Chapter

CHARACTERISTICS AND APPLICATIONS OF SOME DOLOMITIC ROCKS FROM ARGENTINA

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ABSTRACT

Argentina is a vast territory with different geological settings. In this scenery, dolomitic rocks are abundant and widespread. The economic importance of both this lithology and the main mineral constituent (dolomite) is the first cause for the studies carried out on these types of rocks. Dolomitic rocks in Argentina have been exploited for hundreds of years for different purposes. They are used as refractories, concrete aggregates and mastics, among other applications. Marble processing 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. This chapter describes the mineralogical characteristics, textures, origin, mineral assemblages, and application of some dolostones, calcitic dolostones, dolomitic limestones, and marbles from the provinces of Buenos Aires, Río Negro and Córdoba (Argentina). The origin of these rocks varies even in close areas. In the province of Río Negro there are several deposits. One of them is composed of a dolostone formed from a preexisting hydrothermal limestone by circulation of hypersaline fluids rich in Mg and Na. It is a porous fine-grained (10 to 30 µm) rock consisting of dolomite with minor amounts of quartz, feldspar, and rhyolite particles. Clay minerals (montmorillonite, illite and sepiolite) were also identified. The alkali–carbonate reactivity of this rock when used as concrete aggregate has been analyzed. Another deposit is composed of a dolomitic marble generated by the metamorphism of a preexisting dolostone. The only mineral present is dolomite, but the further circulation of hydrothermal fluids in cracks developed talc veins with a sepiolite + calcite + amphibole (tremolite) assemblage. The main use of this rock is in mastics and refractories. The dolomitic limestone from the province of Buenos Aires is a compact medium–to– coarse–grained (1500 to 4500 μm) rock, consisting of calcite, dolomite and minor amount of quartz. This type of rock is one of the most important materials in the area used as concrete aggregate. In the province of Córdoba, marbles appear as lens or tabular banks with different metamorphic grades associated with gneisses, migmatites, amphibolites, and ultramafic rocks. Their composition is variable, where calcitic to dolomitic end members are recognized. 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 (with some asbestiform varieties). These rocks are crushed and used for construction, or discarded in spoil heaps in quarries.

Keywords: dolomite, applications, Argentina

INTRODUCTION

Dolostone (also "dolomite" or "dolomite rock") is in general defined as a sedimentary rock with more than 90% of the mineral dolomite ($CaMg(CO_3)_2$) and makes up more than 50% of the rock (Pettijohn 1957). There are all gradations between dolostones and limestones. In general, the first ones are more even grained and occur in rocks of all ages, usually as dolomitic beds (less than one to more than thousands of meters thick) interstratified with limestones. It is also common to find limestones grading into dolostones in a short distance away. Although some of these sedimentary dolomitic rocks were deposited as such, favored by shallow waters with high salinity (particularly those associated with salt and gypsum beds), most dolostones are clearly replaced limestones (e.g., Mudd 1960, Tucker 1991). In addition, metamorphic processes can affect carbonatic rocks producing marbles of variable composition (dolomitic to calcitic marbles).

Argentina is a vast territory with different geological settings. In this scenery, dolomitic rocks (sedimentary and metamorphic) are abundant and widespread. The economic importance of both this lithology and the main mineral constituent (dolomite) is the first cause for the studies carried out on these types of rocks. They have been exploited for hundreds of years for different purposes (as refractories, concrete aggregates, mastics, among other applications). Processing of these dolomitic rocks varies depending on their use and could include chemical treatments, burning, crushing, milling, polishing, etc. More impure material is discarded in spoil heaps in quarries.

When aggregates containing dolomitic rocks are used as concrete aggregates, special attention should be paid to their potential reactivity because they can produce expansion in concrete. Swenson and Gillot (1960) were the first to suggest that expansion of certain dolomitic limestones may be the result of a dedolomitization reaction (the so-called alkali-carbonate reaction, ACR). X-ray diffraction (XRD) studies performed by Hadley (1961) on expansive rocks that had reacted with alkaline solutions showed a decrease in the amount of dolomite, an increase of calcite and the appearance of brucite.

The explanation for this behavior is that in alkaline conditions, the dolomite present in dolomitic limestones interacts with the alkali hydroxides from the concrete pore solution causing a fine intergrowth of calcite and brucite. This process releases $(CO_3)^{2-}$ from alkaline carbonate, which migrates to the cement paste dissolving the portlandite phase present in the cement paste and releasing Ca^{2+} ions that will react to form a carbonate halo around the aggregate and will keep the solution alkalinity high due to the regeneration of alkali hydroxide, undergoing the following reactions (Hadley 1961):

$$CaMg\,(CO_3)_2 + 2\,MOH \rightarrow Mg(OH)_2 + CaCO_3 + M_2CO_3$$

$$M_2CO_3 + Ca(OH)_2 \rightarrow 2\,MOH + CaCO_3$$

where M represents Na, K or Li.

According to some studies, this process produces a volume change that can cause expansion due to the many voids enclosed by the reaction products (e.g., Deng & Tang 1993). Some others (e.g., Katayama 2004) indicate that the alkali-silica reaction (ASR) is responsible for concrete expansion.

The ASR develops when certain silica species with some kind of internal disorder such as strained quartz, micro- to cryptocrystalline silica (e.g., chalcedony, chert, etc.) or amorphous materials (e.g., opal, volcanic glass) react with hydroxyl ions from alkali hydroxides in the concrete pore solution. This process breaks the siloxane network in siliceous minerals allowing the interaction with alkaline ions (mainly Na^+ and K^+, although Ca^{2+} can effectively participate), generating an alkaline or calc-alkaline hydrated silicate that can absorb water and swell producing internal stresses in the concrete (e.g., Ichikawa & Miura 2007, Ichikawa 2009).

Although it is still a matter of current debate (e.g., Jensen 2012), recent studies point out that the two main processes can occur separately or simultaneously depending on the mineral composition of the aggregates involved in the process: (a) dedolomitization of dolomite crystals in carbonatic aggregates, and (b) ASR caused by reactive silica minerals in the carbonatic aggregates, the first one being non-expansive and the second one, expansive and the cause of concrete deterioration (e.g., Katayama, 2004, 2011, Locati, 2014a, Štukovnik, 2014, Prinčič, 2013).

Many cases of ACR in dolomitic rocks have been reported in structures from different parts of the world (e.g., USA, Canada, China). In Argentina, this reaction has been investigated since 1991, but so far no structures in service affected by the so-called ACR have been reported. Laboratory tests have been conducted on some carbonatic aggregates such as dolomitic rocks from Olavarría (province of Buenos Aires, Argentina), dolostones from “Dolomite” quarry (Valcheta, province of Río Negro, Argentina) and different dolomitic marbles from the province of Córdoba, Argentina) (Batic et al. 1991, Batic & Milanesi 1991, Milanesi et al. 1996, Locati et al. 2012, 2014a, 2014b) in order to evaluate their potential reactivity. According to these studies, all aggregates showed evidence of dedolomitization, but only the dolostone from Valcheta was classified as potentially reactive owing to its expansive behavior (Milanesi et al. 2012). The province of Córdoba is one of the most important suppliers of marbles in Argentina. These rocks have been exploited for different purposes for more than 400 years (lime, cement and paint manufacturing, as rock slabs, as additives for paper manufacturing, additives for soils, aggregates for construction, etc.), 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 phases in 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, Locati et al. 2014c, 2014d). Asbestos is the name given to a group of minerals that occur naturally in the environment as bundles of thin, long, separated fibers 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. 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 fibers into the airways, which accumulate in lungs and can cause lung diseases (Loomis et al. 2010). An example of asbestiform tremolite in a marble quarry from Altautina town (Córdoba, Argentina) is presented.

Figure 1. Location of the study areas: Provinces of Río Negro, Córdoba and Buenos Aires (Argentina).

Study Sites, Sampling and Analyses

This chapter describes the mineralogical characteristics, textures, origin, mineral assemblages of some dolostones, calcitic dolostones, dolomitic limestones, and marbles from three provinces of Argentina (Río Negro, Córdoba and Buenos Aires) (Figure 1). Their application in the construction industries (mainly as concrete aggregate) and the environmental impact caused by the presence of minerals dangerous for human health were also evaluated.

RESULTS

Province of Río Negro (Argentina)

In the province of Río Negro two deposits of different origin were studied: "Dolomite" and "La Adela". The first one is a dolomitic deposit located in the NNE of Somuncurá massif in the province of Río Negro at 7 km NE of Valcheta city (Figure 2). It is composed of a dolostone formed from a preexisting hydrothermal limestone by circulation of hypersaline fluids rich in Mg and Na. It is a porous fine-grained rock (10 to 30 µm) consisting of dolomite with minor amounts of quartz, feldspar, and rhyolite particles. Clay minerals (montmorillonite, illite and sepiolite) were also identified by XRD.

The second one is located in the Department of San Antonio Oeste, 75 km WNW of the village of Sierra Grande, in the province of Río Negro (Figure 2). It is composed of a dolomitic marble formed by the metamorphism of a preexisting dolostone. The most abundant mineral is dolomite, but the further circulation of hydrothermal fluids in cracks developed talc veins with a sepiolite + calcite + amphibole (tremolite) assemblage. The main use of this rock is in mastics and refractories.

The first studies in the area were carried out by Hayase and Maiza (1970). They reported the presence of sepiolite veins in the "Aguada Cecilio" mine, located near the city of Valcheta (Province of Río Negro). The host rock is a dolomitic marble and the veins were attributed to hydrothermal activity. This origin was mentioned by other authors such as Imai and Yamazaki (1967) for dolostones from Japan associated with iron deposits and sepiolite veins. Deguillen (1977) studied the ore minerals, genetic relationships, alteration phenomena, and mineral assemblages of the "Dolomite" mine to compare them with those of other deposits with similar or different genetic types.

