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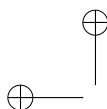
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Characteristics, distribution and diagenetic stages of chert in the La Silla Formation (Lower Ordovician), Argentine Precordillera

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ABSTRACT

The late Cambrian – late Tremadocian La Silla Formation is a carbonate unit of the eastern Precordillera in Argentina whose facies indicate a shallow platform environment. Until this moment, there were no studies that referred to the diagenetic evolution of these rocks. The present study involves the characteristics and distribution of the silicification that affects this unit and determines its different diagenetic stages through petrographic (with cathodoluminescence support) and stratigraphic analyses. An early diagenetic chert, in a stage previous to the compaction, was observed. This chert is related to silica-rich seawater in contact with permeable and porous sediments. A later pulse of chert associated with fracturing, also occurs. The knowledge provided by the characteristics and distribution of chert in these carbonates is significant, especially when considering that the La Silla Formation in San Juan province is the most quarried unit for the elaboration of lime.

Key words: carbonates, chert, early diagenesis, eastern Precordillera, Lower Ordovician.

INTRODUCTION

Chert is a hard, dense or compact sedimentary rock, consisting of micro- or cryptocrystalline quartz crystals that contain amorphous silica (opal) and impurities such as calcite or iron oxide (Bates and Jackson 1980). There are many references to chert associations in carbonates; comprising different depositional environments and ages (Geeslin and Chafetz 1982, Maliva and Siever 1989, Gao and Land 1991, Lawrence 1994, Giménez-Montsant et al. 1999, Pope 2004). Chert can provide a window to the original composition of the sediment, the diagenetic history and the biota of the host rock due to its low susceptibility to further diagenetic alterations (Maliva 2001).

The La Silla Formation (Keller et al. 1994) Cambrian to late Tremadocian age, is a carbonate in the eastern Precordillera whose facies indicate a low platform environment (Cañas 1999, Keller 1999, M.M. Raviolo et al., unpublished data). It is free of diagenetic material and is extensively quarried to produce lime. The present study was carried out in the southern outcrops of the La Silla Formation in the Cerro Pedernal, Cerro Pedernal de los Berros, Loma Redonda, Chica de Zonda, and Sierra de Villicum (Fig. 1).

Among the different studies involving this formation, only the abundance of chert present in the host rock and its importance as a rock-constituting element have been mentioned (Cañas 1999, Keller 1999); in recent isotopic studies (Buggisch et al. 2003, Sial et al.

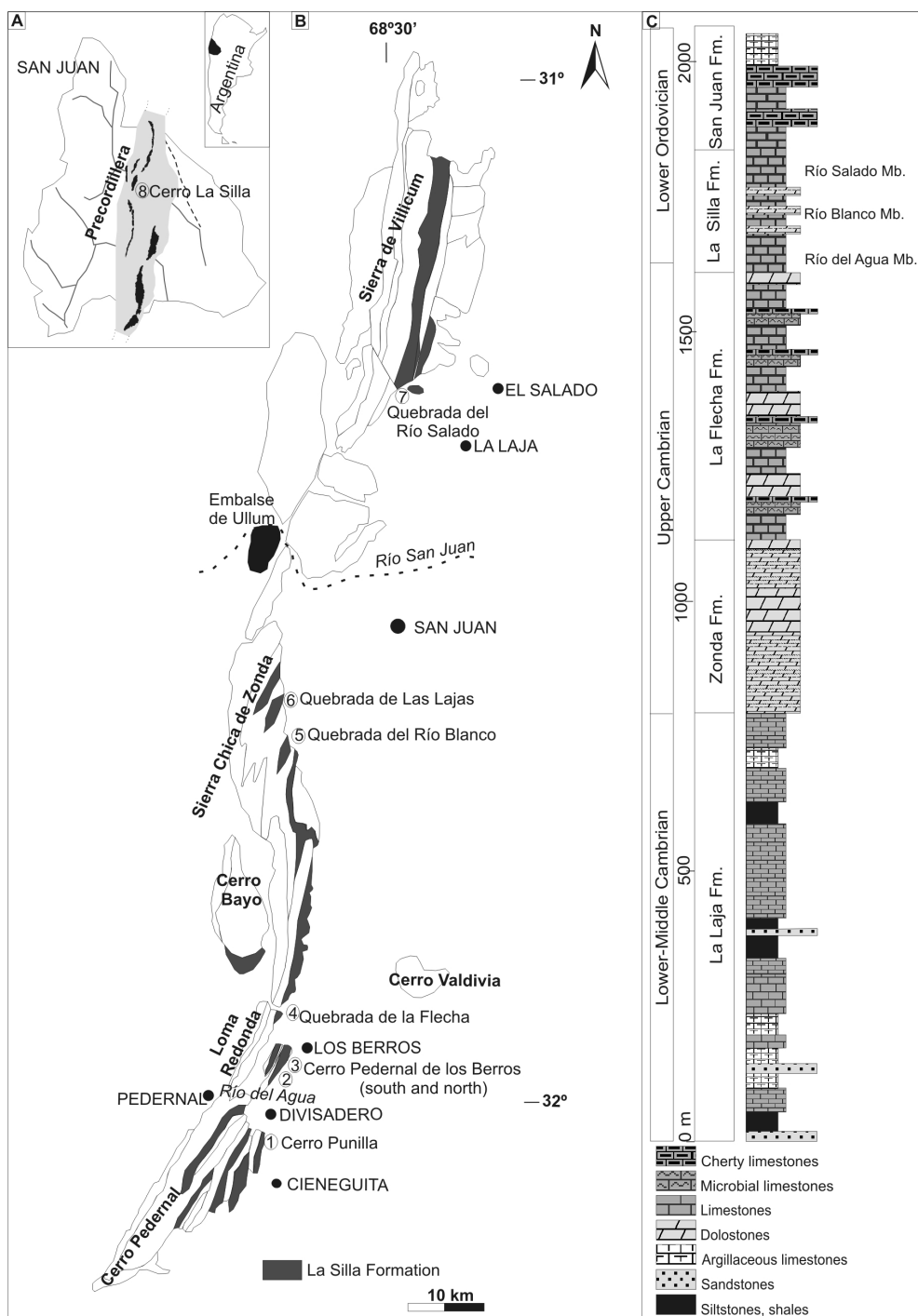
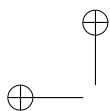


