8.29	F
	9	365	56	6.52	F	9	278	160	1.74	Fr	9	91	13	7.00	Fr
	10	142	28	5.07	F	10	97	32	3.03	Fr	10	42	36	1.17	Fr
	Average	233	45	5.39		Average	198.7	86.7	2.88		Average	64.3	15.78	6.21	
Fine residue from the oven	1	320	110	2.91	Fr	1	105	30	3.5	Fr	1	54	9.23	5.85	F
	2	122	22	5.55	F	2	185	65	2.85	Fr	2	61	9.354	6.52	F
	3	228	86	2.65	Fr	3	325	126	2.58	Fr	3	98	45	2.18	Fr
	4	360	110	3.27	Fr	4	59	10	5.90	F	4	53	10.2	5.20	F
	5	158	24	6.58	F	5	145	75	1.93	Fr	5	75	20	3.75	Fr
	6	272	57	4.77	F	6	236	113	2.09	Fr	6	76	19	4.00	Fr
	7	310	106	2.92	Fr	7	85	32	2.66	Fr	7	68	8.2	8.29	F
	8	110	19	5.79	F	8	185	50	3.70	F	8	82	9	9.11	F
	9	98	15	6.53	F	9	310	112	2.77	Fr	9	65	7.8	8.33	F
	10	142	32	4.44	Fr	10	165	62	2.66	Fr	10	49	7.5	6.53	F
	Average	212	58.1	4.54		Average	180	67.5	3.06		Average	68.1	14.52	5.98	

F fibre, *Fr* cleavage fragments, *l* length, *w* width

habit is extremely small compared to the natural material, with a maximum length of 60 µm and the width not exceeding 2 µm.

After calcination, exfoliated vermiculite was observed in the last stage of production. The minerals of the tremolite–ferroactinolite series are distinguished as elongated and fibrous crystals. In some cases, the fibres have an acicular habit, but angle terminations prevail. These minerals remain, but less frequently than in the dry fine material and even less frequently than in the natural material. The fibre length ranges from 40 to 300 µm and the average width is 10 µm (Fig. 9c).

Material from deposit C

In the natural sample, pre-treated for the production plant, "packages" of vermiculite with intertwined compact sheets are recognized. Amphibole fibres are elongated and occur between the mica sheets, and scattered within the mass of the sample. The ends have an irregular splintery fracture. The sizes vary, exceeding 200 µm in length. Fibres with acicular habit are not recognized. Figure 9d shows how these amphiboles are in contact with vermiculite.

In the fine dry residue, amphibole fibres are less abundant than in the previous sample, but they are over 150 µm in length with an average length/width ratio >15. The ends of the crystals are irregular and brittle. Crystals with acicular habit prevail in the fine residue.

In the finest residue from the chimney, fully exfoliated vermiculite and some particles without expansion were observed. The amphiboles were present, but in a lower content than in the exfoliated coarse material.

Morphological studies

The size and morphology of these minerals in vermiculite mines in production related with the potential environmental impact on the people who work in the mines were evaluated. The morphology, size and length/width ratio of 10 crystals in natural and treated samples from each deposit were analysed.

They were classified as either fragments or fibres based on morphological and optical properties (i.e. extinction characteristics) (Wylie 1979). Observation of extinction conditions has helped past researchers to distinguish monoclinic amphibole fibres from cleavage fragments; in fact, OSHA (1992) mentions this method. The premise for this is that a fibre will show parallel extinction, whereas a fragment will show inclined extinction (Brown and Gunter 2003).

In deposit A, natural sample, the sizes of the fibres vary with an average length of 350 μm. The average length/width ratio is greater than 5, describing a fibrous crystal, as defined by OSHA (1992), which determines that a fibrous form is one that has a length–width ratio >3. In terms of morphology, fibres, cleavage fragments and basal sections of tabular crystals were observed. In this case, cleavage fragments prevailed over fibrous ones. Acicular forms were not distinguished. In the fine dry residue, amphibole sizes were shorter, but the length/width ratio remained relatively constant. The habit observed was similar to that of the natural rock samples.

In deposit B, amphibole fibres have two distinctly different types of morphologies. The minerals that appear as cleavage fragments have a prismatic habit and, in some cases, a tabular habit. The length/width ratio of these fibres is less than 3 and the average length is in excess of 180 μm. The amphibole crystals found in vermiculite sheets have a fibrous acicular habit of smaller size than the cleavage habit. The longest length is 60 μm and the width is 6 μm, with a length/width ratio >5. Prismatic forms prevail over fibres. In the last stage of production (fine residue from the oven), amphibole particles remain, although to a lesser extent, in the composition of the rock, with an average length/width ratio of 3 μm.

