GEOLOGY AND GEOCHEMISTRY OF PALEOPROTEROZOIC MAGNESITE DEPOSITS (~1.8Ga), STATE OF CEARÁ, NORTHEASTERN BRAZIL

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ABSTRACT: Five important magnesite mines and small occurrences in the state of Ceará form a sequence of lenses that extend, discontinuously, for over 140km. The magnesite rocks are hosted by metadolomites with lutecite, sulphate nodules pseudomorphed by fiber-radiated quartz, scapolite and dissolution breccias. This metacarbonate sequence is more voluminous and more calcic in the southwestern extremity of the belt, but less voluminous and more magnesian towards the northeastern portion of the belt, the highest Mg contents being observed in the Alencar-Orós region. Magnesite deposits pass gradually into metadolomites and then to almost pure calcitic marbles westward the belt. This group is hosted in a greenschist to amphibolite-facies metavolcanic-sedimentary sequence crosscut by basic sills and granitic intrusions of variable size, form, composition and age (middle to late Proterozoic ~550Ma).

Two types of magnesite marble may be distinguished: (1) medium-grained (1 to 9mm) and (2) sparry -magnesite marble (1 to 15cm). The latter displays wide textural variation (porphyric, rosette, layered and pisolitic types) and exhibits remnants of the original sedimentary features. The sparry crystals, in spite of their deformation, are hypidiomorphic and pisolitic. The colors vary from white to light or dark gray, or even red. The dark banded term presents traces of microfossils and stromatolites structures. The medium-grained magnesite marble, on the other hand, shows more homogeneous texture and color and anhedral crystals are more abundant.

The sparry-magnesite marble is less enriched in SiO₂, Fe₂O₃, Al₂O₃ and CaO and richer in MgO than the medium-grained ones. The magnesitic marbles display positive Ce, and negative Eu anomalies. This suggests a shallow marine platform environment with continental, reduced influence (lagunar). These magnesitic marbles also show positive Ce and Eu anomalies in relation to the present seawater, suggesting compositional differences, materialized mainly by an enrichment of these elements in the past seawater.

Fluid inclusions in the medium-grained magnesites of the Riacho Fundo deposit are aqueous inclusions, while in the sparry magnesite deposits, particularly in Cabeça de Negro, aquo-carbonic inclusions dominate. Hydrocarbons, however, are found in both cases.

The calcitic marble, deposited on open-marine environment, displays positive ⁰¹C (+0.5 to 2.1 %o PDB), while dolomitic to dolostone marbles, deposited on less open marine environment, display negative shift (0.7 to ~3.2% PDB). This ¹³C fluctuation is within the range for carbonates deposited around 1.8Ga.

The depositional environment of these carbonates is close to a paralic system, lagoon, with strong evaporitic conditions. The depressions were of variable depth and lengths and could be isolated, in particular by Stromatolitic barriers, dried and flooded by seawater with continental inflows. The largest and deepest ones correspond to the sparry magnesite deposits. These magnesites are located in a lateral way to almost pure calcitic marbles, through dolomitic marbles. This points to a process of chemical differentiation within a paralic system, from open sea to landwards, more calcic in the first to more magnesian in the confined environment, in which lagoon waters are progressively purified from Ca through preferential precipitation of calcic carbonates and secondly of gypsum/anhydrite, which increases the Mg/Ca ratio, and lead carbonate deposits towards the magnesite pole. These metacarbonates also reveal a fractionation of the Light REE, starting from the calcitic, through the dolomitic to magnesitic marbles. In the calcitic marbles, REE are in association with calcitic marbles, while in magnesitic marbles, they seem to be in association with organic and/or soluble complexes. The magnesitic marbles are of sedimentary origin and underwent important diagenetic evolution before being metamorphosed during the Brasiliano orogenic cycle.

INTRODUCTION

Magnesite, as an accessory phase or forming small bodies without economic importance, may be found in a series of geological environments, from the Archaean to the Cenozoic. At present, magnesite is associated with lacustrine deposits of arid climate (Elton lake, ex. URSS; Tuz Golu, Turkey) and with saline to hypersaline paralic deposits (Coorong, Australia; sabkha El Melah, Tunisia; sabkhas of the Pirate coast, Arabic Gulf) (Müller et al. 1972; Von der Borg 1965; Busson and Perthusot 1977). It is also associated with calcretes (Australia), with laterites developed on ultrabasic rocks, with contact metamorphic zones and with hydrothermal veins.

The largest magnesite deposits are, however, hosted by Proterozoic and Paleozoic terrains associated to rocks of sedimentary origin, known as of Veitsch type (Pohl and Siegl 1986; Pohl 1989). The origin of the magnesite deposits of this type, however, is controversial and two hypotheses are known (1) syngenetic formation; (2) epigenetic formation or metasomatic.

A genetic model that assumes magnesite to be syn-
sedi\ntary or formed during early diagenesis, if dolomite is a primary precipitated phase, is based on recent sedimentary systems (e.g., Rumpf 1873 in Pohl and Siegl 1986; Nishihara 1956; Gomes de Llarena 1968; Valdiya 1968; Qu\nméneur 1974; Guil\nlo 1973, 1980; Ch\ny d'Albissin and Guil\nlo 1986, 1988; Pohl and Siegl 1986; Pohl 1990; Velasco et al. 1987; Guil\nlo and Lefol\nle 1988; Qiusheng 1988; Almeida 1989; Tufar et al. 1989, Joshi et al. 1993, Melezhik et al. 1997, Melezhik et al. 2001).

A metasomatic hypothesis in which magnesite results from the introduction of ions of Mg2+ during metamorphism of limestones or dolomite precursors, has been proposed by several authors (e.g., Koch 1893 in Pohl and Siegl 1986; Bodenlos 1948, 1954; Morte\nli et al. 1982, 1983; Bone 1983; Aharon 1988; Morte\nli 1989; Kralik et al. 1989; Möller 1989; Preinfalk et al. 1993; Lugli et al. 2000).

Hypotheses on the origin of magnesite associated to metasedimentary rocks are, therefore, numerous and, in general, based on particular characteristics of the studied deposits, normally envolving one single type of occurrence of magnesite.

There are two important types of precambrian magnesite deposits in the state of Ceará. They are 40km apart, but they are related to the same lithostratigraphic unit: (a) fine- to medium-grained and (b) coarse-grained or sparry magnesite deposits.

The present study, based on fluid inclusions, elemental and isotope geochemistry of magnesite deposits of the Ceará state, offers an opportunity to advance with the knowledge of the geology and genesis of precambrian magnesite deposits associated with metasedimentary rocks.

**GEOLOGIC FRAMEWORK OF THE OROS FOLD BELT**

The Orós foldbelt is part of the set of proterozoic foldbelts that comprises the Borborema province, constituted by supracrustal rocks of the late Paleoproterozoic within archean or early paleoproterozoic rocks of the basement. The Orós foldbelt forms a sigmoidal, linear zone whose structural trends vary from ENE-WSW in its western portion, to N-S in the central one, and to NE-SW in its northern extremity. The belt extends for over 600 km with a width that varies from 2 to 13km.