Fig. 1 – Study area in western Argentina. A – Map of the province of San Juan showing the location of the Precordillera terrane and the type



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cerning the type of chert, its location, characteristics and diagenetic history in this area known for heavy exploitation that require high quality for its industrial use.

The aim of this study is to recognize, describe and locate in the stratigraphic columns of the La Silla Formation the different types of chert and to establish the different pulses that provided silicification, related to the depositional environment in early stages.

LOCATION AND GEOLOGY OF THE AREA UNDER STUDY

The Argentine Precordillera is a geological unit located in the central-western part of Argentina, and is distributed among Mendoza, San Juan and La Rioja provinces. It is bordered to the west by the Cordillera Frontal and to the east by the western Sierras Pampeanas. Precordillera was subdivided into three separate belts according to its respective sedimentary successions and structural style: Precordillera Oriental (Ortiz and Zambrano 1981), Occidental, and Central (Baldi and Chebli 1969) (i.e. eastern, western, and central Precordillera).

The Precordillera Oriental, located in San Juan Province, has a regional structure composed of imbricated thrust sheets with westward vergence, elevated as stacked thrust sheets dipping to the east (e.g. Ramos 1988, 1999, Álvarez-Marrón et al. 2006). This study has been carried out in the southern sector of Precordillera Oriental. The southern sector is located at 31°S–32°S and along 68°30'W near the city of San Juan, including the Cerro Pedernal, Cerro Pedernal de Los Berros, Sierra Chica de Zonda and Sierra de Villicum (Fig. 1).

STRATIGRAPHY

The core of the Precordillera Oriental and Central is a 2000 m thick carbonate succession that was accumulated in a wide shallow platform developed during the late Early Cambrian through Middle Ordovician. The Cambro-Ordovician platform succession of the Precordillera Oriental consists of five formations (Fig. 1), from base to top: La Laja, Zonda, La Flecha, La Silla and San Juan (Keller 1999, Bordonaro 2003a, b).

The La Silla Formation was established by Keller et al. (1994) in order to describe thick-bedded, light-

of Jáchal (north of San Juan Province), reaching 360 m in thickness. For the southern sector, Ramos et al. (2007) established a three-fold subdivision based on the presence of dolostone beds, from base to top: Río Agua, Río Blanco and Río Salado members, respectively 85 m, 140 m and 81 m thick in their type section. The interbedding of dolostone (generally with chert nodules and lenses) and limestone distinguishes the Río Salado Member from the lower and upper members that are mainly massive limestones (Fig. 2).

FACIES OF THE LA SILLA FORMATION

Here, the array of carbonate rock types is grouped into eight recurring facies. The facies are described in order of their decreasing relative abundance in the La Silla Formation. Peloidal grainstone is consistent in all measured sections; peloidal grainstone is by far the most common facies, giving the La Silla Formation a monotonous appearance (Fig. 2).