In deposit C, fibres smaller than those recognized in the two deposits mentioned above are observed. Their average length is 52 μm and the length/width ratio is greater than 7. Their width ranges from 3 to 15 μm. The habit is acicular, elongated and with pointed ends.

In plant-processed samples, amphibole fibres ranging from 42 to 100 μm in length and from 17 to 45 μm in width are recognized. The length/width ratio decreases with respect to that of the natural sample, but remains higher than 5.5.

Table 1 lists the results of the morphological studies of the three deposits.

Chemical analyses

The results of chemical analyses of natural and plant-processed samples are listed in Table 2. Results from the mineralogical studies suggest that the calcium content of the samples may be attributed to minerals of the amphibole group.

Table 2 Chemical analyses of natural and plant-processed samples

Deposit/sample	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	LOI
A/N1	44.92	8.19	8.50	21.57	3.25	0.18	1.31	10.06
A/N2	40.07	13.93	5.92	23.70	1.01	0.14	1.66	11.64
A/N3	50.18	9.05	7.52	19.18	1.65	0.16	1.59	8.09
A/FDR	45.72	9.53	7.71	22.02	1.75	0.14	1.18	9.65
A/FCR	43.99	12.01	9.37	22.51	1.85	0.16	1.97	5.26
B/N	36.30	14.79	13.20	10.76	6.08	0.58	3.22	11.20
B/FDR	42.03	10.97	9.81	16.36	4.86	0.44	1.87	10.03
B/FCR	45.13	11.53	10.90	16.91	3.66	0.32	2.26	5.84
C/N1	37.03	14.79	13.77	15.70	1.16	0.36	5.75	8.19
C/N2	36.31	8.56	8.18	27.68	0.24	<0.01	0.32	16.44
C/N3	36.39	15.37	15.09	14.44	0.94	0.99	7.05	5.60
C/FDR	37.75	16.09	14.98	15.87	0.56	0.34	7.22	3.43
C/FCR	39.83	14.80	14.84	18.43	1.47	0.28	4.83	2.00

N natural material, *FDR* fine dry residue, *FCR* fine calcined residue

The analyses conducted for deposit A included three of the natural rock, two of the northern workings (A/N1, A/N2), one of the southern workings (A/N3) and two analyses of the fine residues: dry (A/FDR) and calcined (A/FCR) at the plant. In this case, the calcium content in all the samples is over 1 %, with 3.25 % (A/N1) being determined in the natural sample used at the processing plant. From this value on, the CaO content of the treated samples decreases.

Chemical analyses of natural (B/N) and treated samples (B/FDR, B/FCR) from deposit B were conducted. In this case, the CaO content of the natural sample is over 6 %, but in all the plant-treated samples a slightly lower CaO content was determined.

The chemical analyses for deposit C included studies of three natural samples: C/N1 and C/N2, corresponding to the eastern workings, and C/N3, corresponding to the western workings, which is currently in production. The three natural samples show a low CaO content (<2 %). In the dry residues generated at the plant (C/FDR), calcium percentages are low; though an increase in the fine residue from the oven is observed (C/FCR).

Results of the chemical analyses (Fig. 10) allow the comparison of the CaO content with water loss on ignition (LOI), and the $Fe_2O_3 + MgO$ content for the three deposits. In general, a reduction in LOI and in CaO content as well as an increase in the $Fe_2O_3 + MgO$ and Al_2O_3 content is observed in treated samples, especially in those from deposit B, which presents the highest content of amphiboles. The fact that amphiboles are the only minerals that contain CaO suggests that the amphibole content decreases as the raw material is processed. The reduction in LOI is mainly due to water loss of vermiculite.

