Asbestiform Amphiboles in a Marble Quarry: A Case Study from the Province of Córdoba (Argentina)

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Abstract

Pure and impure marbles in Argentina have been exploited for hundreds of years for different purposes. Marble processing is varies depending on its use and could include chemical treatments, burning, crushing, milling and polishing. More impure marbles are crushed and used for construction, or discarded in spoil heaps in quarries. There are numerous studies related to the physical and mechanical properties of marbles from the province of Córdoba; however, there are no records about the potential presence of asbestos that could be liberated during processing procedures or degraded by natural agents in spoil heaps. Fibrous samples from a metasomatic zone in an abandoned marble quarry in the Altautina area (Córdoba, Argentina) were studied through polarized light microscopy, X-ray diffraction and electron probe microanalyses. Asbestiform (tremolite) and non-asbestiform amphiboles (tremolite and magnesio-hornblende) were identified as the main phases. Asbestiform amphiboles were concentrated and studied through a stirring degradation test to evaluate morphological and size changes in the fibres by simulating natural water degradation. This process was monitored by stereomicroscopy and scanning electron microscopy. During the test, fibres underwent length (L) and width (W) reduction, maintaining or increasing the initial L/W ratio. Although the action of natural agents can differ from data obtained in laboratory tests, results indicate that the asbestiform fibre size decreases reaching values that can be harmful to human health.

Keywords

Asbestos • Amphibole • Tremolite • Degradation

244.1 Introduction

The province of Córdoba is one of the most important suppliers of marbles in Argentina. The main quarries are located in a set of mountain ranges of N–S direction in the centre of the country denominated "Sierras de Córdoba" (SC) (Fig. 244.1). The marbles have been exploited for different purposes for more than 400 years, so active and abandoned quarries are numerous and widely distributed (Sfragulla et al. 1999). A large amount of impure carbonatic material is discarded in spoil heaps in quarries and exposed to weathering processes that could produce its degradation. Fibrous amphiboles are commonly present as accessory

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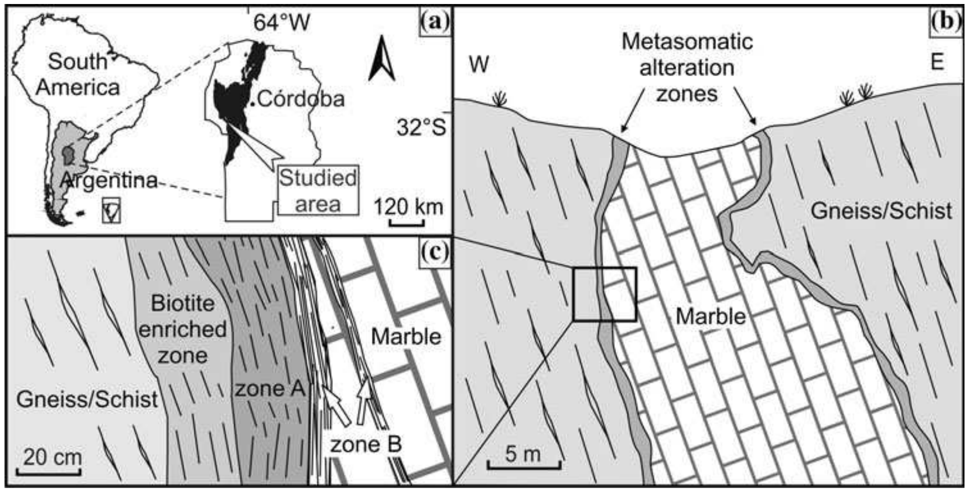

Fig. 244.1 **a** Sierras de Córdoba (Argentina). **b** Geological sketch of the studied quarry. **c** Detail of the metasomatic zone

phases in the marbles (e.g. tremolite), so the determination of asbestiform varieties and their potential degradation should be evaluated in order to avoid potential problems in the community (Lee et al. 2008). Asbestos is the name given to a group of minerals that occur naturally in the environment as bundles of thin, long, separated fibres that are often flexible and resistant to heat and chemicals (Case et al. 2011). For these reasons, for decades, these minerals were used in the industry for different purposes; however, their high dangerousness and capacity to provoke, either directly or indirectly, conditions detrimental to human health have caused their prohibition nationwide, in consonance with other countries in the world (Rodriguez 2004). According to the World Health Organization (WHO 1986) and the Occupational Safety and Health Administration (OSHA 1992) the morphology of asbestos is considered harmful to humans when its length is >5 µm, diameter <3 µm and length/diameter >3, although these limits could vary (Lee et al. 2008). These factors determine the penetration of the fibres into the airways, which accumulate in lungs and can cause lung diseases (Loomis et al. 2010).

In this work, fibrous samples from a metasomatic zone in an abandoned marble quarry in the Altautina area (SC) were studied in order to establish whether they can be classified or not as asbestiform minerals. Then, the mechanical behaviour of fibres was assessed through a stirring degradation test to evaluate morphological and size changes by simulating natural water degradation.