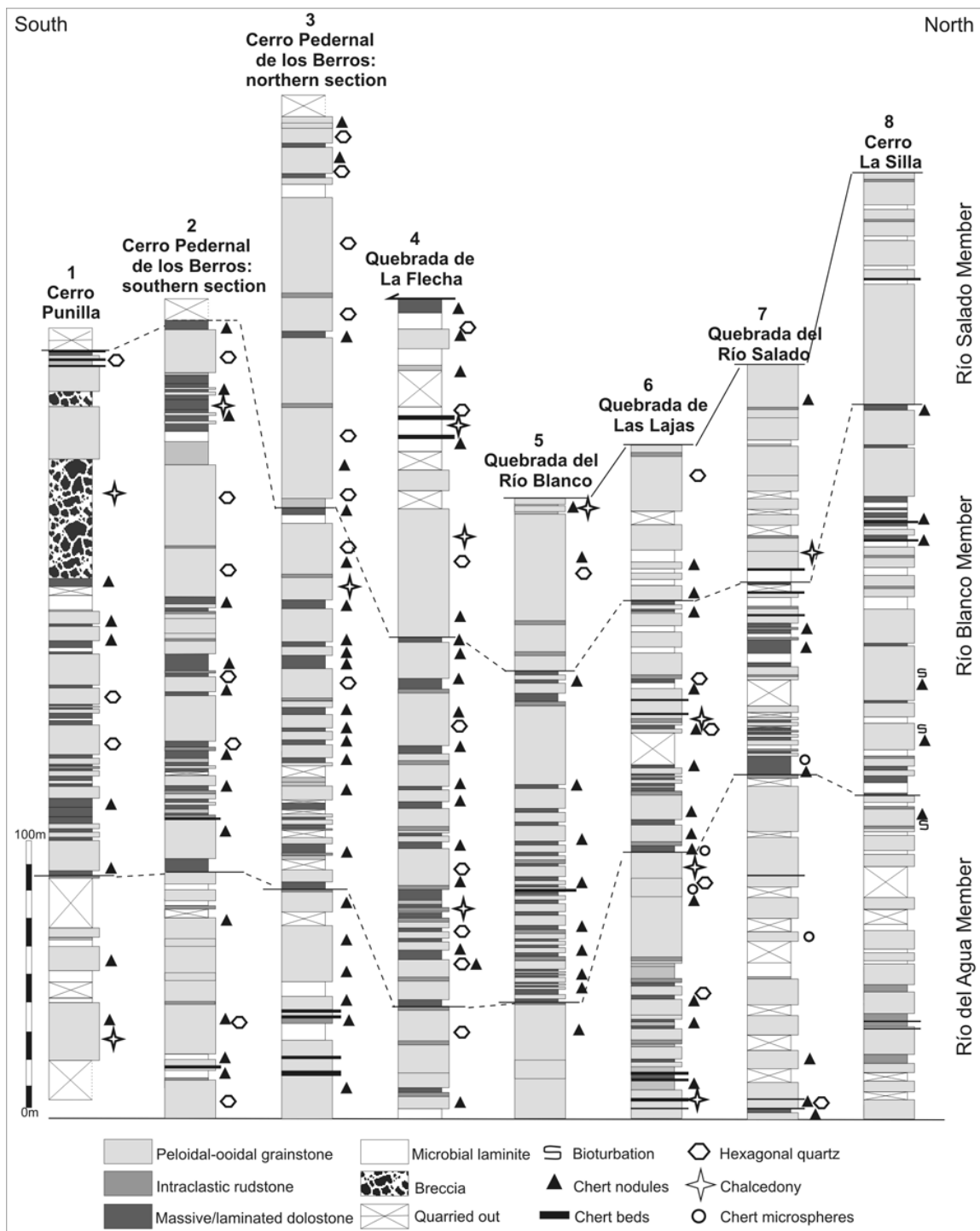
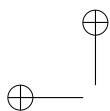
Facies 1: Peloidal grainstone

This facies is composed of generally well-sorted dolostone with a variable amount of admixed lumps; some bioturbated and abraded bioclasts and rare ooids and grapestone are also present. Local packstone textures rarely occur. Bedding is thick to massive and mostly tabular; margins are sharp. Grading is absent. Bioturbation is locally common and some burrows are attributed to *Thalassinoides*. Unidirectional cross-lamination, small ripples and small dunes occur locally. In places, especially in the Río Blanco Member, beds of fine-grained dolomite are replaced by massive, light, buff-coloured, crystalline dolomite. This is generally associated with black chert nodules and beds.

This facies represents deposition under more or less uniformly elevated energy, probably as shifting, accreting sand sheets and rarely as low-relief bars.

Facies 2: Laminated dolostone

Whitish, finely crystalline dolostone is locally interbedded with non-dolomitized Facies 1 and forms medium beds that are tabular to lenticular at met-





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as individual beds with sharp, erosive bases, or gradationally as overlying intraclastic rudstone (Facies 3) that has cut into Facies 1.

The lamination is wave- or current-induced rather than microbial, and is more likely to indicate sporadic events of significantly higher energy than background conditions.

Facies 3: Intraclastic rudstone

This flat-pebble conglomerate facies consists of sub-angular to rounded intraclasts composed of lime mudstone and/or grainstone-packstone, with a matrix of peloidal or ooidal grainstone and locally containing thin lime mudstone intercalations. Intraclasts are horizontal to gently imbricated. In some beds, the intraclasts are preferentially dolomitized. They form thin beds and meter-scale lenses about 10–50 cm thick.

This is the coarsest facies in the La Silla Formation, which is believed to have been formed by major erosive events after a period of relative quiescence, leading to cementation of some of the underlying sediments.

Facies 4: Microbial laminite

This facies consists of parallel planar to wavy laminae, sometimes doming to low-relief, laterally-linked hemispheroidal (LLH) stromatolites, forming beds a few centimetres thick and at least 1 m in lateral extent. In a single bed in Cerro La Silla, relief is up to 20 cm. Laminae are composed of millimetre-scale alternations of dolostone and mudstone or mudstone and peloidal grainstone. Locally laminae are accentuated by preferential silicification. No fossils are present.