The basement is composed of me\no- to leu\nocratic by mesoproterozoic and neopaleozoic granites and by meso- to leucocratic by mesoproterozoic and neopaleozoic granites and by mesoproterozoic and neopaleozoic phosphorite deposits associated with metasedimentary rocks.

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The supracrustal sequence is dominated by metasedimentary rocks and basic to acidic metavolcanics. The metasedimentary rocks are represented by schists and aluminous quartzites discontinuously covered by marine carbonates and evaporites, represented by calcite, dolomite and magnesite and calc-silicate rocks. The schists comprise andalusite-rich schists, garnet-staurolite-andalusite schists, two-mica gneiss-schists, and feldsparitic schists or metagreywackes. The andalusite-rich schists and the garnet-staurolite-andalusite schists are found in the eastern portion near the base of the sequence, while the other lithological types are located in the upper portion of the system.

Quartzites are usually in topographic relief and intercalated in schists as discontinuous, tens of meter thick, few kilometers long bodies (e.g. Orós and Franco hills) and as small, cross-stratified, few meter thick, lenticular bodies within the metapelitic sequence. They are very abundant in the northeastern portion of the belt and, progressively, decrease in volume and extension towards the southwestern extremity of the belt. The carbonate sequence, on the contrary, is more abundant and more calcic in the southeastern extremity of the belt (Pio IX and Aiuaba regions), becoming more magnesian and decreasing in volume and extension, in the northeastern portion of the belt (e.g. Alencar-Orós region). These are features common to a mixed paralic-deltaic system.

The metavolcanic-sedimentary sequence was deformed and metamorphosed under greenschist to amphibolite facies with narrow isoclinal folds, with vertical axial plane foliation and subhorizontal stretching lineations consistent with a Brasiliano transpressional regime. Further details on the geology of this area are found in Sá (1991), Parente (1995) and Parente and Arthaud (1995).

**GEOLOGY OF THE MAGNESITE DEPOSITS**

The main deposits and some magnesite occurrences in the state of Ceará form a string of lenses that integrates a discontinuous carbonate rock set, 140km long, between Pio IX in the state of Piaui, to the west and Orós, Ceará state to the east (Fig. 1). All of these metacarbonate rocks are interlayered in the green-schist to amphibolite facies metavolcanic-sedimentary sequence intruded by mesoproterozoic and neopaleozoic granites and by neoproterozoic basic-ultrabasic plutons.

Thermobarometric studies on aluminous schists (Sá 1991) with or without staurolite, in contact with sparry magnesite marbles, yielded temperature values, respectively, between 443 and 507°C and 436 and 485°C, and pressure P around 3kbar. U-Pb dating for some rhyolites intercalated with
Figure 1. Geological map of the Oros Belt (modified from Sa' 1991 and Parente 1995).
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metasedimentary rocks revealed ages around 1.8Ga (Sá 1991; Van Schmus et al. 1995; Landim 2000), corresponding to the sedimentation age.

Two types of magnesitic marbles have been distinguished: (a) sparry magnesitic (1 to 15cm long magnesite crystals) and (b) medium-grained magnesitic marbles (1 to 9mm crystals).

CHARACTERISTICS OF THE SPARRY MAGNESITE DEPOSITS

The sparry magnesite deposits (Alencar, Malhada Vermelha and Cabeça Negro) and some occurrences are located in the central-eastern portion of the belt between Alencar and Orós. They form a 25km-long string of discontinuous lenticular bodies. The length of these lenticular bodies vary from 20 to 900m long and the width, from 10 to 200m. The largest deposits are found in the Alencar region, but those with best preserved primary structures are in the Cabeça de Negro region.

The magnesites are found in association with dolomitic marbles, where one verifies locally the development of lutecite, scapolite, sulfate nodules pseudomorphically replaced by fiber-radiated quartz crystals, dissolution breccias and dolomitic marbles with petal-shaped texture. All of this association indicates that evaporitic conditions prevailed in the wall rocks of the magnesites. Further details on the formation of evaporitic older associations are found in Shaw (1960), Hietanen (1967), Serdyuchenko (1975), Badham and Stanworth (1977), Hogarth and Griffin (1978), Leake and Farrow (1979), Arbev (1980), Friedman (1980), Friedman and Shukla (1980), Vanko and Bishop (1982), Papaioanou and Carotsieris (1993), Svênningsen (1994) and Parente et al. (1996).

The transition of sparry magnesitic marbles into dolomitic marbles is gradual and well-defined but, sometimes, complex when a mixture between these carbonate rocks occur. This suggests in situ mixture between these two lithological types or an incomplete replacement of one by the other. Sparry magnesitic veins are seen crosscutting metadolomites.

The sparry magnesitic marbles exhibit textural variations where porphyritic, rosette, banded or palisade varieties are common. The last one preserves some of the original sedimentary structures. Traces of microfossils are found with the banded textures, while stromatolitic structures are found with the other textural varieties. The color of these rocks vary from white, to light to dark gray, pink to brick-red. Crystals are usually subidiomorphic to subautomorphic and their size varies from 1 to 15 cm.

Some magnesitites show up to 21% SiO₂ and have talc and chlorite while others are Fe-enriched and show iron oxide minerals and syn-metamorphic pyrite which appears in veins or as nodules.

The two small lenticular deposits of the Alencar region (Fig. 2) exhibit stromatolitic relics and microfossils, besides irregular pyrite veins, with nodular texture. They also exhibit silica-enriched layers with chlorite and talc or some iron-enriched ones. This observation leads to the assumption that these deposits may represent a marginal lagunar zone with periodic inflow of continental water containing silica and probably iron. The stromatolitic facies corresponds either to stromatolite barriers in the lagunar entrance or to intralagunar formations.

The Malhada Vermelha deposit (Fig. 3) is also characterized by iron oxide and silica enrichment. In this deposit, the transition between the magnesites and the dolomitic marbles is marked by a thin layer of metadolomite (1m thick) with quartz nodules in a ferruginous and brecciated
MAGNESITE DEPOSITS (~1.8Ga), STATE OF CEARÁ, NORTHEASTERN BRAZIL

Figure 3. Malhada Vermelha deposit. Geological setting of the main magnesite deposits of the Orós foldbelt (Ceará, NW Brazil).

Figure 4. Cabeça de Negro deposit. Geological setting of the main magnesite deposits of the Orós foldbelt (Ceará, NW Brazil).

These breccias appear to record a temporal-spatial hiatus between the dolomitic and the magnesitic carbonates. One can interpret this as an indication of a late accumulation of continental sabkhas in the contact zone, accompanied by dissolution and/or redistribution of the evaporites.