244.2 Geology and Location

Marbles from SC appear as lens or tabular banks with different metamorphic grades associated with gneisses, migmatites, amphibolites, and ultramafic rocks. Their composition is varies depending on the studied area, where calcitic to dolomitic end members are recognised. The content and type of accessory minerals are also variable depending on the initial composition of the protolith, the metamorphic grade achieved and secondary hydrothermal processes. In the Altautina area, marbles are mainly dolomitic to calc-dolomitic, minerals of the amphibole group being one of the main accessories (Sfragulla et al. 1999). The studied quarry is located 3 km NE from Altautina town in the occidental sector of the SC (Fig. 244.1a) and corresponds to an irregular bank of dolomitic marbles (20 m width, N340°/70° E), limited by quartz-biotite gneisses/schists (Fig. 244.1b). In the contact zone there is a metasomatic belt, 50 cm width, where gneisses/schists are enriched in biotite (Fig. 244.1c). Between this sector and the marble bank there are at least two different zones. A zone rich in green fibrous minerals (~20 cm width) next to the gneisses/schists (Fig. 244.1c, zone A) and a thinner zone (~5 cm width) next to the marble, rich in white fibrous minerals (Fig. 244.1c, zone B). The latter minerals are also observed in discontinuity planes in the marbles near the contact zone.

244.3 Materials and Methods

Samples from zone A and B were characterized by polarized light microscopy, X-ray diffraction (XRD) (Rigaku D-Max IIIC, Cu Kα radiation, λ = 1.54060 Å, 35 kV and 15 mA) and electron probe microanalyses (EPAM) (JEOL JXA 8230, 15 kV, 20 nA, 4 µm beam diameter). Asbestiform material was attacked with HCl acid to eliminate carbonates and concentrated (1 g of sample) for degradation treatments by a permanent stirring test (magnetic stirrer, 500 rpm and 5, 20, 180 and 360 min) simulating natural water torrent conditions. Changes in morphology and size of the fibres were monitored by stereomicroscopy and scanning electron microscopy (JEOL JSM 35 CP, 14 kV). Amphibole classification of Hawthorne et al. (2012) and mineral abbreviations of Whitney and Evans (2010) were used.

244.4 Polarized Light Microscopy, X-ray Diffraction and Electron Probe Microanalyses

Fibrous materials from zone A and B correspond to minerals of the amphibole group (XRD analyses) rich in calcium (EPMA analyses). Material from zone A (Fig. 244.2a) corresponds to a sector rich in prismatic, tabular non-asbestiform Mhb (Amp1) associated with less abundant, long, prismatic, fibrous Tr (Amp2). Crystals are elongated and cleavages are well marked. Accessory minerals are abundant (Cal ± Ttn ± Ep ± Bt ± Chl ± Srp ± Zrn) as inclusions or in the contact between the tabular amphiboles. Material from zone B corresponds to a mixture of long, prismatic, fibrous Tr (Amp2) similar to those in zone A but forming the main accessory phase in the dolomitic marble; and bundles of thin, long Tr fibres of asbestiform habit (Amp3) are mainly present as veins crosscutting marble foliation (Fig. 244.2b) or in discontinuity planes. Asbestiform fibres have a variable grain size (a few microns to 5 mm length and L/W ratio generally >50) and their interweaving produces a mesh-like structure that is difficult to separate.

244.5 Degradation in Aqueous Medium

Degradation treatments in aqueous medium over asbestiform fibres (L: ∼5 mm) from discontinuity planes (zone B, Amp3) were carried out in order to evaluate their physical behaviour by simulating natural torrent waters working at different times. Long fibres were chosen for this test to facilitate the monitoring of the degradation process; however, small fibres (L: >5 µm, W: <3 µm) are naturally present in the metasomatic zone (Amp3). Natural fibres are flexible (Fig. 244.2c and 244.2d) and with increasing stirring time (5 min) they begin to disintegrate and reduce their