The lack of associated high-energy sedimentary structures, the uniformity and laterally extensive planar lamination and occasionally developed fenestral fabrics are evidence of microbial accretion under protected, low-energy conditions.

Facies 5: Peloidal packstone

This facies is scarce and is generally thick-bedded, although locally it can be thin-bedded or somewhat nodular. It commonly possesses a mottling due to moderate

The peloidal nature of the framework grains indicates that this sediment was originally deposited under somewhat turbulent submerged conditions as Facies 1, but modified by extensive bioturbation under lower energy conditions.

Facies 6: Ooidal grainstone

This facies is composed of locally cross-laminated, sorted ooids with variably admixed grapestone, scarce peloids and bioclasts. This facies ranges from thin-bedded to massive, generally tabular beds.

Like Facies 1, the ooidal facies was originated by persistent but relatively gentle turbulence that led to flats and low-relief shoals.

Facies 7: Thrombolite boundstone

Thrombolite patch reefs are less than 0.5 m in diameter and thickness. They consist of thromboids flanked by burrowed to sporadically burrowed, peloidal grainstone-packstone, commonly with trilobite sclerites. Generally they display a radial-columnar fabric that imparts a mottled aspect due to contrasting texture and colour between the internal thromboids and matrix that in some cases is picked out by preferential dolomitization. The patch-reef boundstones formed in a shallow environment of moderate and intermittent turbulence.

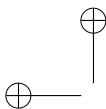
Facies 8: Mudstone

Lime mudstones and peloidal or bioclastic wackestone are very scarce as well. They form laminae interbedded with Facies 1 and Facies 3. Thus, they are too scarce to be portrayed in Figure 2.

The rarity of mudstone over the large portion of the platform studied indicates that very little lime mud was generated. The mud laminae observed within the other facies point to brief spells of quiet conditions and removal from suspension.

MATERIALS AND METHODS

This study is based on eight detailed sections: Punilla, Cerro Pedernal de los Berros, Quebrada



and especially the characteristics of silicification were identified and described. In order to perform specific analyses, a detailed sampling of the different lithologies recognized was obtained. Abundant thin sections (300) and polished sections (100) of rock samples were carried out in the laboratory of Petrology of the Universidad Nacional de San Juan (INGEO), Argentina. These sections were studied using a petrographic-calceographic microscope Olympus BH-2 with an Olympus digital camera.

Samples with interesting features related to silicification were chosen, and special thin sections (30) were made for cathodoluminescence (CL) analysis. The CL equipment used consists of a petrographic microscope NIKON E600 ECLIPSES W POL, with a NIKON (model H-III) camera. Cathodoluminescence module for optic microscope is CLmk4 8200 of Cambridge Technology LTD, with a hot-cathode technique. The analyses were carried out in the Laboratory of Sedimentary Geology (LAGESE) on the CL Laboratory (LCT) of the Department of Geology, Federal University of Pernambuco (UFPE), Recife, Pernambuco, Brazil.

CHERT CHARACTERISTICS

On a regional scale, chert is very common; it is found in all the stratigraphic sections. Chert is more abundant in dolostones, but it is also found in limestones. Because most of the dolostone banks have chert, it is very important in the Río Blanco Member (see Figs. 2 and 3).

On a local scale (meters to centimetres), chert can be seen as: beds with planar base and top, up to 1 m thick, in agreement with a stratification that can be laterally followed by several meters (Fig. 3A). It has lenses about 10–50 cm thick (Fig. 3B, C), also with lateral extension; ellipsoidal nodules of few centimetres; irregularly distributed mottles (Fig. 3D); and laminae. The colour ranges from white to black.

In a more detailed view, some of the chert types are associated to specific facies: nodules, for example, are more common in peloidal or ooidal grainstones; irregular mottles are connected with bioturbation, and laminae are associated with planar or stromatolitic microbial structures

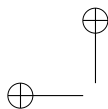
This quartz is so fine-grained that, when replace micritic grains (peloids, ooids), the shape of these grains is conserved; thus, they are called “ghosts”; megaquartz, grains $> 20\mu\text{m}$ (Fig. 4C); and chalcedony, which develop radial fibers until $700\mu\text{m}$ (Fig. 4D). The megaquartz presents a varied range of colours from gray to orange; when the grain size increases towards the inner side of the pore, it gives a drusy texture. The contacts among these crystals are planar to sub-rounded. Chalcedony has a radial texture and variable coloration. Another feature observed in thin sections is authigenic quartz, hexagonal to pseudo-hexagonal, with calcite inclusions in the core of the crystal. The maximum size of these crystals is $250\mu\text{m}$ (Fig. 4E). In some cases, there are silica microspheres with radial extinction, $200\mu\text{m}$ of average diameter (Fig. 4F). Microscopic chert is randomly distributed in all facies, without a specific pattern.