The Cabeça de Negro deposit shows boudinated mega- and micro-structures, where the magnesites, enclosed by metadolomites with scapolite, correspond to the more competent terms or less deformed ones in this set (Fig. 4). Magnesitic marbles exhibit, in general, palisade texture marked by alternance of magnesite crystals with dolomitic matrix. These nodules are ellipsoidal, with major axis between 1 and 10cm. They are constituted by fiber-radiated quartz as rosettes, indicating they are sulphate pseudomorphs replaced by silica. There are also even more brecciated metadolomites, typical of dissolution breccias found in evaporite deposits. In these breccias, one finds lutecite crystals with dolomite inclusions, some of them automorphic and cubic, indicating they are halite pseudomorphs replaced by dolomite.
dark millimetric zones, enriched in pelitic and/or organic material. The magnesite crystals are of the pinolitic type, sub-automorphic and with an average size of 1 cm, exhibit a bi-polar growth in symmetry to pelitic and/or organogenic levels (Fig. 5a). These crystals are deformed, curved and, under the microscope, are marked by wavy extinction, deformation bands and recrystallization into subgrains, and this indicates that they are pre-tectonic crystals. The color of these rocks varies from white, light to dark gray, to pink to brick-red.

The predominance of small lenticular magnesitite with palisade structures/textures with metadolomites, appear to reflect rhythmic variation in the middle of the carbonate sedimentation. These variations can be associated with other phenomena, oscillations of the sea level. Besides these features, there are also Al-silicate and Fe-enriched magnesite and metadolomite levels with detrital zircon which could indicate freshwater inflow during the formation of this deposit.

All of these features indicate that sparry magnesitic marbles formed in paralic systems, lagunar with marked evaporitic tendency, receiving periodical inflow of freshwater.

**CHARACTERISTICS OF MEDIUM-GRAINED MAGNESITE DEPOSITS**

The medium-grained magnesitic deposits are represented by small lenticular bodies in the central-western portion of the belt (Jucás region), known as Riacho Fundo and

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**Figure 5.** (A) Outcrop of sparry magnesitic marble with palisade structure. S0 // S1 stratification marked by thin layers of organic matter or dark gray pelite in alternance with light gray sparry magnesite. Cabeça de Negro deposit. Notice the hammer at the left upper side. (B) Sparry magnesitic marbles with deformed palisade structure. Bent magnesite crystals apparently indicate left-lateral movement.

**Figure 6.** Riacho Fundo deposit. Geological setting of the main magnesite deposits of the Orós foldbelt (Ceará, NW Brazil).
Torto (Figs. 6 and 7). They occupy two small basins, presently separated by a structural accident, which preclude comparing them stratigraphically: the metavolcanic acidic rocks and Jucás porphyritic metagranites represent the central portion of this structural accident. The Riacho Fundo magnesite deposits display a lenticular shape and irregular thickness, due to a pinch-and-swell megastructure, partially controlled by ductile shear zones. This well-exploited deposit is about 100m long and about 30 to 50m thick, and its extremities are covered by cenozoic sediments. It is intercalated in light gray metadolomites, in basic schists with biotite, phlogopite and tremolite and in scapolite-bearing calc-silicate rocks.

From the petrographic viewpoint, the magnesitic marbles are very homogeneous and characterized by a fine to medium-grained dominant facies (1 to 8mm), white color, sometimes with light to dark gray patches. Locally, some textural/structural variations are observed, and subrounded magnesite grains, 3 to 6mm in diameter, are seen in a matrix with talc and chlorite (Fig. 8a) or in veins filling extensional fractures opened during deformation. In this case, the magnesitic marble is characterized by 1 cm-long, translucid, prismatic magnesite crystals, developed perpendicular to the walls of the talc-chloritic levels.

Under the microscope, the fine- to medium-grained facies is characterized by an allotriomorphic, granoblastic texture essentially composed by magnesite, with talc, chlorite and pyrite accessory phases. The largest magnesite crystals, up to 8mm long, are marked by sutured boundaries, wavy extinctions, deformational bands and recrystallization and are usually clouded with small dark inclusions (organic matter?), oriented or not. Small magnesite grains, usually pure, display straight boundaries or slightly bent and triple junctions and are product of recrystallization. Subrounded magnesite, sometimes sigmoidal, when deformed displays a pyrite-, talc- and chlorite-rich nucleus, besides fluid inclusions disposed in radial lines (Fig. 8b). This spheroidal texture, only seen in this deposit suggests three possibilities: (a) replacement of oolitic structures or pre-existing carbonate oolites (radial magnesian calcite);
Table 1. Chemical analyses of major elements (%) of meta carbonate rocks from the Orós foldbelt.

<table>
<thead>
<tr>
<th>Calcitic marble</th>
<th>Dolomitic marble</th>
<th>Magnesitic marble</th>
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<tbody>
<tr>
<td>%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CaO</td>
<td>49.8</td>
<td>29.9</td>
</tr>
<tr>
<td>MgO</td>
<td>3</td>
<td>1.5</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>0.69</td>
<td>0.12</td>
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<tr>
<td>Fe₂O₃</td>
<td>0.45</td>
<td>0.41</td>
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<tr>
<td>FeO</td>
<td>0.14</td>
<td>0.14</td>
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<tr>
<td>SiO₂</td>
<td>5.7</td>
<td>6.9</td>
</tr>
<tr>
<td>MnO</td>
<td>0.01</td>
<td>0.01</td>
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<tr>
<td>P₃O₅</td>
<td>0.05</td>
<td>0.05</td>
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<tr>
<td>TiO₂</td>
<td>0.05</td>
<td>0.05</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiO₂</td>
<td>43.4</td>
<td>46.4</td>
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<tr>
<td>Al₂O₃</td>
<td>0.11</td>
<td>0.11</td>
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<tr>
<td>Fe₂O₃</td>
<td>0.33</td>
<td>0.53</td>
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<tr>
<td>FeO</td>
<td>0.42</td>
<td>0.42</td>
</tr>
<tr>
<td>SiO₂</td>
<td>1.4</td>
<td>1.8</td>
</tr>
<tr>
<td>MnO</td>
<td>0.23</td>
<td>0.29</td>
</tr>
<tr>
<td>P₃O₅</td>
<td>0.11</td>
<td>0.05</td>
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<tr>
<td>TiO₂</td>
<td>0.18</td>
<td>0.05</td>
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(b) pseudomorphs of crystals precursors of magnesite, like nesquehonite or huntite; (c) the original shape of magnesite.

The Torto mine is characterized by two small lenses, roughly sigmoidal, with up to 400m long and up to 120m wide, trending NE-SW, and dipping subvertically. The transition between these two lenticular bodies is covered by clayey soil. These lenticular bodies are bordered to the south by metadolomites, pyrite-rich graphite-schists, quartzites, calc-silicate rocks and porphyritic metabasite, while, to the north, one finds thin films of metarhyolites and mylonitized quartzites. From the petrographic viewpoint, two facies are identified: a fine-grained facies (1-2mm) located in the center of the quarry and a very deformed, equigranular, medium-grained (3-5mm) in the southern portion of the southern lenticular body. Both are dominated by magnesite; talc and chlorite are secondary minerals as well as dolomite in veins that filled one-cm wide fractures.