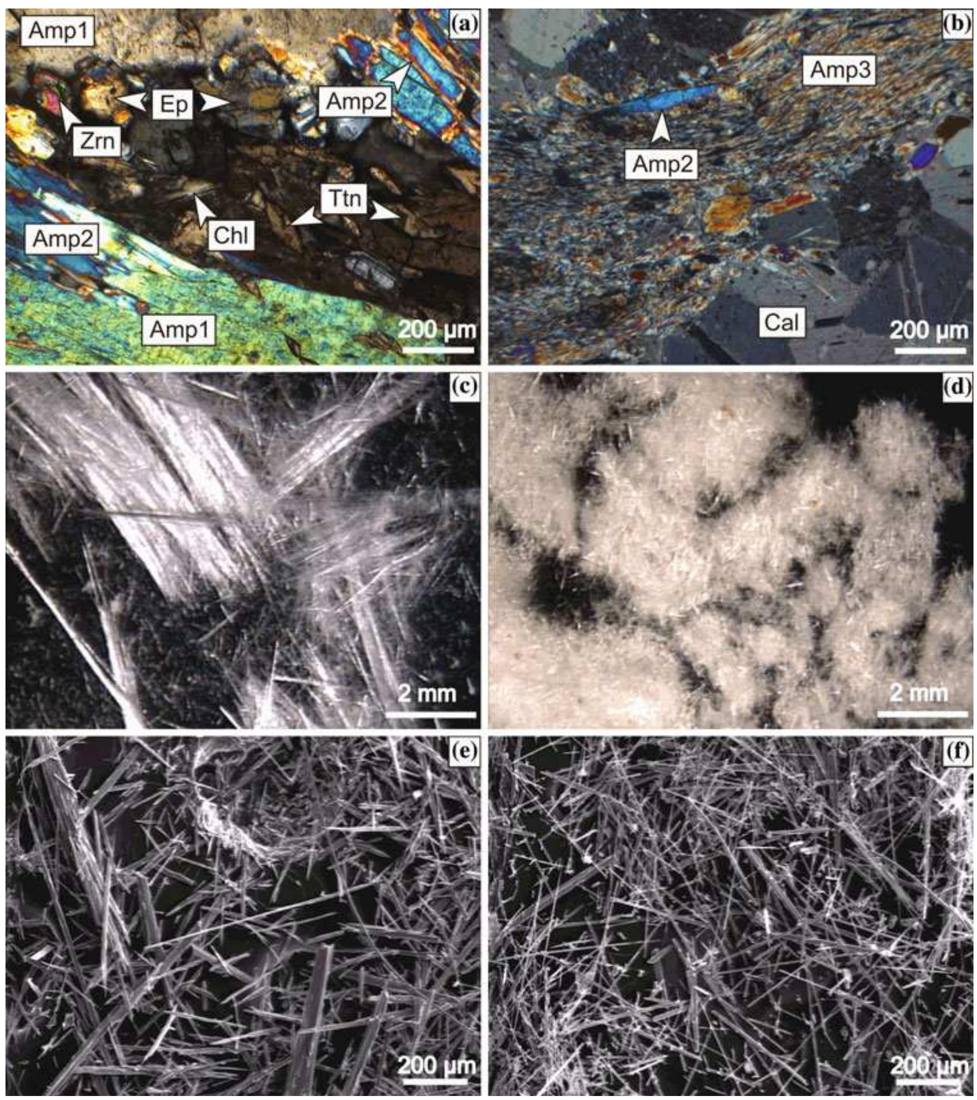

Fig. 244.2 Tabular (*Amp1*) and long prismatic amphiboles (*Amp2*) from zone A (**a**), and fibrous amphiboles (*Amp3*) filling a vein in a carbonate mass (**b**) from zone B. Natural fibres (∼5 mm length) under stereomicroscope (**c**) and SEM (**d**) collected from a discontinuity plane in zone B, and fibres after 6 h of stirring test under stereomicroscope (**e**) and SEM (**f**)

Table 244.1 Morphological changes as stirring time increases

Time exposure	Natural		5 min		20 min		3 h		6 h	
Length/Width (mm)	L	W	L	W	L	W	L	W	L	W
Average	5	0.2	4.2	0.2	3.8	0.18	0.6	0.02	0.4	0.01
L/W ratio	>30		21		22		30		40	

length by ~20 % (Table 244.1). At 20 min their size continues reducing and agglutinating, forming an incipient meshing structure (fibres above 2 mm length still persist). After 3 h numerous micrometric fibres form relevant meshing structures and fibres 1 mm in length are less common. At 6 h millimetric fibres are scarce and the micrometric meshing is almost complete (Fig. 244.2e and f).

244.6 Discussion and Conclusions

In the studied quarry a metasomatic belt (~50 cm width) in the contact between a dolomitic marble and quartz-biotite gneisses/schists was found. Two different zones were identified: zone A: ~20 cm width (next to the gneisses/schists) where prismatic crystals of Mhb (Amp1) of tabular habits prevail and are associated with scarce fibrous Tr (Amp2) ± Cal ± Ttn ± Ep ± Bt ± Chl ± Srp ± Zrn; and zone B: ~5 cm width (next to the dolomitic marble) where long prismatic crystals of fibrous Tr (Amp2) form the main accessory phase in the marble and bundles of thin, long Tr fibres of asbestiform habit (Amp3) are mainly present as veins crosscutting marble foliation or in discontinuity planes. It is important to point out that some of these Tr fibres naturally meet the conditions set by the WHO and OSHA to consider this material as dangerous for human health. Additionally, degradation treatments in aqueous medium over fibrous Tr from zone B (Amp3) reveal that even "long" and "wide" fibres may decrease in size (from L: 5 mm, W: 0.2 mm to L: 0.4 mm, W: 0.01 mm at 6 h of test) and maintain or increase their L/W ratio (>30), reaching values considered harmful to human health. Therefore, under certain conditions, natural water torrents might degrade long and wide Tr fibres forming cleavage fragments. The dangerousness of these broken fibres should be evaluated taking into account that there are controversies about their impact on human health (Case et al. 2011; Oyarzun et al. 2009). Then, it is not only important to verify the presence of natural hazardous asbestiform amphiboles in other marble quarries of the SC, but also monitor deposits with asbestiform amphiboles that could be exposed to weathering and transformed into potentially dangerous asbestiform materials.

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