SILICIFICATION AND OTHER DIAGENETIC PROCESSES

As previously mentioned, the association between chert and dolostones is very common; at a microscopic scale, some typical characteristics are: dolomite crystals that develop between the contact of chert and limestone; dolomite rhombs floating in a siliceous matrix, and dolomite laminae crossing chert nodules.

Another important relationship that could be clearly observed under the microscope is between silicification and compaction. In the same thin section, it is possible to observe different responses of the carbonate grains to compaction (Fig. 5). While in one sector of the thin section peloids and ooids are completely replaced by chert, keeping their original shape (Fig. 5A), in another sector unsilicified carbonate grains have experienced a high degree of deformation (Fig. 5B). The same response is observed in examples of non-silicified dolomites vs. silicified dolomites.

The connection between chert and fractures is also noted. It is possible to observe silicification pulses contemporaneous with fracturing. This is better described in Cathodoluminescence section.



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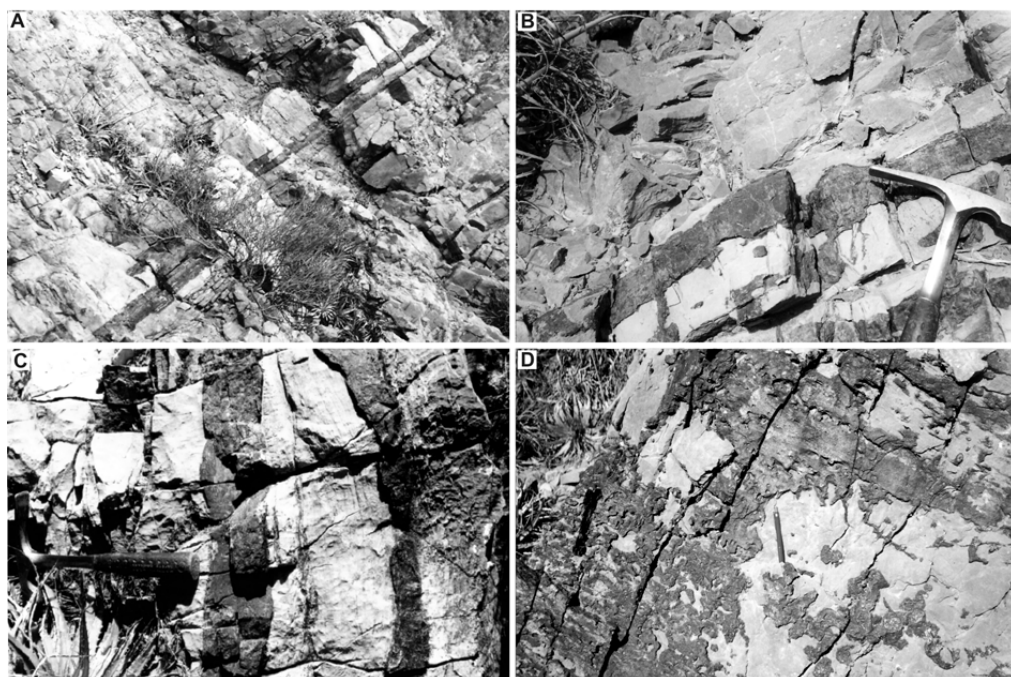


Fig. 3 – Chert in outcrop. A – Beds of black chert, Quebrada de Las Lajas. B – Lenses of chert, Quebrada del Río Salado. C – Beds of chert associated with a stromatolite (top to the left of the picture), Cerro Pederal de Los Berros, northern section. D – Bioturbation replaced by chert, Cerro La Silla. All pictures correspond to examples in Río del Agua member, in dolostone banks.

petrographic microscope. In Figure 6A, carbonate grains (OO) and the cement among them are totally replaced by micro-quartz (CQ) that gives a dark colour to the complete thin section. The fracture cuts diagonally, and it is filled by Mn calcite (bright colour); there is a later replacement of the quartz cement with calcite around the fracture; it is clearly observed in the rim of the ooids (arrow). Figure 6B shows the same thin section in a different sector; to the left of the picture, the non-luminescent micro-quartz that rims the grains (OO) is more intense than to the right. The fracture is filled with Mn calcite containing a fragment of dark filling (arrow) that probably corresponds to a previous siliceous filling. Later pulses of Mn calcite are found replacing the micro-quartz (C). In this example, it is clear that silicification was intense and affects the entire rock components. It is possible to observe in Figure 6C the relationship between silicification and fracturation and

group of fractures almost perpendicular to A, in as B and C. They are also sealed by a dark filling, indicating that they were the first ones to be formed. The fluid composition at the moment were silica rich. After A, B, and C, a new group of horizontal fractures (D and E) is formed; the thickest one (D) is sealed by Mn rich calcite. This indicates that there was a change in the fluids that circulated through these new fractures. Mn calcite was not precipitated in the first ones as they were sealed. It is observed that D was re-opened and sealed by a dark Fe rich calcite (vertical arrows). The fourth stage of fractures: F, G and H that have a different orientation to A. The F, G and H cut D and E and are sealed by calcite. There is a sector of F and A (vertical arrows) showing a non-luminescent filling, and a sector with light colour (calcite) indicating probably the reactivation of fractures. There are, at least, four fracture phases. The first and the last phases agree in the