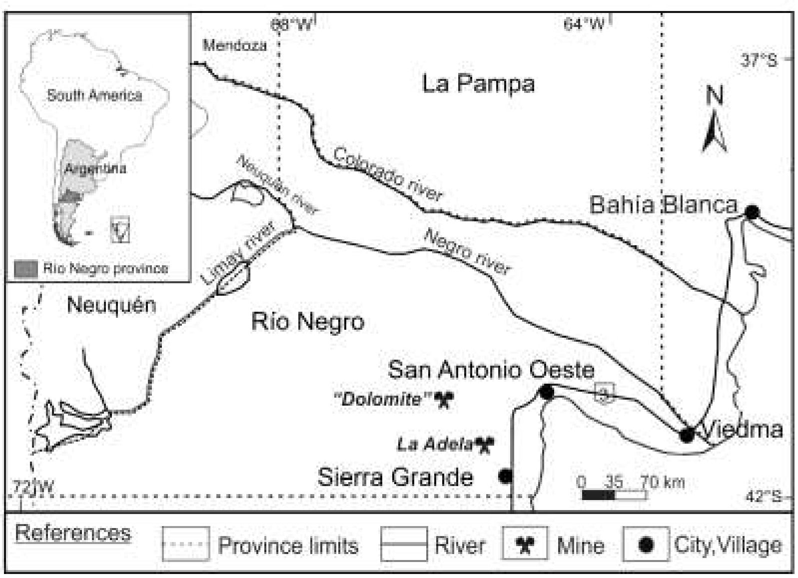

Figure 2. Location map of "Dolomite" and "La Adela" deposits in the province of Río Negro.

The "Dolomite" Mine

The host rock is a tuffaceous sandstone from Upper Cretaceous to Lower Tertiary age (Dequillen 1977). Dolostone is green to light green, very compact, with a thickness greater than two meters, with <10% impurities, consisting of quartz grains with minor amounts of feldspars, altered volcanic rock particles, plagioclase, volcanic glass, hornblende, pyroxenes and biotite, among others. In some places of the quarry, the dolostone is 4 meters thick and the tuffaceous sandstone cannot even be observed on the floor of the mining works. In the WNW it lies over a sandy limestone with marine fossils of Lower Triassic age (Deguillen 1977). The ore body has a surface area of 0.14 km^2 with a length of 700 meters in NE-SW direction and variable width (between 100 and 220 meters) (Figure 3).

Mineralogical Characteristics

Dolomite is the main ore mineral, with very scarce amount of associated calcite, gypsum and sepiolite (Deguillen 1977). The gypsum is filling carbonate voids or covering cracks, with inhomogeneous distribution. It is present mainly in the upper half of the working fronts. Sepiolite forms veins up to 1 cm thick in the dolomitic rock.

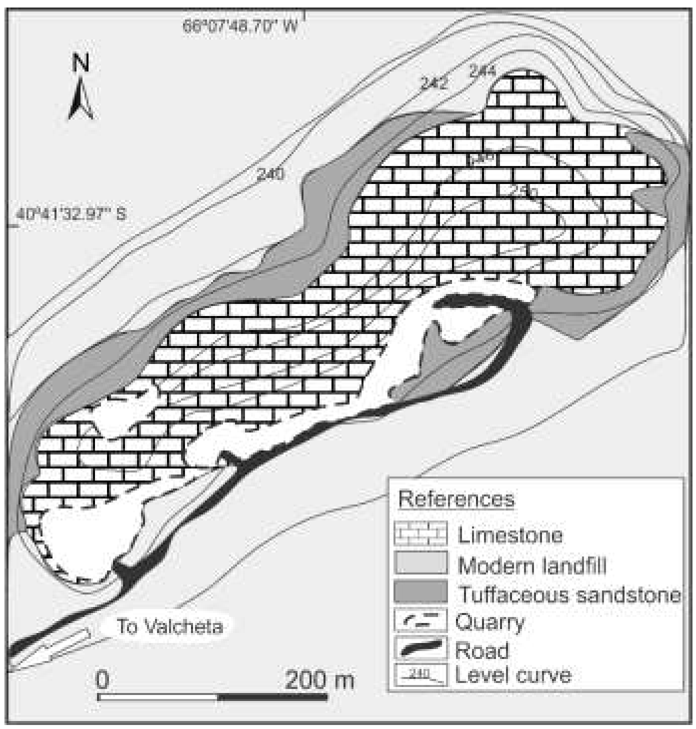

Figure 3. The "Dolomite" mine. Quarry map (modified after Maiza et al. 1982).

Macroscopically, dolomite has a very fine grain size, is very compact and massive, and has a white to yellowish white color.

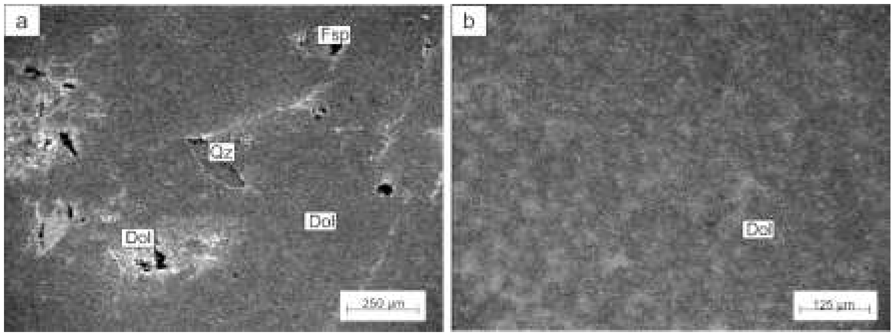

Figure 4. Photomicrographs. a) Fine grained texture with quartz and feldspar particles (with crossed nichols (XN)). b) Detail showing the fine grain size (XN). Qtz: quartz, Dol: dolomite, Fsp. Feldspar.

Two types of dolomite crystals were seen on thin sections. The first type is composed of rounded to subrounded grains with sizes ranging between 3 µm and 20 µm, with fine equigranular texture (Figure 4a). The second type is subrounded, transparent and bigger (8 µm–40 µm), has perfect cleavage, twins and is crossed by secondary quartz veins with mosaic texture (Figure 4b). These crystals form veins cutting the texture of the first ones. Rock or mineral fragments partially corroded with reaction rings consisting of the first type of dolomite crystals but with larger grain size are also common. Some rocks and mineral fragments are crossed by thin carbonate veins. In this chapter, mineral abbreviations after Whitney and Evans (2010) are used.

Paragenetic Sequence

The sequence of crystallization of the ore minerals and mineral assemblages is: 1) First type of dolomite, characterized by small rounded to subrounded crystals with equigranular fine texture. 2) Second type of dolomite filling and covering voids and in veins crossing the texture of the first type of dolomite. 3) Secondary quartz with mosaic texture present both in the tuffaceous sandstone and in the ore developing thin veins. 4) Sepiolite in fine veinlets no more than 1 cm thick crossing the dolomite and the modern landfill. Gypsum nodules and sheets were also deposited. Another evidence of the mineralizing solution actions on the tuffaceous sandstone is the presence of zones totally altered to montmorillonite (mainly in the NE and E).

Chemical Analysis

Table 1 lists the chemical analyses of samples from the "Dolomite" mine compared with those obtained by Deguillén et al. (1967).

Table 1. Chemical composition of dolostones from the "Dolomite" mine

Sample	CaO (%)	MgO (%)	R_2O_3 (%)	Insoluble residue (%)	Loss on ignition
1	28.1	16.8	1.2	10.7	41.5
2	29.4	22.5	0.0	2.6	45.0
3	23.6	18.0	1.3	17.9	40.0
*	29.5	17.9	0.4	10.5	41.7
*	34.7	16.6	0.0	3.5	45.2
*	30.5	18.8	0.0	6.4	44.3

* Analyses after Deguillén et al. (1977). R_2O_3: $Fe_2O_3 + Al_2O_3$.

X-Ray Diffraction

Figure 5 shows the X-ray spectra of dolostone. It is possible to observe the characteristic reflections of dolomite and the good crystallinity of the material (sharp narrow peaks) with very scarce amounts of quartz, feldspar and gypsum.

Isotopes

Isotopic analyses were performed to better constrain the origin of the deposit. The results of $\delta^{13}C$ and $\delta^{18}O$ are listed in Table 2.

Keith and Weber (1964) introduced an empirical Z-value $Z = 2.048(\delta^{13}C + 50) + 0.498(\delta^{18}O + 50)$ in order to discriminate between marine ($Z > 120$) and continental ($Z < 120$) carbonates that has also been successfully applied in more recent studies (e.g., Hofer et al. 2013). This criterion is valid for Jurassic sandstones and more modern rocks, so it is applicable to this deposit. The Z value was calculated using the means $\delta^{13}C$ and $\delta^{18}O$ of the 14 samples analyzed (-3.39 and 28.61, respectively). The result (119.3) indicates a continental origin.