MAJOR, TRACE AND RARE EARTH ELEMENT GEOCHEMISTRY

A total of twenty two carbonate samples in this study were analyzed in the GEOSOL Laboratories (GEOLAB), in Belo Horizonte. SiO₂, Al₂O₃, total FeO, CaO, MgO, MnO, P₂O₅ and TiO₂ have been determined by X-ray fluorescence in samples fused with Li₂B₄O₇. FeO was analyzed after reaction with HF + H₂SO₄ in a platinum crucible, release of CO₂ and titration of FeO with KMnO₄ and boric acid. Rare-earth elements were analyzed in an ARL ICP 3500.

Among these samples, 5 are from calcitic marbles of the western zone of the belt, between Cruzeta (Ceará) and Pio IX (Piauí); 9 samples are from dolomitic marbles, that are wall rocks of the sparry magnesites, in the central-eastern portion of the belt, next to the Malhada Vermelha and Cabeça de Negro deposits, and 8 are from sparry magnesites from the Cabeça de Negro deposit. Among the dolomitic marble samples, 3 are of brecciated dolomitic marbles, cemented by sparry calcite (Tables 1 and 2).

**Major Element Behavior**

Major elements in the metacarbonates under consideration have been plotted in the Fe₂O₃+FeO-CaO – MgO (Fig. 9a) and Fe₂O₃+FeO+SiO₂-CaO – MgO (Fig. 9b) diagrams. These rocks plot preferentially in the magnesitic, dolomitic and calcitic marble fields.
In the sparry magnesitic marbles, MgO varies from 39.20 to 46.60% with the lowest contents in the transition zones to the metadolomites. In turn, CaO varies from 0.41 to 8.40% with the highest values in the contacts with the dolomitic marbles. SiO₂ varies from 0.47 to 7.10%; Al₂O₃ from 0.11 to 1.30% and Fe₂O₃ values are lower than 1% (0.14 to 0.98%). MnO varies from 0.03 to 0.08% with highest values found next to the dolomitic marbles. P₂O₅ presents low contents and usually around 0.05% while TiO₂ varies from 0.05 to 0.07%.

Dolomitic marbles exhibit MgO from 5.70 to 23.10% (avg. 17.69%) the lowest values found in calciferous dolomitic marbles. SiO₂ varies from 0.92 to 10.60% (avg. 3.70%); Al₂O₃ ranges from 0.06 to 1.50% (avg. 0.55%) and total FeO lower than 2% (0.24 to 1.62). CaO varies from 25.70 to 48.30% (avg. 33.39%) and MnO, from 0.02 to 0.37% (avg. 0.12%) much higher than values found in the associated to the sparry magnesites. The P₂O₅ varies from 0.05 to 0.11% (avg. 0.06) and TiO₂ range from 0.05 to 0.18% (avg. 0.07%).

The calcitic marbles located to the west of the belt display CaO from 47.40 to 54.10%. The lowest contents are in the samples next to the dolomitic marbles. SiO₂ is relatively low, varying from 0.79 to 5.70%, typical of platalinal limestone (e.g. Veizer et al. 1990); Al₂O₃ varies from 0.12 to 1.10% and total FeO is lower to 1% (0.15 to 0.73%). MgO values are progressively higher from west to east and ranges from 0.65 to 4.60%. MnO ranges from 0.01 to 0.02% whereas P₂O₅ and TiO₂ display average values around 0.05%.

In the magnesitic marbles, SiO₂ displays a strong positive
SiO$_2$+Fe$_2$O$_3$+FeO

In the dolomitic marbles, SiO$_2$ shows positive correlation with Al$_2$O$_3$, Fe$_2$O$_3$ and MgO and negative with MnO, although with a correlation factor (r) lower than that for magnesites (Table 4). Fe$_2$O$_3$ varies sympathetically with MnO and both with CaO present a negative correlation with MgO. The weak correlation, positive or negative, between Fe$_2$O$_3$ and Al$_2$O$_3$ and between Fe$_2$O$_3$ and SiO$_2$ demonstrate that the Al-silicate minerals correspond to Fe-poor chlorite (clinochlore) or to illite, as depicted from Fig. 10a. Other oxides like P$_2$O$_5$ and TiO$_2$ do not display co-variation with MgO as shown by a low correlation factor (r < 0.3, Table 3).

In the calcitic marbles, SiO$_2$ displays positive correlation with Al$_2$O$_3$, Fe$_2$O$_3$ and MgO (Table 5). Fe$_2$O$_3$ presents a negative correlation with MnO, as well as CaO vs. MgO. The positive correlation between Fe$_2$O$_3$ with Al$_2$O$_3$ and Fe$_2$O$_3$ with SiO$_2$ suggests that the Al-silicate phase associated with the limestones corresponds to a chlorite, more Fe-enriched, or to an illite, as one can see in Fig. 10a. P$_2$O$_5$ and TiO$_2$ show very low correlation with MgO (r < 0.3).

The transition between the calcitic to magnesitic marbles is attained through dolomitic marble, marked by a sharp decrease of Ca from the calcitic into the sparry magnesitic marbles (Fig. 10b). Parente (1995) also observed a decrease from silica and alumina from metadolomites towards magnesites. The decrease of silica and alumina in a carbonate sequence may reflect a chemical differentiation.
process (e.g., Pohl and Siegl 1986), because Al and Si are tied to the clay fraction of the carbonate rocks while CaO gradually decreases from the calcitic to the magnesitic marbles.

Mn seems to decrease from the calcitic marbles to magnesites (Fig. 10c). However, if we eliminate three samples corresponding to calcitic dolomitic marbles, a progressive Mn enrichment from the calcitic to the magnesitic marbles is observed (Fig 10d). According to Niedermayer et al. (1989), Fe and Mn contents are higher in continental or meteoric water than in seawater. Regarding that the dolomitic calcitic marbles represent brecciated material with calcitic cement, the abnormal concentrations in these rocks may be related to a secondary enrichment. On the other hand, in the normal sequence of the carbonate rocks, Fe$^{3+}$ presents more irregularity and higher contents next to the magnesites. The enrichment of Fe$_2$O$_3$ and MnO next to the magnesitic marbles may be associated with the more soluble character of the Mn and Fe ions in an alkaline environment that makes them to precipitate together with Mg in more differentiated stages of the carbonate sequence.
Table 4. Correlation matrix for dolomitic marbles.