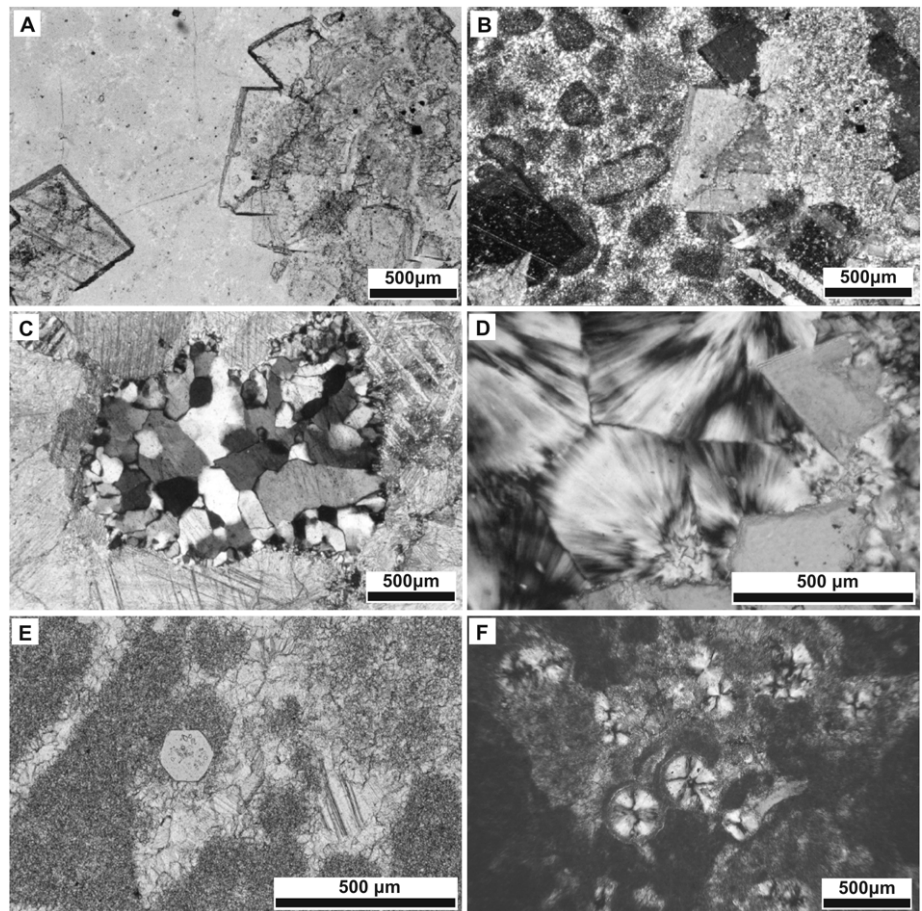


Fig. 4 – Different types of chert in thin section. A – Micro-quartz associated with well developed dolomitic rhombs. Plane-polarized light. B – Same section that A, crossed nicols. It is possible to see the carbonate grains (peloids) completely replaced by micro-quartz. C – Cavity occupied by mega-quartz, drusy texture. Crossed nicols. D – Fibrous chalcedony associated with dolomite. Crossed nicols. E – Autigenic hexagonal quartz. Crossed nicols. F – Silica microspheres. Crossed nicols.

rich calcite, and then possibly of dark Fe rich calcite. In Figure 6D there are other fractures in the same thin section as 6C. The oldest one corresponds to A and show dark calcite and silica filling. Then, B cuts A and is Mn rich calcite (bright colour). After that, C cuts B. Fractures A and C have a similar orientation. When C was generated, it became sealed by variable proportions of Mn calcite (light and dark areas). This also indicates that different stages of the crack-seal process in the frac-

DIAGENETIC INTERPRETATION

The distribution of nodules, lenses, and beds of chert conformable with the stratification and mainly associated with grainstones facies can be related with the permeability of the original sediments that favoured the circulation of silica rich fluids in an early diagenetic stage (Gao and Land 1991). Silicification took place before the compaction that destroyed the trace fossils in the case of bioturbations replaced by chert (Pon-