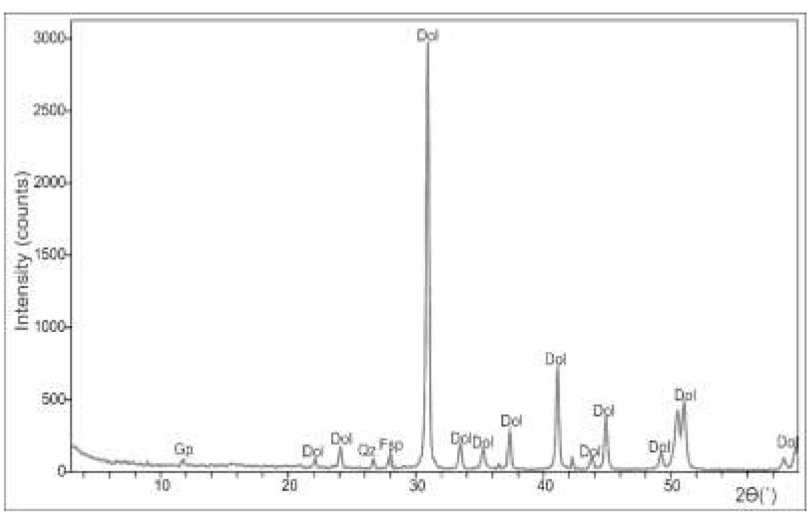

Figure 5. XRD of dolostone from the "Dolomite" mine. Dol: dolomite, Qtz: quartz, Fsp: feldspar, Gp: gypsum.

Table 2. Isotopic analyses of dolostone from the "Dolomite" mine (Maiza et al. 1982)

Sample	$\delta^{13}C$ ‰ (PDB)	$\delta^{18}O$‰ (V-SMOW)
1	-3.9	27.5
2	-3.3	27.0
3	-3.1	29.0
4	-3.3	27.1
5	-3.6	28.6
6	-3.8	29.1
7	-3.8	28.7
8	-3.6	28.9
9	-3.3	29.1
10	-3.4	29.3
11	-3.3	29.8
12	-2.7	31.4
13	-3.4	27.5
14	-2.9	27.5

Fluid Inclusions

The homogenization temperature of fluid inclusions measured in dolomite crystals indicates a hydrothermal origin (Table 3).

Origin

The ore as well as fluorite, kaolin, Pb, Cu, Zn and W hydrothermal deposits are emplaced in parallel bands NNW of Somuncurá massif. They are located in a topographically elevated area, in isolated outcrops without lateral continuity. The strike is NE-SW, coincident with the structural features in the zone, establishing a close relationship between faults and mineralization processes in the area. The ore was first made up of calcite and/or aragonite. Then, by dolomitization, the calcite was transformed into dolomite. This process was favored by the presence of salts, hydroxides and temperature, in this case, related to the hydrothermal activity.

Table 3. Homogenization temperature in fluid inclusions (Maiza et al. 1982)

Sample	1	2	3	4	5	6	7	8
Temperature (ºC)	89	92	92	87	90	84	83	89

The results of the isotopic analyses, fluid inclusions, field evidence, and mineralogical assemblages allow classifying the "Dolomite" mine as continental type, originated by the hydrothermal replacement of tuffaceous sandstones.

Applications

Dolomitic rocks are frequently used as concrete aggregate. Although the physical characteristics are good, a dedolomitization reaction may develop when they are used as concrete aggregate. Milanesi et al. (1996) evaluated the potential reactivity of the "Dolomite" mine rock using standard test methods (ASTM C586, ASTM C227 and CSA A23.2-14A). The results indicated that the expansion exceeded the maximum allowed in the tests (Table 4). A modified version of the ASTM C586 test method was also applied in this study to measure length changes in rock cylinders (19 mm in diameter and 75 mm in length) immersed in 1N NaOH solutions at room temperature for 16 weeks.

Table 4. ASTM C586, ASTM C227 and CSA A23.2 14A test expansions

Expansion (%)					
ASTM C586 (16 weeks)	ASTM C227			CSA A23.2-14A	
	6 months	12 months	5 years	12 months	5 years
1.929	0.060	0.069	0.100	0.032	0.205

In order to evaluate the mineralogical changes of the rocks during the test, the samples were examined by XRD. The results revealed the occurrence of strong dedolomitization, evidenced by the presence of the main reflections of calcite, dolomite and brucite (Figure 6). By polarizing microscopy on thin sections, it was possible to observe the phenomena developing reaction rims on the particle boundaries (Figure 7).

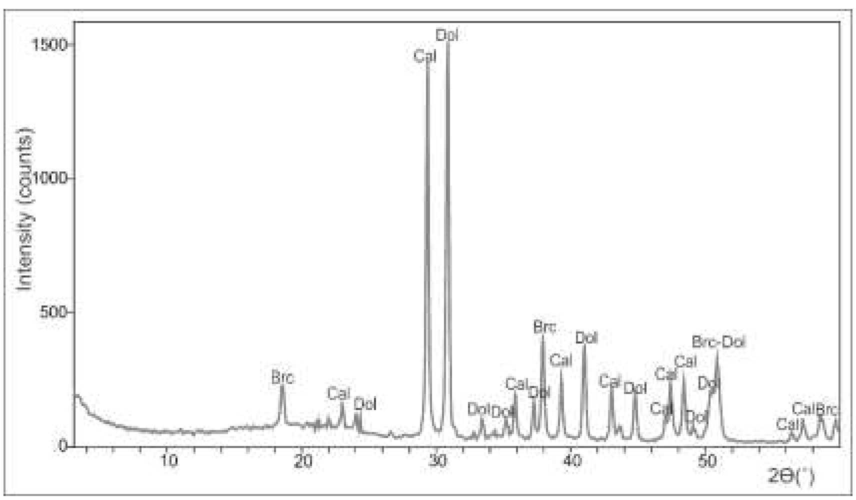

Figure 6. XRD of dolomitic rock after the test. Dol: dolomite, Cal: calcite, Brc: brucite.

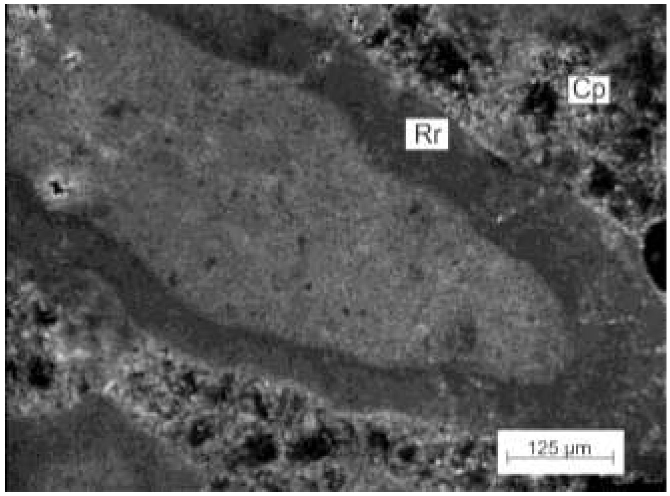

Figure 7. Photomicrograph. Reaction rim (Rr) on dolostone particle (XN). Cp: cement paste.

The "La Adela" Mine

In the area, eight small hills can be recognized; they are mainly composed of dolomite layers with strike EW to N80ºW and dip between 45º and 65º N, affected by metamorphic processes that produced a dolomitic marble outcropping in the zone. The body subject to mining work is 600 meters long, 70–90 meters wide and 50 meters thick. It is emplaced in pre-Silurian micaceous schists (Valcheta Group) (Caminos & Llambías 1984).

Mineralogical Characteristics

The main mineral is dolomite with rare presence of quartz. The mineralogical assemblage is made up of sepiolite, talc, illite, montmorillonite, calcite, phlogopite and amphiboles (tremolite, anthophyllite). From the top to the floor of the working levels, there are abundant mineralized joints (Figure 8).

Host Rock

The dolomite is massive, compact, of blushed to gray color, and sometimes slightly reddish. It shows evidence of weathering on the surface, but it is fresh inside. The texture of the rock is granoblastic, sometimes saccharoidal, with medium to coarse grain size (in some areas reaching 0.5 cm). The crystals are twined, have high birefringence, slight evidence of deformation, and strong cleavage (Figure 9a).

The purity grade of dolomite is 98%, determined by chemical analyses (Angelelli et al. 1976). The main impurities are phlogopite and amphiboles. Tremolite is present as small tabular crystals, of light green color, weakly pleochroic, with oblique extinction and moderate birefringence. It is usually associated with talc (Figure 9b). Anthophyllite_is closely associated with tremolite. It exhibits right extinction, positive elongation and low interference color. Talc is the most common alteration mineral. Phlogopite has a light green color and is in general associated with amphiboles, and arranged in bands nearly concordant with the foliation. On thin sections, it is brownish, slightly pleochroic, with near right extinction and marked cleavage in one direction.

Alteration Minerals

Dolomitic marble hosts an alteration association composed of the following minerals:

- Sepiolite: Macroscopically, sepiolite occurs in flexible, fibrous aggregates; it is white, very light, relatively soft to the touch and of low hardness (2–2.5). The fibers are arranged in bundles and are oriented parallel to cracks within the diaclases of dolomitic rocks, commonly associated with calcite and other minerals (XRD analyses) (Figure 9b). They show noticeable crystalline development since in some areas the fibers are longer than 10 cm. On thin sections, sepiolite is colorless to gray, has low relief and weak birefringence. Extinction is approximately parallel, with positive elongation (length-slow). It occurs in the contact with the dolomitic host rock. Scanning electron microscopy (SEM) analyses showed no individual fibers but an interlocking texture.
- Calcite: It appears in veins 250 µm wide, extended along the contact between the dolomitic rock and sepiolite. These veins developed together with the sepiolite and after dolomite formation. It is possible to recognize two different carbonate generations, the first corresponding to the original rock with an important crystalline development and the second having smaller crystals in veins.
- Talc: It is present as interstitial masses distributed into the sepiolite or as alteration product of amphiboles. Very fine crystalline aggregates with tabular habit, high birefringence and positive elongation are observed on thin sections. Sometimes they appear as amphibole pseudomorphs and frequently in veins interstitially between deformed sepiolite grains (Figure 9b).