<table>
<thead>
<tr>
<th></th>
<th>CaO</th>
<th>MgO</th>
<th>Al₂O₃</th>
<th>FeO</th>
<th>SiO₂</th>
<th>MnO</th>
<th>P₂O₅</th>
<th>TiO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO₂</td>
<td>-0.02</td>
<td>-0.09</td>
<td>0.78</td>
<td>0.71</td>
<td>0.56</td>
<td>0.26</td>
<td>0.22</td>
<td>0.97</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.07</td>
<td>-0.17</td>
<td>0.66</td>
<td>0.74</td>
<td>0.53</td>
<td>0.19</td>
<td>0.29</td>
<td></td>
</tr>
<tr>
<td>MnO</td>
<td>0.93</td>
<td>-0.97</td>
<td>-0.12</td>
<td>0.40</td>
<td>0.44</td>
<td>-0.24</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiO₂</td>
<td>-0.48</td>
<td>0.31</td>
<td>0.62</td>
<td>0.58</td>
<td>0.16</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FeO</td>
<td>0.16</td>
<td>-0.22</td>
<td>0.49</td>
<td>0.42</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>0.13</td>
<td>-0.29</td>
<td>0.67</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>-0.39</td>
<td>0.26</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MgO</td>
<td>-0.98</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

Table 5. Correlation matrix for calcitic marbles.

<table>
<thead>
<tr>
<th></th>
<th>CaO</th>
<th>MgO</th>
<th>Al₂O₃</th>
<th>FeO</th>
<th>SiO₂</th>
<th>MnO</th>
<th>P₂O₅</th>
<th>TiO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO₂</td>
<td>-0.81</td>
<td>0.84</td>
<td>0.82</td>
<td>-0.19</td>
<td>0.61</td>
<td>0.44</td>
<td>-0.25</td>
<td>0.34</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>-0.25</td>
<td>0.28</td>
<td>0.40</td>
<td>-0.20</td>
<td>-0.04</td>
<td>-0.08</td>
<td>-0.39</td>
<td></td>
</tr>
<tr>
<td>MnO</td>
<td>0.47</td>
<td>-0.59</td>
<td>-0.46</td>
<td>-0.49</td>
<td>0.61</td>
<td>-0.32</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiO₂</td>
<td>-0.86</td>
<td>0.78</td>
<td>0.81</td>
<td>0.74</td>
<td>0.10</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FeO</td>
<td>-0.27</td>
<td>0.20</td>
<td>0.30</td>
<td>-0.56</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>-0.42</td>
<td>0.36</td>
<td>0.34</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>-0.98</td>
<td>0.96</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MgO</td>
<td>-0.98</td>
<td></td>
<td></td>
<td></td>
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</tbody>
</table>

It is also plausible to think that continental water may have carried these elements to the original depositional environment.

Mn varies, therefore, as a result of the evolution of Eh and pH. Under conditions of Eh and pH close to neutral, the Mn²⁺ ion remains in solution and is available to precipitate as a carbonate component. The MnO content of the limestones is lower than of the dolomites (Holland 1984). This suggests that Mn can be more soluble than Ca and as so should remain in solution and precipitate as MgO, independently from late mobilizations. Even so, Fe and Mn of carbonate rocks are susceptible to late mobilizations, either associated with diagenesis or with metamorphism. On the other hand, such rocks probably developed at the end of the Paleoproterozoic. In this era, the Fe and Mn behavior was different from today. In this regard, carbonates of the Paleoproterozoic (2.25 ± 0.25Ga) were far more Fe- and Mn-enriched than their phanerozoic analogues (e.g., Veizer et al. 1992).

The chemical variations and irregular dispersion of these elements within the carbonate rocks also suggest that the sedimentation occurred under variable environmental conditions, at shallow depth. The presence of at least 4 thin layers of metapelites, intercalated with metadolomites in the Alencar region, described by Parente (1995), constitutes a further evidence.

With regard to the medium-grained magnesites, Parente (1995) observed that such rocks present a more irregular composition and the SiO₂, Al₂O₃, Fe₂O₃ and CaO contents are higher than in the sparry correspondents. According to Parente, SiO₂ ranges from 1.1 to 21.9% (avg. 7.19%). Al₂O₃ oscillates from 0.1 to 4.5% (avg. 0.76%), Fe₂O₃ ranges from 1.5 to 4.5% (avg. 2.4%), CaO from 0.8 to 10.1% (avg. 2.29%) and MgO varies from 75 to 95% (avg. 87.15%).

If the two magnesitic types of marbles are compared, it becomes evident that the sparry type is more Mg-enriched and less enriched in Si, Al, Fe⁺⁺ and Ca than the medium-grained type. In the medium-grained magnesites, these elements exhibit a more irregular distribution, while in the sparry magnesites their distribution is more regular. The dolomitic marbles are more Si, Al, Ca⁺⁺ and Mn-enriched and less enriched in Mg, and in a less extent in Fe⁺⁺, than the magnesitic marbles.

Rare-Earth Elements (REE)

The calcitic marbles display ΣREE from 6.4 to 23.47ppm, calcitic dolomitic marbles from 30.2 to 114.4ppm, dolomitic marbles from 11.3 to 20.6ppm and sparry magnesitic marbles, between 5.3 and 11.5ppm. The (La/Lu)N ratio decreases from the calcitic marbles (21.0-61.03) to magnesitic marbles (3.9-19.6), with the calcitic dolomitic marbles (4.6-28.6) and the dolomitic marbles (10.01 to 21.50) presenting intermediate values between these two lithological types, indicating a fractionation of light REE between these rocks.

Chondrite-normalized REE patterns (values from Evensen et al. 1978) display a more REE enrichment next to the brecciated calcitic dolomitic marbles and a progressive decrease of REE from the calcitic to the magnesitic marbles and a light heavy REE enrichment next to the sparry magnesitic marbles (Fig. 11). It is also observed a negative Eu anomaly (Eu/Eu* from 0.4 to 0.9 in the calcitic marbles; 0.6 to 0.7 in the calcitic dolomitic marbles; 0.5 to 0.9 in the dolomitic marbles and from 0.5 to 0.7 in the magnesitic ones) while Ce displays a slightly positive anomaly.
Comparing these REE patterns to the pattern for the seawater, one observes that all the metacarbonate sequence presents a strong positive Ce anomaly and a weak positive Eu anomaly (Fig. 12).

In the calcitic marbles, REE display a significant negative correlation with CaO (r varies from -0.75 to -0.95) and a positive one in relation to MgO (r varies from 0.72 to 0.92) and with Al$_2$O$_3$ (r varies from 0.81 to 0.98). As Al$_2$O$_3$ varies sympathetically with SiO$_2$ and MgO and, to a lesser extent, with Fe$_2$O$_3$ indicating that the Al-silicate phase associated with the calcitic marbles is a magnesian chlorite with Fe, it is likely that REE can be associated with clay minerals rather than with the calcite of the calcitic marbles.
In the dolomitic marbles, there is no significant correlation between the REE and the major elements as for Mg and Ca (r ~ 0.6). However, the REE shows a weak positive correlation with Al₂O₃ and Fe₂O₃ (r varies, respectively, from 0.45 to 0.68 and from 0.72 to 0.78). La and Ce display a weak positive correlation with MnO (r = 0.74 and 0.51 respectively) what suggests an affinity with Fe-Mn-oxide/hydroxide.