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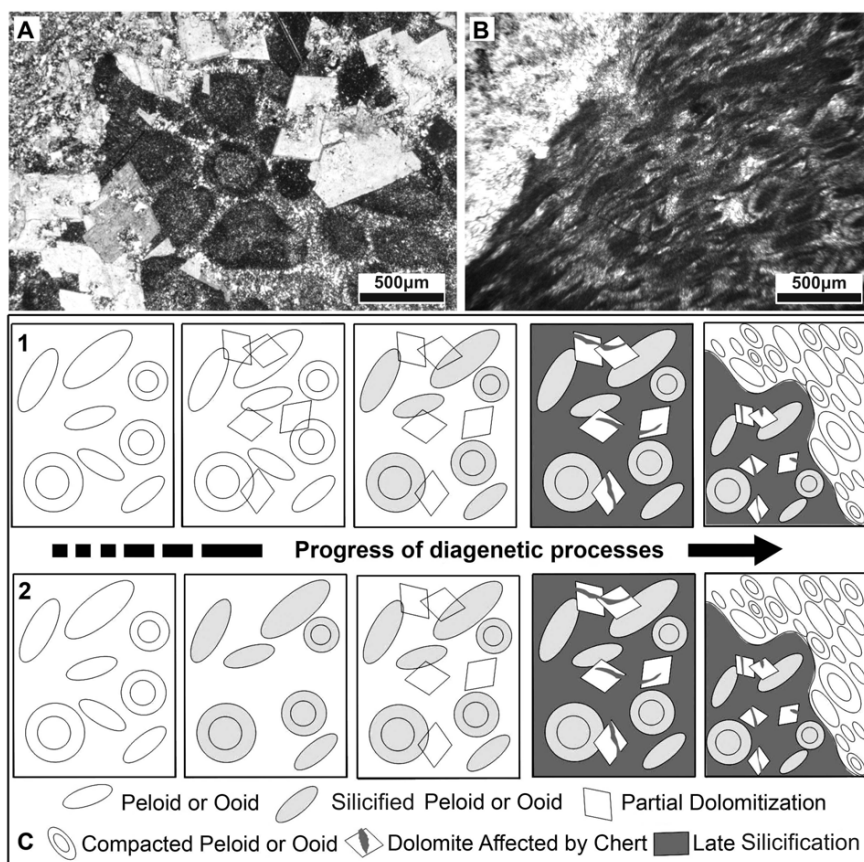


Fig. 5 – Chert and compaction. A – Thin section showing carbonate grains (peloids, ooids) totally silicified, associated with dolomite rhombs. Plane-polarized light. B – Same thin section of A, another sector, highly compacted carbonate grains in contact with chert nodule. C – Schematic models of the diagenetic evolution: 1 – Formation of early dolomite followed by an early selective silicification of the carbonate grains; another pulse of chert that constitutes the cement begins to affect partially the dolomite crystals. Intense compaction of non silicified components. 2 – Early silicification of the carbonate grains, partial dolomitization; later silicification that constitutes the cement and affects the dolomite. Intense compaction of non silicified components.

of chert associated with microbial structures, it is worth mentioning that the organic matter would act by absorbing the silica in the fluids. This occurs in the case of silicification during early diagenesis, when the bacterial activity and the oxidation of the organic matter are still active (Gao and Land 1991). The micro-quartz mainly replaces carbonate grains; the mega-quartz and chalcidony are mainly pore-filling cements. The micro-quartz and the hexagonal quartz are generally found

Dolomitization in the La Silla Formation is related to the high permeability of the host rock (Raviolo et al., unpublished data). Its already mentioned petrographical characteristics point to a very close relationship between this process and the silicification during early diagenetic stage. Dolomite rhombs in the contact between chert and limestone indicate a selective dolomitization during an early diagenetic stage, while silicification of the host sediments intercepts organic

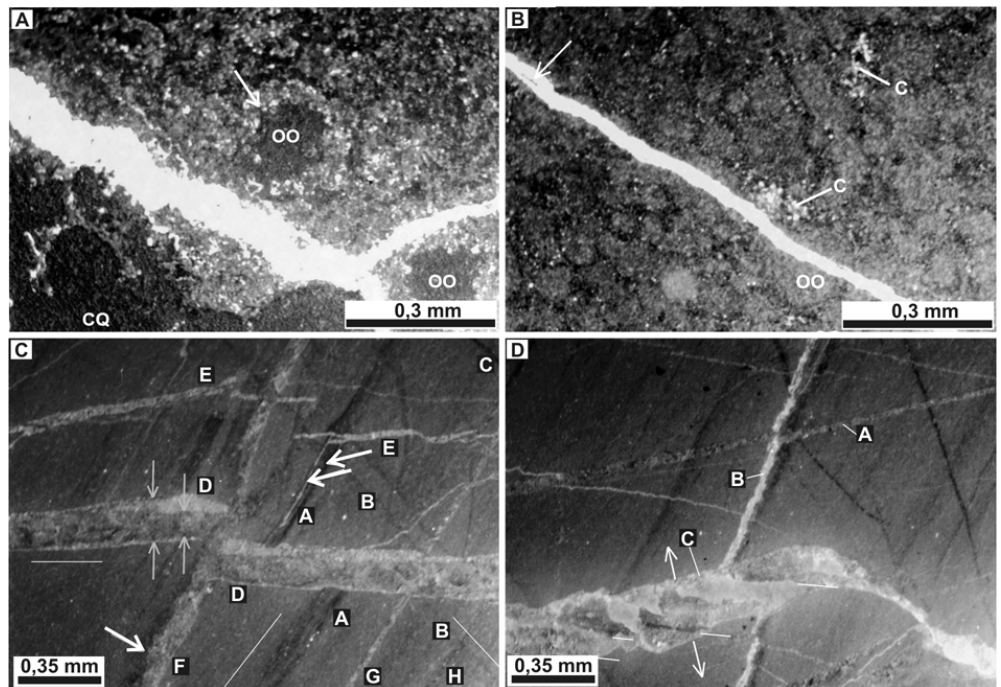


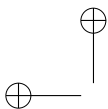
Fig. 6 – Cathodoluminescence. A – Carbonate grains (OO) and cement are strongly silicified (CQ), a big fracture is observed (Mn calcite filling). The arrow points to the later replacement of the quartz cement by calcite. B – Another sector of the same thin section of A. Light areas to the right are carbonate grains (OO), the quartz cement that rims the grains is more intense to the left of the picture. The fracture is Mn calcite, but it has a relict of the previous non luminescent filling (arrow). Later pulses of Mn calcite are replacing the micro-quartz (C). C–D: Different stages of fracturing in the same thin section.