Paragenetic Sequence

The sequence of crystallization of the ore minerals and mineral assemblages is: 1) Dol + Qz + Amp + Phl; 2) Cal + Tlc + Sepiolite + Phl + Amp + clay minerals (illite + montmorillonite). Two generations of carbonates were identified: the first one corresponds to very good crystalline metamorphic dolomite and the second one, to small calcite crystals in veins. Talc is a common alteration mineral. Elongated amphibole crystals were observed in the carbonatic mass (Figure 9c). In some cases, they are altered to talc on their edges and in others, pseudomorphism occurs showing shades of amphiboles with esteatization. Figure 9d shows a tabular amphibole crystal, altered and fractured.

Origin

The mineralization process that formed sepiolite developed by hydrothermal activity, following the fracturing and the foliation of dolomite, behaving as lithological and structural control. The sequence of crystallization from acid medium at temperature of ~300ºC to alkaline medium at environmental temperature is: talc, phlogopite, illite, sepiolite, montmorillonite, dolomite + calcite + brucite. In the “La Adela” mine, talc and phlogopite crystallized from the alteration of the original rock in the principal stage of mineralization. Illite is formed when the medium reached a pH near 7. In the presence of alkaline elements, dedolomitization of the host rock developed with the crystallization of calcite and leaching of an important amount of magnesium. Finally, in alkaline medium at low temperature, the sepiolite crystallizes using the silica leached from the clay minerals contained as impurities in dolomite, and magnesium.

The crystallization of calcite caused a volume increase developing stress with the consequent deformation observed in the phyllosilicates.

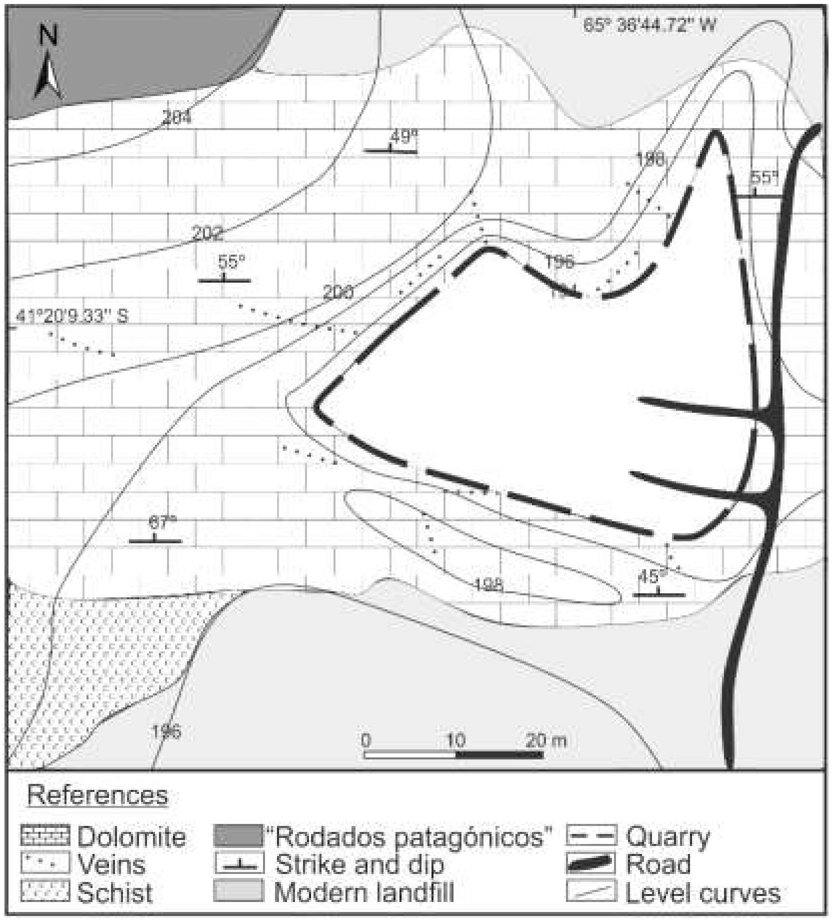

Figure 8. The “La Adela” mine. Quarry map (modified after Maiza and Marfil 1993).

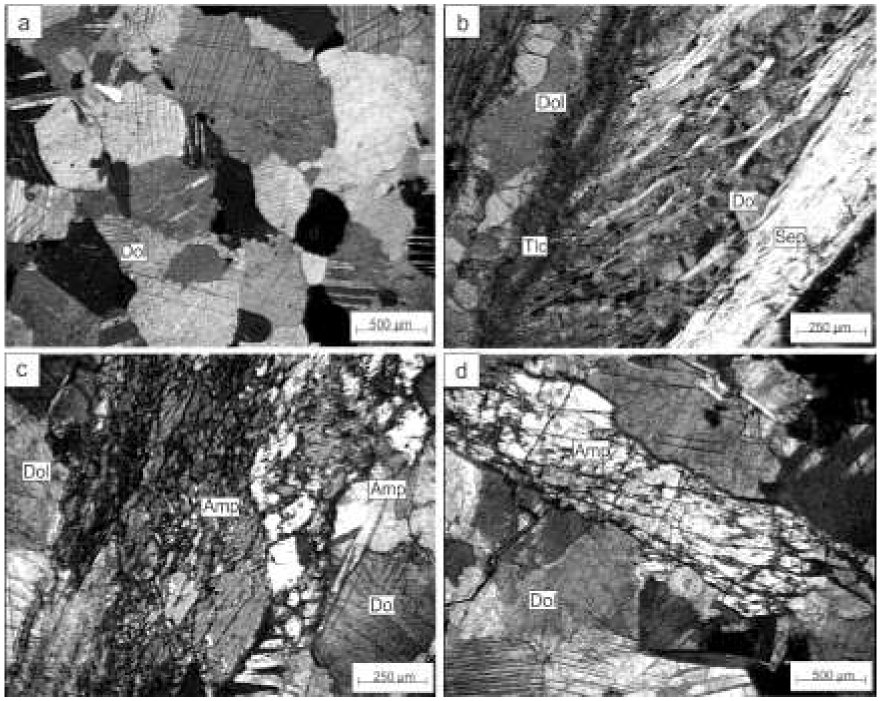

Figure 9. Photomicrographs. Dolomitic marble from the "La Adela" mine. a) Detail of the granoblastic texture (XN); b) distribution of sepiolite and talc in the dolomitic rock (XN); c) and d) elongated amphibole crystals associated with dolomite (XN). Dol: dolomite, Tlc: talc, Am: amphibol, Sep: sepiolite.

Applications

The material from this quarry was used in metallurgical processes in a very important nearby iron mine ("Sierra Grande", Figure 2). Nowadays, it is not exploited but the mineralogical assemblage, mainly sepiolite, has important commercial value because it is used in a wide range of technological applications. Due to its fibrous morphology and surface characteristics, it is considered an excellent reinforcement in polymer-based nanocomposites and is used in photocatalysis, heavy metal adsorption, as metallic nanoparticle support with biocide or plasmonic properties, as well as vaccine support and electronic conductor.

Any attempt to obtain individualized fibers from natural sepiolite micrometric aggregates would profit from the development of technological applications, taking advantage of the silanol-based chemistry and the nanometric diameter of isolated fibers. Sepiolite from the "La Adela" mine, which was first described by Cortelezzi et al. (1994), shows a peculiar feature related to its high crystalline development. However, this clay mineral is emplaced within dolomitic rock bodies, which are responsible for the presence of impurities. Lescano et al. (2014) analyzed lyophilization and acid treatments comparatively evaluating mainly the defibering effect on high crystalline sepiolite from "La Adela" and its purification, in order to make it applicable at an industrial scale. For this purpose, the treatment effect on sepiolite structure and purity was studied based on mineral characterization, electronic and polarizing microscopy, XRD, and Fourier transform infrared spectroscopy (FT-IR). Taking into account that the "La Adela" mine is not commercially exploited, the defibering and purification of sepiolite samples through any of the proposed methods is an interesting added value to this clay mineral. Acid treatments and lyophilization were proposed as a relatively simple alternative for defibering sepiolite bundles and, eventually, for its purification in order to be used at the industrial scale. Acid treatments allowed sepiolite purification by removing carbonates. This method permitted the conservation of the clay mineral structure, and fiber crystallinity was sensitively reduced. The efficiency of this method resides in the fact that the freezing of water within sepiolite channels causes a volume increase that induces fiber separation when ice sublimates.

Table 5 summarizes the main mineralogical characteristics and applications of the deposits distributed in the province of Río Negro.

Table 5. Summary of the main characteristics of Río Negro deposits

Characteristics	“Dolomite” mine	“La Adela” mine
Surface	Not greater than 1.5 km^2	600 m^2
Shape	Irregular	Tabular
Associated rocks	Tuffaceous sandstone	Micaceous schists
Fossils	Does not contain any	Does not contain any
Thickness	Up to 20 meters	50 meters
Texture	Equigranular with fine grain size	Granoblastic with medium to coarse grain size.
Mineral assemblages	Dolomite, quartz, feldspar, lithic fragments, sepiolite, montmorillonite, gypsum	Dolomite, sepiolite, talc, illite, montmorillonite, calcite, brucite, phlogopite and amphiboles (tremolite, anthophyllite).
Structure	Massive in the lower part of the working fronts to banded and with voids towards the top	Massive, with mineralization located in joints
Origin	Replacement by hydrothermal solutions	Metamorphism of dolomites and subsequent hydrothermal processes
Applications	Concrete aggregate and industrial products	In metallurgical and other processes (under study)

Province of Córdoba (Argentina)

Marbles from Córdoba appear as lens or tabular banks with different metamorphic grades (generally medium to high) associated with gneisses, migmatites, amphibolites, and ultramafic rocks. Their composition is variable depending on the studied area, where calcitic to dolomitic end members are recognized (Sfragulla et al. 1999). 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.