In the sparry magnesitic marbles, there is a weak negative correlation between REE and CaO (r = from -0.46 to -0.81) and MnO (r = -0.63 and -0.82), a positive one between REE and MgO (r = 0.5 to 0.75) and a poor correlation with Al₂O₃ (< 0.4) and with Fe₂O₃ (r = -0.16 and -0.42).

Regarding that REE concentrate particularly in the clay fraction of the carbonate rocks, it is likely that this difference in favor of the calcitic marbles can be tied to its less fractionated character than that of the dolomitic and magnesitic marbles. This would explain the observed differences in the behavior of the REE in the calcitic, dolomitic and magnesitic marbles.
Ce and Eu Anomalies

The knowledge of the behavior of these two elements is very useful in paleo-environmental reconstitution. The negative anomaly of Ce in sedimentary rocks, particularly in carbonate rocks, has been many times used to invoke a marine origin, due to its easier remotion in oxidation zone. In the oceans, Ce³⁺ is oxidized to Ce⁴⁺ that is soluble precipitating as CeO₂, resulting in a depletion of this element in the seawater in relation to the other REE (Elderfield and Graves 1982). As to the Ce positive anomaly, this could be related either to a reducing marine environment or to a shallow marine environment with influence of continental water (Tlig 1987). In the evaporitic lacustrine environment (Möller and Bau 1993), this anomaly is usually related to the negative Eu anomaly.

According to Fleet (1984) the lack of Ce depletion in marine sediments close to the coast (nearshore and coastal) could be associated with: (a) areas close to the continent, platformal regions, involving mixture between Ce-undepleted continental waters, that causes a more or less pronounced deficiency in Ce, influenced by formation of authigenic minerals near the coast; (b) areas of shallow seas, marginal basins to epicontinental, in which Ce is apparently in suspended solid particles with the remaining REE. In this case, even being tetravalent, Ce behaves just like the other REE.

In remote areas of the continents, this element is submitted to selective remotion within fine-grained solid particles (<0.1 μm, Fe-Mn flakes). In consequence, Ce is separated from its neighbor elements (La and Nd) and a Ce anomaly may occur in the sediments.

This way, as pointed by Fleet (1984), it seems that seawater is not necessarily impoverished in Ce and that remotion of this element likely occurs in the open ocean rather than in platformal or estuarine waters. It should be also stressed that the absence of Ce anomaly in carbonate rocks is not due to diagenetic influence nor to dolomitization, but probably to formation of these rocks in environments with water not depleted in Ce.

Some authors admit, however, that marine sediments are depleted in Ce and consider that Ce depletion in modern oceanic waters is associated with the preferential incorporation of Ce⁴⁺ in authigenic minerals as Mn nodules and phosphorites (e.g. Piper 1974; McLennant et al. 1979).

Positive anomaly of Eu in the marine sediments or in seawater has been attributed to a hydrothermal inflow whose REE enrichment (e.g. Michard et al. 1983, Tlig 1987). This is typical of Archean sediments when primitive seas received a strong contribution of hydrothermal fluids. The negative anomaly of Eu is regarded as being characteristic of a reducing environment in which Eu³⁺ is reduced to Eu²⁺ although some authors have suggested that metamorphism or metasomatism could cause Eu reduction (e.g. Jarvis et al. 1975 in Fleet 1984).

Morteani et al. (1983), however, regard that the negative Eu anomaly is found in minerals formed from low-Eh solutions, while the positive Eu anomaly is ascribed to minerals formed in fluids with high oxygen fugacity that interacted in the decomposition of feldspars. Möller (1989) considers that similar behavior of REE and the same types of negative anomalies of Ce and Eu between magnesites and dolomites is the product of magnesian metasomatism on dolomitic rocks. He also considers that the negative anomalies of Eu and Ce are associated, respectively, to a marine and to a reducing environment.

In the present case, a negative Eu anomaly and absence of a negative Ce anomaly may indicate that the studied magnesian carbonate sequence was developed in a paralic marine environment, platformal with euxinic influence. Metapelites intercalated in the dolomites of Alencar, dissolution breccias, mineral associations of evaporitic environment (Parente 1995; Parente et al. 1996) and hydrocarbon inclusions in magnesites, further support this contention. Perhaps REE were not in the seawater that equilibrated with Mn nodules, or there was no Mn nodule when the studied Mg carbonate sequence was deposited.

The REE patterns for the studied sparry magnesitic marbles keep some similarities to REE patterns obtained for petrographically equivalent Paleoproterozoic marbles of Liaodong, China (Fig. 13). However, some differences should be pointed out. The magnesian marbles of the Liaodong province are more enriched in REE than those studied here and usually display Eu positive anomaly while those from Ceará, in Brazil, exhibit Eu negative anomaly. Magnesites of the Liaodong province developed in the late Archean to early Paleoproterozoic (~2.5 Ga), a time when there was more hydrothermal fluid inflow in the primitive ocean water, implying in a REE enrichment and in a Eu positive anomaly. Although there are some divergences, the available data altogether suggest that these two associations were developed in similar platformal environments and that the magnesitic rocks, mainly the sparry ones, are chiefly of sedimentary origin.

FLUID INCLUSIONS

Twenty two polished sections of dolomitic, sparry magnesitic and medium-grained marbles were examined for fluid inclusion studies. However, only in magnesite from the Riacho Fundo and Cabeça de Negro deposits, fluid inclusions with size, transparency and in adequate amount for a detailed study, were found. From the petrographic study, fluid inclusions have been classified and a detailed study of microthermometry and Raman microspectrometry was carried out. A Dilor multichannel Raman spectrometer
There are several types of fluid and solid inclusions in the medium-grained magnesite of the Riacho Fundo deposit, some of which display a regular distribution as shown in Fig. 14. In the first place, we see a light zone without fluid or solid inclusions (number 1 in Fig. 14). Next, we have a narrow zone with biphasic aqueous (aqueous LC, 2 in Fig. 14) with polygonal shapes, walls parallel to the growth walls and size that can reach 30 μm. Eventually, one can see monophasic aqueous inclusions associated with the biphasic group, probably a metastable process. There is a third central zone (AC type, 3 in Fig. 14) much wider that displays solid inclusions, normally rounded to oval, of dolomites (determined by Raman spectrometry), aquo-carbonic inclusions with or without associated dolomite. The size and shape of these inclusions are variable and could reach up to 30 μm. Their distribution is aleatory, being roughly parallel to the growth lines of magnesite. Finally, one repeats the narrow zone 2 with aqueous biphasic inclusions and the first zone without solid or fluid inclusion. This distribution of the inclusions probably reflects the process of growth of the magnesite crystal during a metamorphic recrystallization, implying in that these fluid inclusions are primary in relation to the metamorphic process.