nae crossing chert nodules; this indicates that the compaction and loss of water of the un-lithified carbonate took place after the silicification (Geeslin and Chafetz 1982, Gao and Land 1991). It is common to find dolomitic rhombs floating in a siliceous micro-quartz matrix; this characteristic has been considered by some authors as an evidence of dolomitization previous to silicification, and the selective replacement of the calcium carbonate of the host rock by silica (Dietrich et al. 1963, Harris and Meyers 1987). It seems easier to explain that euhedral dolomite crystals developed in a carbonate mud matrix rather than in a siliceous mass. However, there is a possibility of the process being the opposite: an early silicification of the matrix and a later replacement of this silicification by partial dolomitiza-

Silicification that preserves carbonate grains from strong deformation is interpreted as an early diagenetic stage process pre-compaction (Gao and Land 1991). Figure 5C shows that, independently of what kind of process takes place before, whether it is dolomitization or silicification, both processes are previous to compaction. This early pulse of silicification is obviously previous to spar cementation and fracturing (observed with CL), but later silicification pulses associated with fracturing were also observed.

DISCUSSION

There is no evidence of subaerial exposure or indications of environmental restriction associated to the chert loca-



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No spicules (or only very few) and very scarce bioclasts were found, which generates doubts about the origin of the silica. The fact that the sediments were affected by the silicification during early diagenesis may have caused the dissolution of these components (Maliva and Siever 1989); this means that, in these carbonates, one of the silica sources may be biogenic, although there are no organisms' remains.

Gao and Land (1991), in an example similar to this study, inferred that chert could have been formed during early diagenesis in marine environments, and they propose silica enriched seawater as a source of it. Another consideration given by these authors is the fact that the nucleation of chert is favoured by the sediment porosity and permeability.

Other possible sources of silica that cannot be discarded are those connected with the participation of meteoric water that, in contact with seawater, generates a favourable model of silicification in shallow platform carbonates. There are mentions of hydrothermalism connected with fracturation in the area of eastern Precordillera, in Paleozoic rocks (Ormeño 2002), and also the volcanic influence: there are K-bentonites in neighbouring areas of the basin (eastern and central belts of the Precordillera) of Lower Ordovician age (Huff et al. 2003, Huff 2008). Later chert stages may represent periods of dissolution and reprecipitation of silica present in the rocks since early diagenesis.

According to the descriptions made in the Cathodoluminescence section, it is clear that the fluids that circulated through these rocks were varying their composition, which could generate the different types of chert.

CONCLUSIONS

Chert is an important component in the carbonates of the La Silla Formation; different types of chert were identified, described, interpreted, and located in the stratigraphic sections.

Using petrographical analyses with cathodoluminescence support, it is possible to confirm the existence of an early pulse of chert connected with porous and permeable sediments in contact with silica rich seawater.

turation is also recognized.

ACKNOWLEDGMENTS

We are grateful to the Laboratório de Catodoluminescência, Departamento de Geologia, Universidade Federal de Pernambuco (UFPE), Recife, Pernambuco, for the cathodoluminescence analyses. We also thank J.M. Mabesoone for critics and suggestions. Comments from F.G. Aceñolaza and an anonymous reviewer helped to improve the manuscript.

RESUMO

A Formação La Silla (Neo Cambriano-Neo Tremadocense) é formada por depósitos carbonáticos da região da Precordilheira leste, Argentina. As faciologias encontradas em depósitos indicam um ambiente de deposição caracterizado por uma plataforma rasa. Até o momento, nenhum estudo específico da evolução diagenética dessas rochas. Este estudo envolve as características e distribuição da silicificação que afeta esta formação e apresenta os diferentes processos diagenéticos ocorridos, através de análises petrográficas (realizadas por catodoluminescência) e estratigráficas. Foi observado um pulso precoce de silicificação, anterior ao processo de compactação das rochas afetadas. Esta silicificação foi evidenciada pela presença de água do mar rica em sílica em contato com sedimentos porosos e permeáveis. Também foi observado um pulso de silicificação tardia, associado a eventos de fraturamento das rochas. O conhecimento adquirido sobre as características e a distribuição da silicificação nestes depósitos carbonáticos é importante, especialmente quando se considera que a Formação La Silla, na Província de San Juan, Argentina, é uma formação mais minerada para a produção de calcário.

Palavras-chave: carbonatos, chert, diagênese inicial, Precordilheira Oriental, Ordoviciano Inferior.

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