Recent studies have proposed a sedimentary age of ~630–545 Ma for the carbonatic deposits (Murra et al. 2014). These deposits were then affected by metamorphic processes of

Lower Cambrian age (Rapela et al. 1998, Steenken et al. 2011) that transformed these sediments into dolomitic to calcitic marbles.

The main marble quarries are located in a set of mountain ranges of N–S direction in the center of the country called “Sierras de Córdoba” (Figure 10) and an important percentage of these rocks are used as aggregates in concrete. Locati et al. (2012, 2014a, 2014b) studied several marble quarries from this province (especially those in the E of the ranges) in order to characterize and evaluate the potential reactivity of these rocks. A general description of the marbles from “San Agustín” belt, “Alta Gracia-Bosque Alegre” belt, and El Manzano Formation, and a summary of the most important results from the studied samples from each sector are given below. In addition, asbestiform varieties were identified, and their potential degradation in an abandoned marble quarry from Altautina town (Córdoba) was evaluated.

“San Agustín” Marble Belt

In the SE of Sierras de Córdoba (4 km to the SW of San Agustín city) there are several outcrops of marbles of white to light green color intercalated with pelitic gneisses. This is the so-called “San Agustín” belt (Figure 10), which is dominated by dolomitic marbles (± calcite) with phlogopite, tremolite, quartz, talc, chlorite, diopside, and serpentine as the main accessories.

“Alta Gracia-Bosque Alegre” Marble Belt

In the east of Sierras de Córdoba (5 km to the NW of Alta Gracia city) there is a marble belt denominated “Alta Gracia - Bosque Alegre” (Figure 10).

It is composed of serpentinitic marbles (mainly dolomitic, although in some sectors calcite can predominate over dolomite) of white to light green or gray color. Phlogopite, diopside, epidote, serpentine, tremolite, chlorite, olivine, quartz, garnet, opaque minerals, and iron oxides are the main accessory minerals.

“El Manzano” Formation

In the NE of Sierras de Córdoba (2 km to the E of El Manzano town and near “El Sauce” quarries), there is a series of marble outcrops, of white to gray color, named “El Manzano” Formation (Figure 10). They are mainly dolomitic or calc-dolomitic, although in some sectors calcitic varieties predominate. The main accessories are quartz, olivine, tremolite, serpentine, phlogopite, diopside, epidote, spinel, chlorite, and opaque minerals.

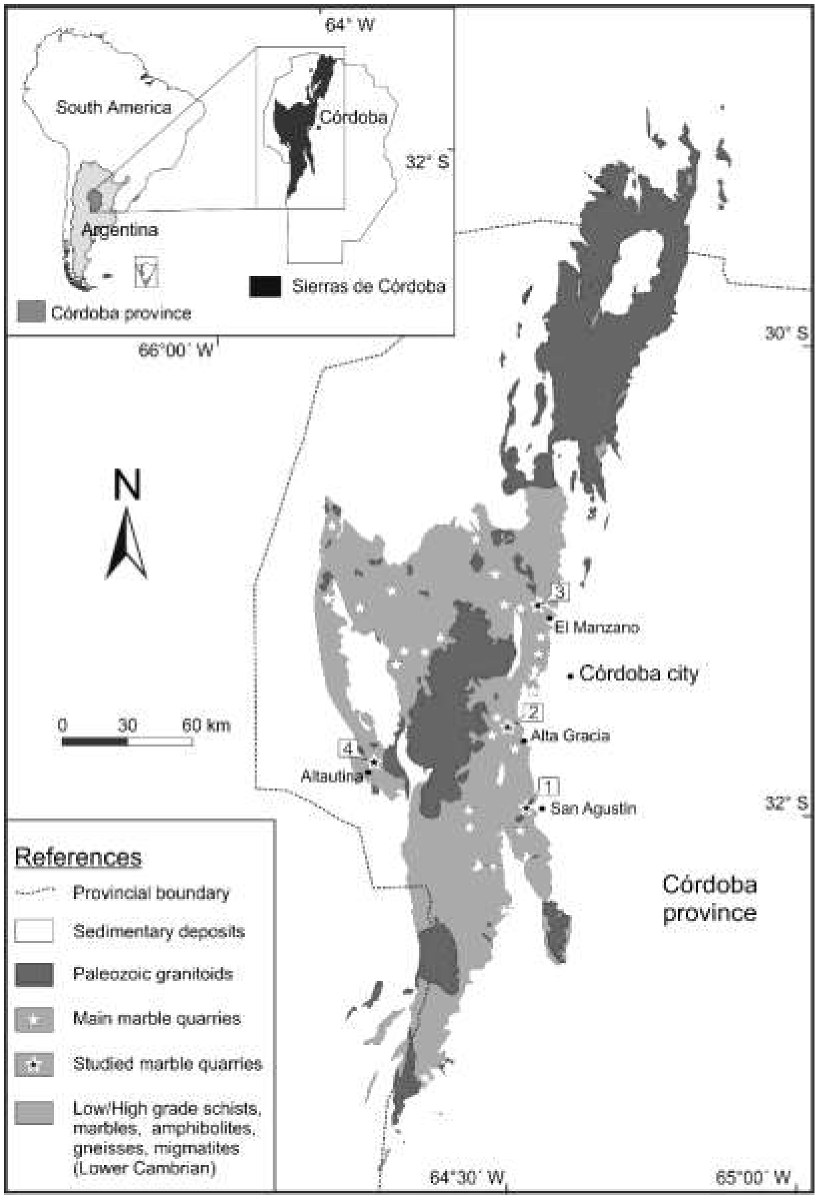

Figure 10. Location map of the main marble quarries in the province of Córdoba (modified after Murra et al. 2014). 1) Marble from San Agustín belt. 2) Marble from Alta Gracia-Bosque Alegre belt. 3) Marble from El Manzano Formation. 4) Marble near Altautina town ("Altautina quarry").

Mineralogical Characteristics

In Table 6 and Figure 11 the most important characteristics of the studied sampled are presented.

X-Ray Diffraction and Insoluble Residue

The mineralogical characterization of marbles from the province of Córdoba was supplemented with XRD studies on natural samples (Figure 12) and on the insoluble residue fraction (Table 7). In addition, semi-quantification of dolomite mass fractions (Figure 12) was performed with X'Pert HighScore software (PANalytical) using the scale factor and Reference Intensity Ratio (RIR) values from ICDD (International Centre for Diffraction Data) database. The program uses the RIR method proposed by Chung (1974).

Table 6. Characteristics of the studied samples

Provenance	San Agustín marble belt	Alta Gracia -Bosque Alegre marble belt	El Manzano Formation
Texture	Granoblastic with anhedral crystals with irregular boundaries due to recrystallization	Granoblastic with subhedral to anhedral crystals.	Granoblastic with subhedral to anhedral crystals.
Grain size	Grains: ≤ 8 mm, new grains at the boundaries: ≤ 100 μm	≤ 1 mm	≤ 3 mm
Main minerals identified by petrography	Dol>>Cal (~95%) ± Srp ± Tlc ± Chl ± Phl ± Di (~5%)	Cal > Dol (~60%) ± Phl ± Di ± Srp ± Tr ± Ol (~40%)	Dol > Cal (~75%) ± Srp (~15%) ± Phl (~5%) ± Spl ± Qz ± Ol ± Opq (~5%).
Other character-ristics		Serpentine replaces almost all olivine crystals	Serpentine completely replaces olivine crystals leaving olivine pseudomorphs. Iron oxides appear associated with cracks in the original olivine crystals.

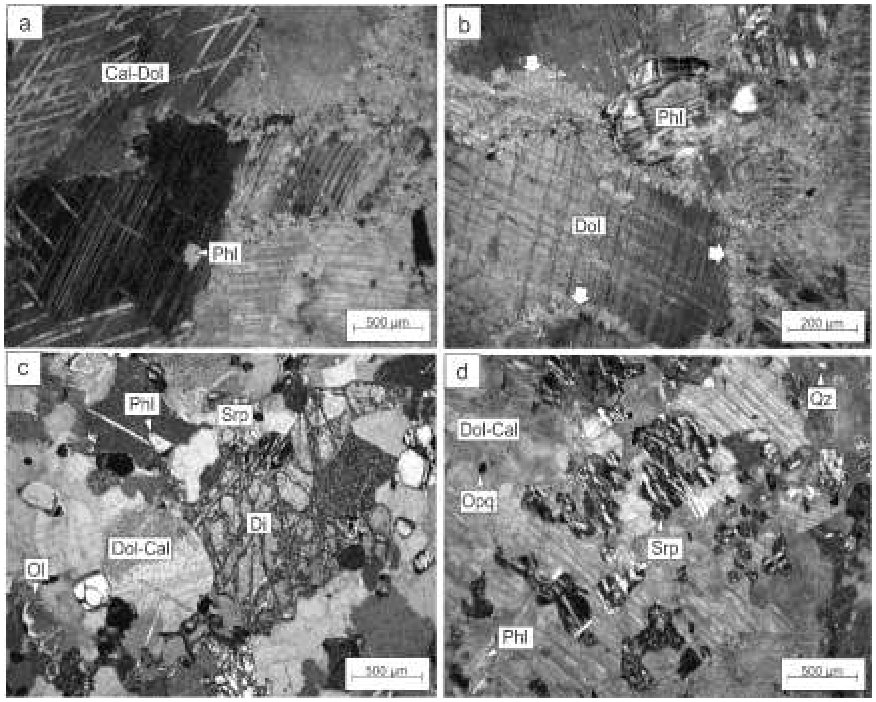

Figure 11. Photomicrographs (XN). a) Dolomitic marble (Dol >> Cal) with evidence of recrystallization at grain boundaries. b) Calc-dolomitic marble (Cal > Dol). d) Calc-dolomitic marble (Dol > Cal) (modified after Locati et al. 2014a). Dol: dolomite, Cal:calcite, Phl: flogopite, Srp: serpentine, Opq: opaque minerals, Qz: quartz, Di: diopside, Ol: olivine.