One fluid inclusion of the LC type (liquid aqueous) revealed traces of CO₂ and N₂ in the Raman spectrometry, while in the aquo-carbonic inclusions, only CO₂ was detected, although CH₄ and N₂ were also investigated. A third type of inclusion, partially or totally filled by an opaque, black material that may form rounded inclusions with small light aqueous appendices, that is usually associated with rounded solid inclusions of dolomites (Fig. 15). The size of the black phase is less than 5 μm and its composition could not be determined by Raman spectrometry due to a high fluorescence generated during the analysis that masks completely the Raman signal (Pironon et al. 1991). This behavior is characteristic of inclusions with hydrocarbon. The carbon peaks are of 1300 and 1580 cm⁻¹ and according to McMillan (1989) graphite has two sharp peaks (1582 and 140 cm⁻¹) well marked in Raman spectrometry without...
MAGNESITE DEPOSITS (~1.8Ga), STATE OF CEARÁ, NORTHEASTERN BRAZIL

Figure 15. (A) Rounded solid of dolomite with a black portion of probably hydrocarbon and associated aqueous portion. (B) Inclusions with hydrocarbon and aqueous appendices. A little trail of aqueous inclusions and the occurrence of monophasic and biphasic inclusions apparently associated with inclusions with hydrocarbon.

Figure 16. Main kinds of fluid inclusions found in sparry magnesite from the Cabeça de Negro Deposit: 1. aqueous-carbonic inclusions, probably secondary; 2. Fluid-inclusion-free magnesite zone; 3. Biphasic aqueous fluid-inclusion-zone, probably primary; 4. Secondary monophasic and biphasic fluid inclusions; 5. Fine-grained white inclusion-free magnesite.

fluorescence. Its composition could only be determined with infrared microspectrometry, if its size were larger than 15 µm which is not the case (Pironon et al. 1991). The pasty nature was evidenced during the exposure to the laser beam, when a small hole was formed and that expontaneously closed again after some weeks.

Besides these inclusions, probably primary in relation to the metamorphism, one has another very small aqueous, monophasic and biphasic, inclusions (< 5 micrometers) in secondary trails.

Sparry Magnesite from Cabeça de Negro Deposit

In this type of sparry magnesite, one found fluid inclusions similar to those described in the Riacho Fundo deposit, at different proportions. Whereas in the Riacho Fundo deposit aqueous inclusions predominate, in the Cabeça de Negro deposit aquo-carbonic inclusions predominate. Even so, it is evident that the occurrence of these two types of fluid inclusions are in neighbor crystals. The Fig. 16 is a typical example of what happens in this sample where we have a longitudinal trail with aquo-carbonic inclusions (AC type, 1 in Fig. 16) restrict to a single crystal and probably pseudo-secondary. In the neighbor crystal, two well limited zones, one clean without any type of inclusion (2 in Fig. 16) and another with aqueous inclusions (type LC) in the form of negative crystals with aleatory distribution and possibly primary, are observed. The trail marked as 4 in the same Fig. 16, transversal to a tabular crystal of magnesite is composed by tiny (<2 µm) inclusions apparently aqueous monophasic, biphasic and secondary, once the trail cuts
more than one crystal. In five of them, one has a fine, white, translucent magnesite mass, without fluid inclusions. In general, there is very little solid inclusions of dolomite or with hydrocarbons.

**ISOTOPIC GEOCHEMISTRY**

Carbon and oxygen isotopes were analyzed in sixteen samples of calcitic and dolomitic marbles at the stable isotope laboratory (LABISE) of the Federal University of Pernambuco. About 10 to 20 mg of powdered sample have been put to react with 100% orthophosphoric acid at 25°C. CO₂ released from this reaction was cryogenically purified to remove water, that results from the reaction of the carbonate with the orthophosphoric acid, and analyzed for C and O isotopes in a VG ISOTECH SIRA 11 dual inlet, triple collector mass spectrometer, using the BSC (Bororema skarn calcite) as the reference gas that was calibrated against international standards (NBS-18, NBS-19, NBS-20). Results are expressed in notation (Table 6).

These metacarbonates exhibit ¹³C_pdb values from -3.2 to +2.1%. Such a variation may reflect modification occurred during metamorphism or the original isotope values acquired during the sedimentation of these carbonates. As these rocks underwent metamorphism in the greenschist to low amphibolite facies, probably did not go through decarbonation reactions that would have caused isotopic changes (Hoefs 1997). Therefore, the carbon-isotope values can be used to estimate environmental conditions during deposition of the carbonates. In this case, calcitic marbles display ¹³C_pdb from +0.5 to +2.1% a range typical for open sea environment while calcitic dolomitic marbles, with values between -0.51 and -3.14%, could have been deposited in brackish or confined marine environments with strong continental influence. This data set is also in agreement with ¹³C fluctuations observed in late Paleoproterozoic carbonates (~1.8Ga; e.g. Veizer et al. 1992; Sial et al. 2000).

The ¹⁸O_pdb values for the calcitic marbles vary from -6.6 to -10.5%o_pdb while for the dolomitic marbles vary from -9.4 to -14.8%o_pdb. The oxygen isotope ratios are more susceptible to modifications during metamorphism, even at a low degree, in a way they are of little use to trace the thermal history of deposition of the carbonates. However, the highest values, which are associated with the salmon red dolomitic marbles (CMMD-6G) and pink dolomitic marbles (CMMD-6H), could represent the least altered dolomitic rocks or formed in shallower marine water, while those of lower oxygen isotope values may indicate oxygen mobility during metamorphism or a deeper marine environment.

**GENETIC MODEL**

A difficult problem in the study of magnesite deposits associated with metasedimentary rocks is to determine whether these deposits are metasedimentary or metasomatic rocks.

In this study, the presence of two types of magnesite of different grain size poses an interesting problem. It is known that, in general, grain size of the carbonates is linked to the concentration of ions and to the salinity of the environment (Folk and Land 1975; Guillo 1980). Two processes are common: co-precipitation and maturation of the precipitate.

Co-precipitation is a chemical precipitation related to
the presence of impurities. These impurities can be adsorbed or hidden in the structure of the host mineral during the crystallization stage. This process happens in supersaturated environment rich in impurities where crystallization is rapid (Catani et al. 1970 in Almeida 1989). This way, in a strongly saturated evaporitic environment, germs are numerous, crystallization is fast and sediments will evolve little, preserving fine-grain size. Folk and Land (1975) showed that the formation of ordered dolomite is inhibited, at the same time, by the rapidity of the crystallization process in an oversaturated medium and by the concentration of strange ions in this process.

Maturation of the precipitate, by its turn, is related to the more diluted solution, weakly oversaturated where germs are more rare. The strange ions, due to their longer time in solution are eliminated, leaving only two dominant ions (Catani et al. 1970 in Almeida 1989). The crystallization is slow and the sedimentary evolution is faster and this allows for larger, well-defined crystals (Guillou 1980). Folk and Land (1975) pointed out that in the mixing zone of marine and freshwater (schizohaline zone) or of reduced salinity, dolomite crystals are larger and cleaner than those ones formed in an oversaturated environment.