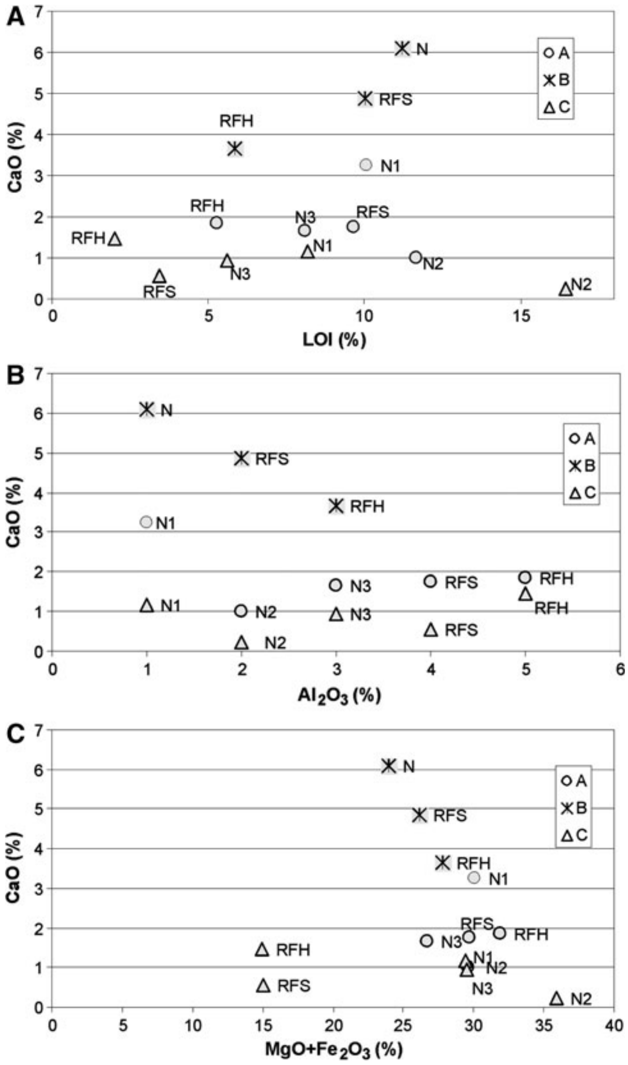

Fig. 10 **a** CaO vs. LOI diagram. **b** CaO vs. Al_2O_3 diagram. **c** CaO vs. $MgO + Fe_2O_3$ diagram

Discussion

Minerals of the amphibole group are present in all deposits and materials processed in the treatment plants studied in the present work. Over the past decades, studies to determine amphiboles as impurities have focused mainly on the fact that these minerals may have deleterious effects on human health. Results of X-ray diffraction, scanning electron microscopy and chemical analyses indicated that the material examined is mainly composed of vermiculite and phlogopite with subordinate amounts of quartz, chlorites and amphiboles.

In terms of morphology, there are four major types of calcic amphiboles: massive, prismatic, finely acicular and asbestiform. There has been considerable controversy for over 20 years about distinguishing cleavage fragments, or single crystals of amphiboles, from fibres of amphiboles (Nolan et al. 1991; Zoltai 1979). The underlying reason is that cleavage fragments, when inhaled, appear to be less harmful than fibres (Davis et al. 1991; Langer et al. 1991; OSHA 1992).

In this study, the terms “fibre” or “fibrous” were applied in accordance with OSHA asbestos regulation standards [which define an asbestos fibre as: “A particle that is 5 μm or longer, with a length-to-width ratio of 3 to 1 or longer” (OSHA, 1992)]. On the other hand, Zoltai (1979) define asbestos crystals as having asbestiform habit that occur as bundles of elongated, strong, resistant and flexible fibres, which are frequently in parallel or columnar assemblages or in tangled masses.

The crystals analysed show long, prismatic, fibrous and acicular habits. They are “fibres” in accordance with OSHA asbestos regulation standards, but, taking into account the definition by Zoltai (1979), the samples studied should not be considered asbestiform.

There are several studies related to the toxicity of amphiboles due to their morphological characteristics (Davis et al. 1991; Oyarzun et al. 2009). However, if the same material is observed in its non-triturated or weathered forms, this characteristic will probably be absent and the material would be considered non-asbestiform. In this sense, trituration and subsequent weathering contribute to the increase in the length/width ratio of the particles allowed by the prismatic cleavage of the mineral, and expressed in the development of the acicular particles with high harmful potential for the pulmonary tissue. This is the case of the minerals of the amphibole group from the deposits examined, which typically present elongated prismatic habits and cleavage fragments. Although these minerals do not present asbestiform characteristics, the sole presence of amphibole crystals (asbestiform or non-asbestiform) in vermiculites in exploitation may be risky to human health, due to fragmentation during the process, generation of abundant dust during the different stages and high volatility as size decreases.

Conclusions

1. Amphibole minerals are present in all deposits and materials processed in the treatment plants studied in the present work.
2. Optical microscopy and XRD showed that the amphiboles belong to the tremolite—ferroactinolite series.
3. The amphibole content decreases as the raw material is processed.
4. Elongated, prismatic cleavage fragments and less acicular habit were identified in all the samples studied, but asbestiform acicular habits were only recognized in deposit C.
5. Chemical analyses and XRD showed that amphibole contents are deposit C < deposit A < deposit B.
6. Due to the negative environmental impact caused by the presence of asbestiform minerals in active vermiculite mines, it would be interesting to evaluate their effect on human health.

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