Table 7. Insoluble residue (%) and minerals identified by XRD

	San Agustín	Alta Gracia - Bosque Alegre	El Manzano
Insoluble residue (%)	10.95	30.33	14.15
Minerals by XRD	Serpentine, talc, chlorite	Phlogopite, diopside, serpentine, tremolite	Phlogopite, serpentine, quartz

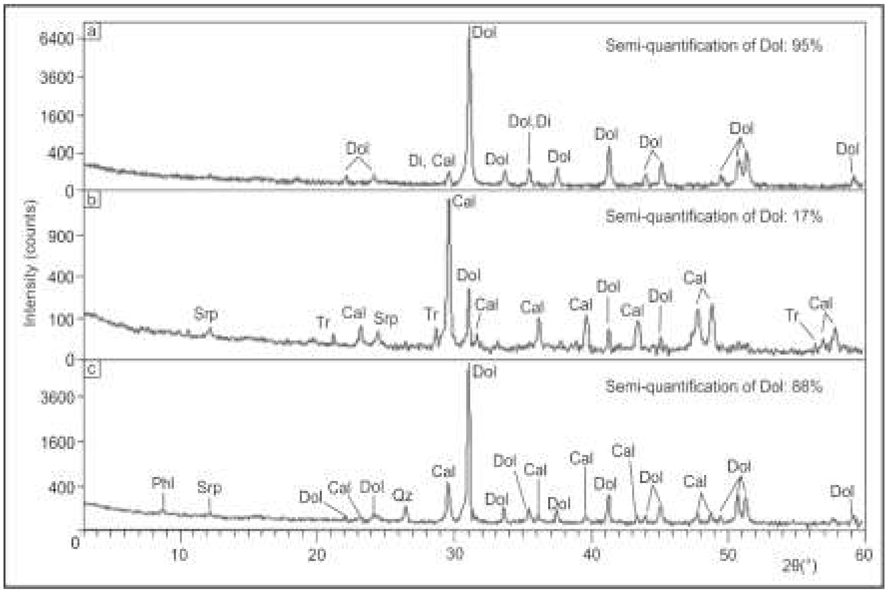

Figure 12. XRD of natural samples. a) Marble from “San Agustín” belt. b) Marble from “Alta Gracia-Bosque Alegre” belt. c) Marble from “El Manzano” Fm. Dol: dolomite, Cal: calcite, Di: diopside, Tr: tremolita, Srp: serpentine, Phl: flogopite, Qz: quartz.

Chemical Composition

Table 8 lists the chemical analyses of marbles from San Agustín, Alta Gracia-Bosque Alegre and El Manzano (near El Sauce quarries) areas after Sfragulla et al. (1999).

Applications

Most of these marbles are used as aggregates in concrete. Locati et al. (2014a) examined the behavior of dolomitic to calcitic marbles from the province of Córdoba with respect to the alkali-carbonate reaction. They concluded that although none of the mortar bars made with the studied aggregates exceeded the limits established by standard methods, low expansions were detected. Detailed studies allowed correlating those expansions with microcracks and reaction products related to the ASR rather than to dedolomitization. The relict strained quartz and possibly the fine-grained phlogopite (≤100 μm) in the marbles acted as silica sources for the development of neoformation silicates of variable composition (Ca, Na, K, Mg, Al), recognized in cavities and microcracks as a result of the ASR. The metamorphic rocks of the province of Córdoba have textures (medium to coarse grain size with a densely packed texture) that differ from that of sedimentary carbonates studied worldwide and typically associated with the so-called ACR (argillaceous dolomitic limestones with dolomite rhombs scattered in the fine-grained matrix). Therefore, the presence and distribution of the dedolomitization process appear not to be related to the texture of the aggregates (or the clay content) but to the amount of dolomite in the rock. In summary, although dolomitic and calc-dolomitic marbles can develop dedolomitization, they can be used as concrete aggregates because there is no evidence of deterioration associated with this process (provided they are physically and mechanically suitable for their specific use). However, care must be taken with those rocks where strained quartz or another kind of reactive phase can act as silica source for ASR (Locati et al. 2014a).

Table 8. Chemical composition of marbles. Average of 18[(1)], 7[(2)], 30[(3)] and 18[(4)] analyses

Sample provenance	CaO (%)	MgO (%)	R_2O_3 (%)	Insoluble residue (%)
[1]San Agustín	33.66	17.28	3.22	3.53
[2]Alta Gracia	33.21	17.13	0.85	5.50
[3]Bosque Alegre	32.09	17.47	1.91	3.63
[4]El Manzano (El Sauce quarries)	39.49	11.91	1.00	4.50

Altautina

In the occidental sector of the “Sierras de Córdoba”, 3 km NE from Altautina town (Figure 10), there is an abandoned marble quarry (Figure 13a) that corresponds to an irregular bank of dolomitic marbles of white to slightly gray color (20 m wide, N340°/70°E), limited by quartz-biotite gneisses/schists.

In the contact zone there is a metasomatic belt, 50 cm wide, where gneisses/schists are enriched in biotite (Figure 13b). Between this sector and the marble bank there are at least two different zones (zone A and B) rich in fibrous amphiboles.

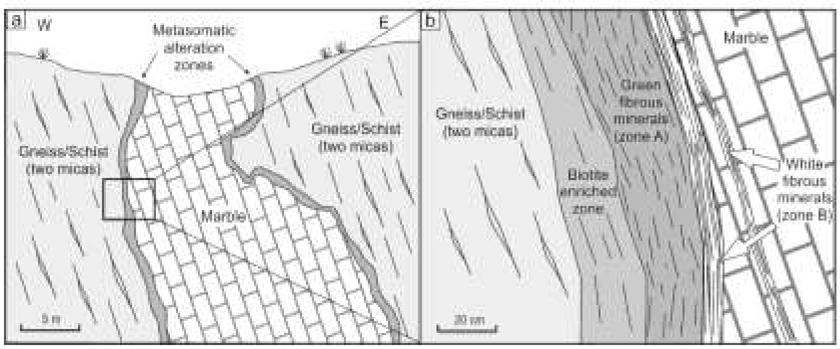

Figure 13. Altautina quarry. a) Geological sketch of the studied quarry. b) Detail of the metasomatic zone (modified after Locati et al. 2014d).

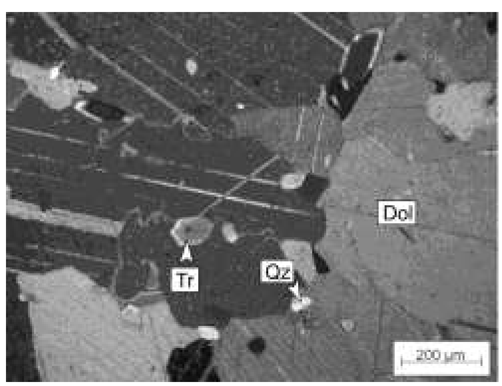

Figure 14. Photomicrograph of dolomitic marble from Altautina quarry (XN). Dol: dolomite, Qz: quartz, Tr: tremolite.

Marbles have medium to fine grain size and granoblastic texture, tremolite being the main accessory mineral (Figure 14), with minor phlogopite, serpentine, quartz, diopside and talc. According to Sfragulla et al. (1999), marbles from Altautina area are predominantly dolomitic (Table 9).

Table 9. Chemical composition of marble from Altautina after Sfragulla (1999). Average of 14 analyses

Sample	CaO (%)	MgO (%)	R_2O_3 (%)	Insoluble residue (%)
Altautina	31.85	17.03	2.24	9.25

Characterization of the Metasomatic Zone

In the metasomatic zone at least three different types of amphiboles distributed in zone A and B were recognized. Zone A corresponds to a discrete belt (~20 cm wide) next to the gneisses/schists enriched in biotite, composed predominantly of prismatic magnesio-hornblende crystals (Amp1) of tabular habit and green to gray color. They are oriented parallel to the contact zone and associated with elongated crystals of tabular to fibrous habit of tremolite, of light green to white color (Amp2) ± calcite ± titanite ± epidote ± biotite ± chlorite ± serpentine ± zircon (Figure 15a). Zone B corresponds to a thinner belt (~5 cm wide) in the marble, rich in prismatic crystals of tremolite (a few microns to 5 mm long) of white color (similar to Amp2 in zone A) oriented and giving the marble a rough foliation. In discrete sectors of this zone (Figure 15b) Amp2 is associated with bundles of thin, long tremolite fibers of white color (Amp3) and asbestiform habit (>5 µm long and <3 µm wide). These types of asbestiform fiber were also observed as veins crosscutting marble foliation (Figure 15c) near the contact zone and in discontinuity planes (Figure 15d).

Chemical Composition of Amphiboles

Amphiboles were analyzed by electron probe microanalyses (EPMA) and classified according to Hawthorne et al. (2012) criteria (Figure 16). All tremolite amphiboles (Amp2 and Amp3) are chemically similar (SiO_2 = 57.07–58.61%, MgO = 22.94–24.09%, CaO = 12.85%–13.52%, Al_2O_3 = 0.48%–3.17%, FeO_T = 0.55%–1.78%, Na_2O = 0.03%–0.32%, MnO = 0.05%–0.08%).