Therefore, it is plausible to assume that the two types of magnesite studied developed in environment with different confining or salinity index: medium-grained magnesitic marbles would have been formed in a more confined or saturated environment than the sparry magnesitic marbles, where the influence of freshwater able to modify the salinity of the original environment was negligible. Abundant pyrite inclusions in subrounded magnesite, a result from bacterial activity in a saline or hypersaline environment, is a further support to this idea. Sparry magnesitic marbles were developed in a paralic, lagunar environment, less saturated than the former and wherein ion concentration was similar to that of seawater, taking into account the balance between evaporation and influence of freshwater inflows. This allowed a slower carbonate crystallization accompanied by important diagenetic processes, responsible for the crystallographic evolution. The common association between red, ferruginous, sparry magnesites and Fe-enriched metadolomites, Al-silicates and detrital zircons are an indication of a strong contribution of freshwater to these deposits.

Most investigations on the formation of magnesite in recent sedimentary environment have shown that the Ca\(^{2+}/(\text{Ca}^{2+} + \text{Mg}^{2+})\) decrease in the carbonate rocks in the paralic systems from open sea to landwards, that is, one goes from more calcic in open sea to more magnesian in confined environment. The Ca\(^{2+}\) decrease could be related to initial crystallization of calcic carbonates or gypsum or both (Müller et al. 1972; Von der Borg 1965, 1976).

In ancient environments, this differentiation was already demonstrated by Guillou (1980) in Cambrian rocks in Spain (Pacios and Mallecina) whose sequence dominated by dolomitic and magnesitic carbonates developed progressively from open sea to lagunar environment. In this study, we found one of the alternatives proposed by Guillou (1980), that is, magnesites are found in the central part in a paleo-lagoon and not in marginal positions as in the Spanish Cambrian. Guillou (1980) also associated the decrease and disappearance of sparry magnesite, to the atmospheric CO\(_2\) decrease by the action of carbon-intaker organisms. The CO\(_2\) decrease is today accepted by unanimity. One can also think on Ca solubility that, compared to that for Mg, increases with the elevation of pCO\(_2\).

Another worth-mentioning point is that the hypermagnesian carbonates are more resistant to tectonic deformation and pressure solution than their calcic analogues. Once submitted to deformation and metamorphism, magnesian carbonates resist more to ion exchange than the calcic carbonates. In a metasomatic hypothesis, where it is assumed that the introduction of Mg\(^{2+}\) was during metamorphism limestones or dolomites, the magnesite and its precursor dolomite would have a similar signature of trace elements of little mobility like Al. The sparry magnesitic marbles and host metadolomites exhibit important differences in \(\text{Al}_2\text{O}_3\), \(\text{Fe}_2\text{O}_3\), and MnO and, therefore, a large-scale metasomatism cannot explain these differences that are probably related to simple sedimentary phenomena, such as progressive depuration of lagunar water from clays (\(\text{Al}_2\text{O}_3\) and \(\text{SiO}_2\)) and, on the contrary, its Fe\(^{2+}\) enrichment, very stable at the time of formation of these rocks. Besides, three other facts are in support of a sedimentary origin: (a) abundant dolomitic and ferriferous magnesitic marbles as well as detrital zircon in the host metadolomites; (b) red dissolution breccias (evaporite dissolution) with luteite, sulphate nodules pseudomorphosed by fiber-radiated quartz in the contact between metadolomites and magnesites, and also presence of scapolite that indicates evaporitic conditions. In this case, the early saline fraction would have been partially dissolved during the emersion stage in oxidizing conditions since pseudomorphosed sulphate nodules are still observed; (c) dissolution breccias and thin films of metapelite, within the metadolomites, suggest a hiatus in the carbonate sedimentation.

The studied magnesites are in a border of an emerging zone, submitted to a pronounced alteration, but subjected to a reduced erosion under climatic conditions that vary from humid to arid. It is well known that under arid climate, evolved aluminous and detrital inflows characterize the sedimentary context. Therefore, it is possible to assume that periodical inflows of continental freshwater brought Fe and heavy minerals during the formation of magnesite. Dolomites are situated in large intra-deltaic paralic depressions (lagoons). Limestones are more distal and correspond to more open marine environments. Altogether, these carbonates appear during periods of weak erosion,
under arid climate and evaporites fit well in this context. Besides, occurrence of organic matter (oil in particular) suggests a biological activity in a confined medium.

As a whole, the present data seem more consistent with a sedimentary hypothesis than to metasomatism. The latter does not explain the granulometric variations observed in the studied magnesites, developed in environments relatively close to each other.

Finally, regarding that the set of magnesite occurrences passes, westward, through metadolomites into almost pure calcitic marbles, the chemical differentiation model proposed by Guillou (1971, 1980) and Chayé d’Albissin and Guillou (1986, 1988) in which the sparry magnesite appears towards the end of the carbonated chain, can be invoked to explain it. In the present case, this model involves an epicontinental marine gulf paleogeography, where the lagunar water loses Ca, from west to east, by preferential precipitation of calcic carbonates and further, in a more arid climate, gypsum was precipitated, raising its Mg/Ca ratio, driving the carbonate evolution toward the magnesian pole. The Figure 1 presents a scheme of the paleogeography and Figure 17 synthetizes the studied magnesian carbonate sequence evolution.

CONCLUSIONS

The geological, geochemical and fluid inclusion study of this magnesian carbonate sequence of the Orós foldbelt show two types of magnesite (sparry and of medium-grain size) of dominantly sedimentary origin.

The textural and compositional variations in the magnesite domain indicate that such rocks developed in different environments. The sparry magnesite formed in a paralic environment, weakly saturated wherein the germs were rare, slow crystallization and important diagenetic
evolution. Magnesites of medium-grain size developed in the same paralic environment, but more confined and/or saturated than that of the sparry magnesite. The greater concentration of ions of different composition associated with the magnesian ions favor a rapid crystallization and a lesser diagenetic evolution.

The distribution of the aqueous and aquo-carbonic fluid inclusions in both magnesite deposits indicate that these fluid inclusions are primary in relation to the tectono-metamorphic event, reflecting magnesite crystal growth during the metamorphism.

We can reconstitute the paleogeography, probably diachronic, configuring a series of paralic gulfs where evaporitic associations mix with continental influences. In this model, the magnesite deposits seem to be situated in the middle of two main paralic gulfs, both in distal position in relation to the sea. The sparry magnesite deposit was formed in the largest and more distal one in a more stable environment than that for the medium-grained magnesites.

This model confirms the major lines of previously analyzed cases, especially regarding Ca and Mg segregations in a sea-continent gradient; ratifies the existing data about the formation of other magnesite deposits and underlines the originality of the supergenic domain in the formation of evaporitic and carbonatic deposits, in the Proterozoic, marked by a strong pCO₂.

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