Applications

Marbles from Altautina area are not exploited nowadays. However, during the operation of the quarry, a large amount of material was crushed and used for construction, or discarded in spoil heaps. All this accumulated material is currently exposed to weathering processes. In order to evaluate its physical behavior and potential degradation in aqueous medium, Locati et al. (2014d) carried out some experiments (a stirring test) simulating natural torrents working at different times using the fibrous amphiboles from zone B (Amp3). They found that with increasing stirring time during the test, fibers began to disintegrate and reduce their size forming a tight micrometric mesh, reaching values considered harmful for human health.

It is important to point out that some of the tremolite fibers recognized in Altautina area naturally meet the conditions set by WHO (1986) and OSHA (1992) to consider this material as dangerous for human health. However, under certain conditions, natural water torrents might degrade long and wide tremolite forming a mesh of separated fibers or cleavage fragments. The dangerousness of these broken fibers 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, but also monitor deposits with asbestiform amphiboles that could be exposed to weathering and transformed into potentially dangerous asbestiform materials (Locati et al. 2014d).

Table 10 summarizes the main mineralogical characteristics and applications of the deposits studied in the province of Córdoba.

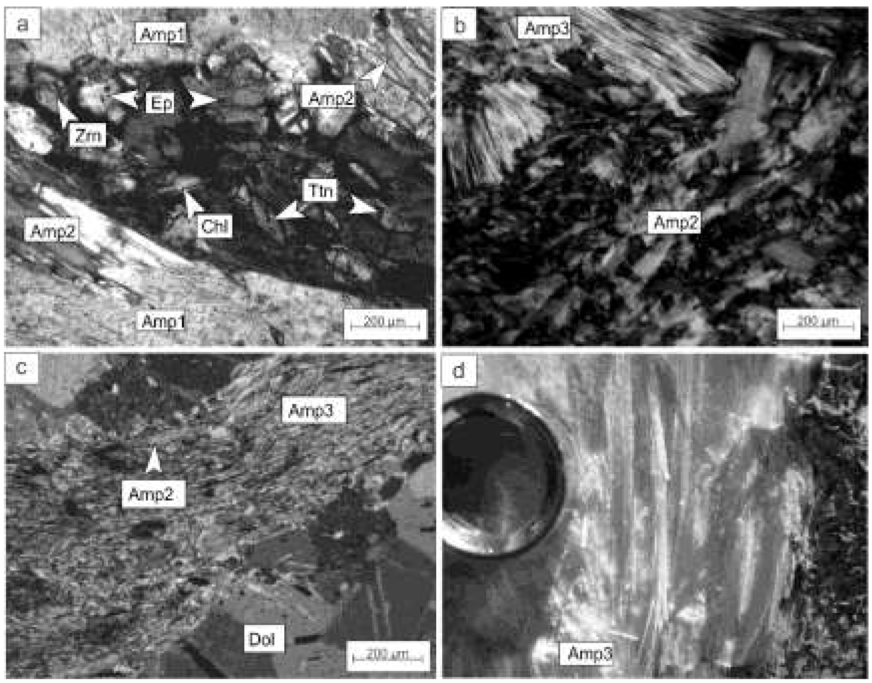

Figure 15. Photomicrographs (XN) of amphiboles (Amp1 and Amp2) in zone A (a) and amphiboles (Amp 2 and Amp3) in zone B (b and c). d) White asbestiform amphiboles (Amp3) in a discontinuity plane (modified after Locati et al. 2014c, 2014d). Amp: amphibole, Dol: dolomite, Chl: chlorite, Ttn: titanite, Zrn: zircon, Ep: epidoto.

Table 10. Summary of the main characteristics of Córdoba deposits

Characteristics	"San Agustín"	"Alta Gracia - Bosque Alegre"	"El Manzano"	"Altautina"
Surface	1.5 km^2 (approx.)	5.1 km^2 (approx.)	108.000 m^2 the main outcrop	3000 m^2 the main outcrop
Shape	Lenticular or tabular bodies	Lenticular or tabular bodies	Lenticular or tabular bodies	Lenticular or tabular bodies
Associated rocks	Pelitic gneisses intruded by aplopegmatites	Gneisses, anatexites, amphibolites and serpentinitic bodies	Gneisses, amphibolites intruded by aplopegmatites	Pelitic gneisses/schists
Fossils	Does not contain any	Does not contain any	Does not contain any	Does not contain any
Thickness	600 m (max.)	1700 m (max.)	200 m the main outcrop	20 m the studied quarry
Texture	Granoblastic with coarse to medium grain size	Granoblastic with medium to fine grain size	Granoblastic with medium to coarse grain size	Granoblastic with medium to fine grain size
Mineral assemblages	Dol>>Cal ± Srp ± Tlc ± Chl ± Phl ± Di	Cal>Dol ± Phl ± Di ± Srp ± Tr ± Ol	Dol>Cal ± Srp ± Phl ± Spl ± Qz ± Ol ± Opq	Dol>>Cal ± Phl ± Srp ± Qz ± Di ± Tr ± Tlc
Structure	Massive and locally banded	Massive and banded	Massive and locally banded	Massive and banded
Origin	Metamorphic with metasomatic processes superimposed	Metamorphic with metasomatic processes superimposed	Metamorphic with metasomatic processes superimposed	Metamorphic with metasomatic processes superimposed
Applications	Concrete aggregate and industrial products (lime production, for paints and soils)	Concrete aggregate and industrial products (for paints and paper industry)	Concrete aggregate and lime production	Not working nowadays

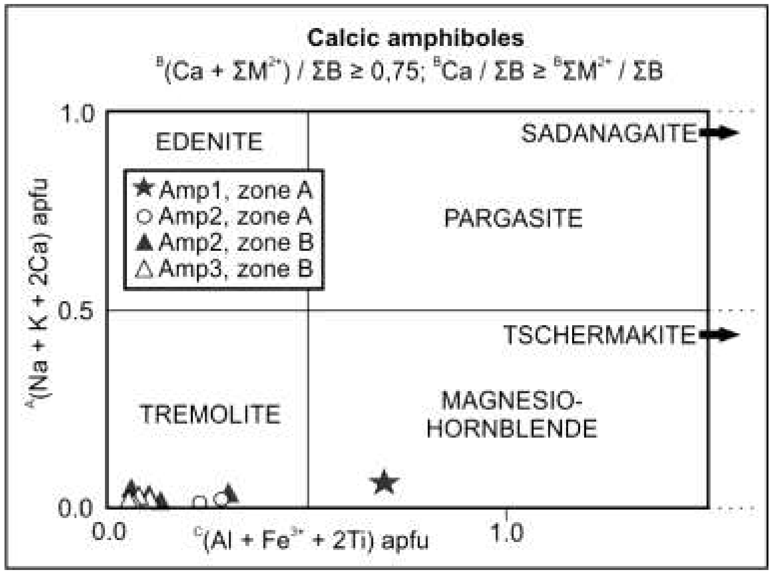

Figure 16. Chemical composition of amphiboles (Locati et al. 2014c).

Province of Buenos Aires

The province of Buenos Aires consists of an extensive plain with Cenozoic and recent sediments where the mountains of “Tandilla” and “Ventania” rise (Figure 17). The first one has strike NW-SE with outcrops in an area 350 km long and 60 km wide, with Olavarría mountains in the northern end. They are the oldest rocks of the country, named Buenos Aires Complex (2100-2200 Ma), and are composed of gneisses, migmatites, amphibolites, granites, schists, marbles, metavolcanic rocks, and basic and acid dikes. Carbonatic rocks are present in the sedimentary Precambrian cover, located between 36º 30´ and 38º S, and 57º 30´ and 61º E (Poiré et al. 2005). In “Sierras Bayas” area, the homonymous Group is composed of Villa Mónica, Cerro Largo and Loma Negra Formations. The first one presents a dolomitic bank up to 36 meters thick. This is one of the most important economic resources of this province.

Olavarría (Province of Buenos Aires, Argentina) is an important mining center where lime, limestone, dolomite, clay, sand and gravel are extracted. The local primary production has been integrated with other industrial processes, obtaining high value-added products such as cement, tiles, ceramics, bricks, etc. The development of other mining-related industries has transformed the region into an industrial hub.

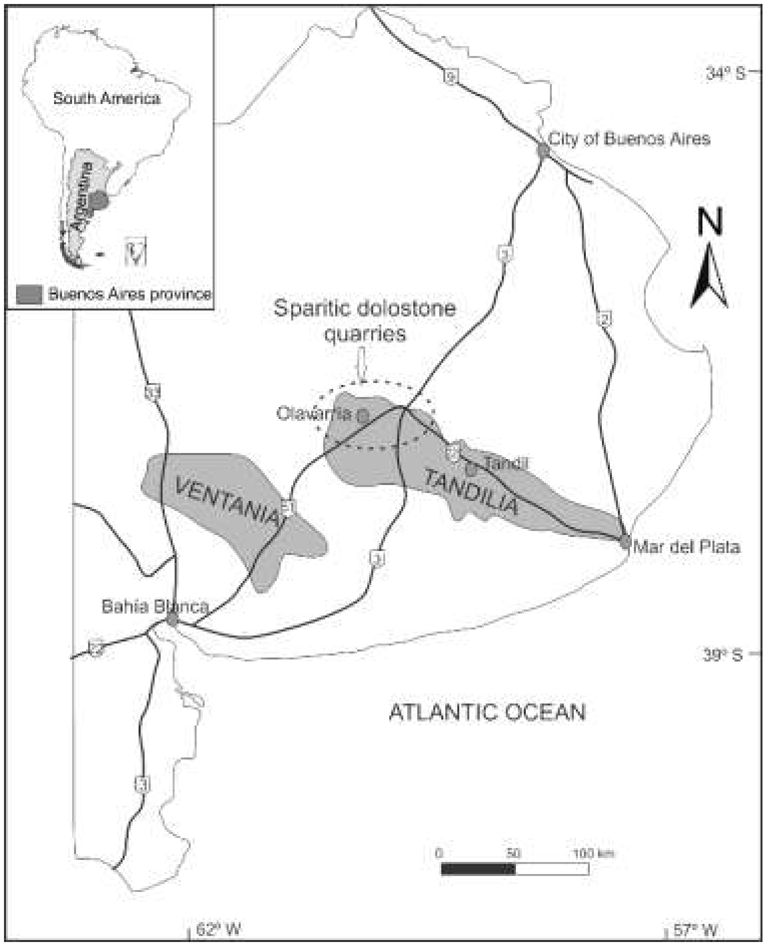

Figure 17. Location of Olavarría deposits in the province of Buenos Aires.

The Olavarría Mine

The Villa Mónica Formation starts with a basal quartz-arkosic conglomerate followed by arkosic wackes, subarkosic arenites, and quartzitic arenites. At a certain time, environmental changes led to the transition from a siliciclastic sequence to an essentially carbonatic sequence composed of 36–52 meters of yellowish dolomites in three packages: a basal stromatolitic package, a middle laminated one, and an upper stromatolitic package again. They were originally magnesian limestones that were transformed via different diagenetic stages into dolostones (Poiré 1987, Poiré & Spaletti 2005). Towards the Barker zone, dolostones grade laterally into reddish and yellowish pelitic facies, composed of quartz and illite, with isolated stromatilitic phthanite lenses (Allo 2001).

Mineralogical Characteristics

The dolostone is a massive, homogeneous rock of light yellowish brown color, with fine grain size, slightly marked stratification and no alteration. On thin sections it shows a sparitic texture, consisting of euhedral to subhedral crystals of dolomite ranging between 100 μm and 200 μm in size, with about 90% of them being between 140 and 150 μm long. The rock is composed mainly of dolomite, minor amount of calcite (especially in veins) and interstitial quartz (Figure 18a and b). There are scarce irregular cracks filled by recrystallized dolomite and iron oxides. The rock is classified as sparitic dolostone.

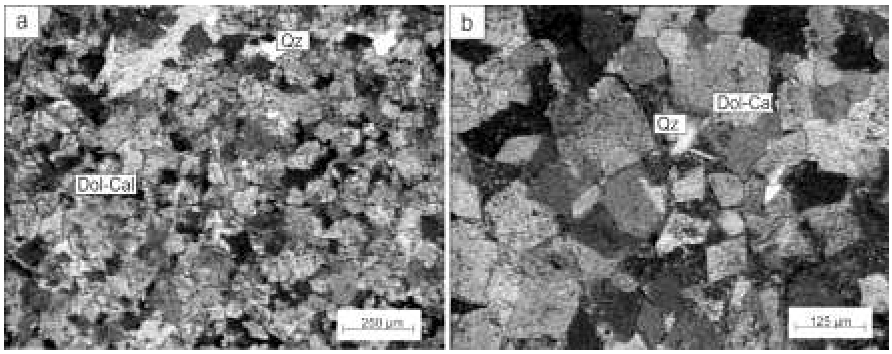

Figure 18. Photomicrographs (XN). a) Fine grain texture of the rock. b) Details showing rhombs of dolomite (Dol) surrounded by calcite (Cal) and minor quartz (Qz).

Alteration Minerals

Illite, hematite, goethite and kaolinite were identified by XRD and microscopy. In the very fine-grained carbonate mass, iron oxide is abundant, in general crystallized in the intercrystalline spaces with diffuse boundaries.
Calcite veins consisting of big crystals with associated silica (quartz, cryptocrystalline silica and opal) with minor illite and kaolinite are also observed (Marfil & Maiza 2011).

Table 11. Chemical composition of the dolomitic rocks from Olavarría (Buenos Aires)

Sample	CaO (%)	MgO (%)	R_2O_3 (%)	Insoluble residue (%)	Loss on ignition
1	23.1	16.5	1.5	23.3	34.4
2	23.8	19.5	1.6	13.7	40.1
3	26.5	18.3	1.0	3.3	51.0

Chemical Analyses

On the basis of chemical analyses, the estimated calcite content does not exceed 10% (Table 11). The insoluble residue is composed mainly of clay minerals with low crystallinity (Milanesi 2013).

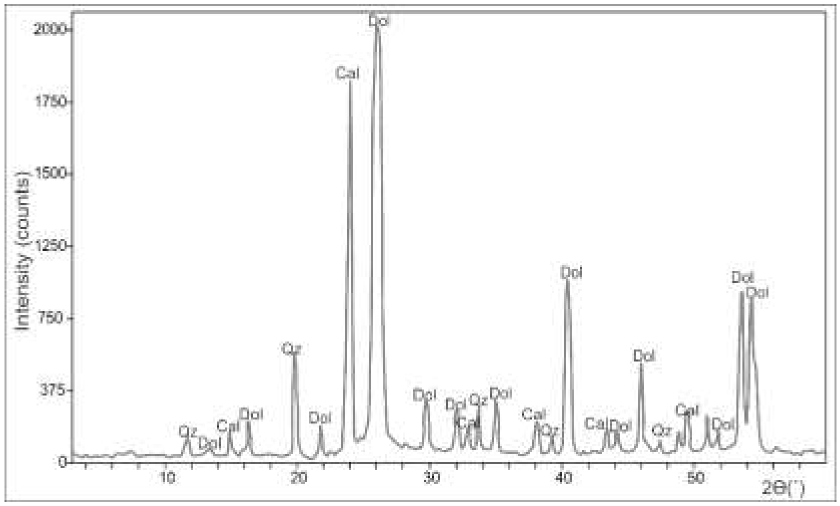

Figure 19. XRD pattern of Olavarría dolostone. Dol: dolomite, Cal: calcite, Qz: quartz.

X-ray Diffraction

By XRD analysis, the dolomite was identified as the main mineral with subordinate amount of calcite and very scarce quartz (Figure 19).

Applications

Olavarría dolostones are mainly used as ornamental rocks, as slagging additive in the steel industry, in the production of lime, and as aggregate for concrete. In previous work (Milanesi et al. 1996, Milanesi 2012) the potential reactivity of these rocks was evaluated using standard test methods (ASTM C586, ASTM C227 and CSA A23.2-14A). According to the results obtained (Table 12) the expansion does not exceed the maximum value allowed in the tests. A modified version of ASTM C586 test method was also applied in this study to measure the length changes in rock cylinders (19 mm in diameter and 75 mm in length) immersed in 1N NaOH solutions at room temperature.

Table 12. ASTM C586, ASTM C227 and CSA A23.2 14A test expansions

Expansion (%)					
ASTM C586 (16 weeks)	ASTM C227			CSA A23.2-14A	
	6 months	12 months	5 years	12 months	5 years
-0.103	0.017	0.023	0.030	0.004	0.013

Table 13 summarizes the main mineralogical characteristics and applications of the deposits studied in the province of Buenos Aires.

Table 13. Summary of the main characteristics of Buenos Aires deposits

Characteristics	Olavarría mine
Surface	10 km^2
Shape	Interlayer in quartzite, arkose and ortoconglomerate
Associated rocks	Gneisses, migmatites, amphibolites, granites, schists, marbles, metavolcanic rocks
Fossils	Stromatolites
Thickness	20/50 meters
Texture	Sparitic
Mineral assemblages	Calcite, quartz, hematite, magnetite, illite, and cryptocrystalline silica.
Origin	Sedimentary
Applications	Crushed stone, cement, industrial uses.

In order to evaluate the mineralogical changes during the test, the samples were examined by XRD. The results showed that a strong dedolomitization had occurred, as evidenced by the presence of the main reflections of calcite and brucite with minor amount of dolomite. Reaction rims on particle boundaries were observed by polarizing microscopy on thin sections.

CONCLUSION

In this chapter we revealed the genetic differences in some Argentine carbonatic-dolomitic deposits, their associated minerals, and the processes that led to the crystallization of different minerals, some of them to be carefully considered at the time of exploitation as they may be hazardous to human health.

Results showed that almost all the deposits have experienced different grades of metamorphism, forming magnesian marbles, except for the "Dolomite" quarry and Olavarría dolostone that were identified as hydrothermal and sedimentary respectively.

In Argentina, the use of dolomitic materials both as aggregate for concrete and ballast and in other industrial applications dates back to the early 20th century. Their degree of exploitation varies, but they have never been exploited at a large scale since in its vast territory, Argentina has alternative materials that have hindered their development. They have been used in the metallurgical, cement and construction industries. The minerals associated with the dolomite are still under study, namely sepiolite due to its application as nanoparticles in plastics and pharmaceutical products. At the same time, the asbestiform amphiboles are likely to be hazardous to human health.

ACKNOWLEDGMENTS

Financial support was provided by Proyecto de Investigación Científica y Tecnológica 2011 (FONCyT) and Secretaría de Ciencia y Tecnología - Universidad Nacional del Sur. The authors thank Centro de Investigaciones en Ciencias de la Tierra (Consejo Nacional de Investigaciones Científicas y Técnicas -Universidad Nacional de Córdoba), Comisión de Investigaciones Científicas from the province of Buenos Aires and the Geology Department of the Universidad Nacional del Sur.

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