FIRST CARBON AND OXYGEN ISOTOPIC ANALYSES OF CARBONATES FROM THE SAN GREGORIO AND MELO FORMATIONS (CARBONIFEROUS-PERMIAN, PARANA BASIN, URUGUAY): PALAEOENVIRONMENTAL IMPLICATIONS

Cernuschi, F.[1], Gaucher, C.[1], Sial, A.N.[2] and Beri, A.[1]

1. Departamento de Geología, Facultad de Ciencias, Iguá 4225, 11400 Montevideo, Uruguay
2. NEG-LABISE, Dept. de Geol. UFPE, C.P. 7852, Recife, 50670-000, Brasil

Keywords: Paraná Basin, Uruguay, isotopes, Carboniferous, Permian

INTRODUCTION

This contribution presents the first isotopic data of five samples, one from the San Gregorio Formation and four of the Melo Formation extracted from the "Paso de las Toscas" borehole (Table 1).

The "Paso de las Toscas" borehole is located in the department of Tacuarembó in Uruguay, and was drilled by DINAMIGE. (Uruguayan Geological Survey; Fig. 1). This borehole cuts through some of the Eogondwanan Formations of the Paraná Basin in Uruguay. The following units were encountered from top to base: Yaguarí, Melo and San Gregorio formations. The final depth of the borehole is at 357m, where the Precambrian basement was reached (Fig. 2). There are no previous chemostratigraphic studies on the mentioned Formations in Uruguay, being also scarce in the rest of the Paraná Basin (De Giovani et al., 1974). Palynological macerations were also performed to study the relationship between palynofacies and isotopic composition of the carbonates.

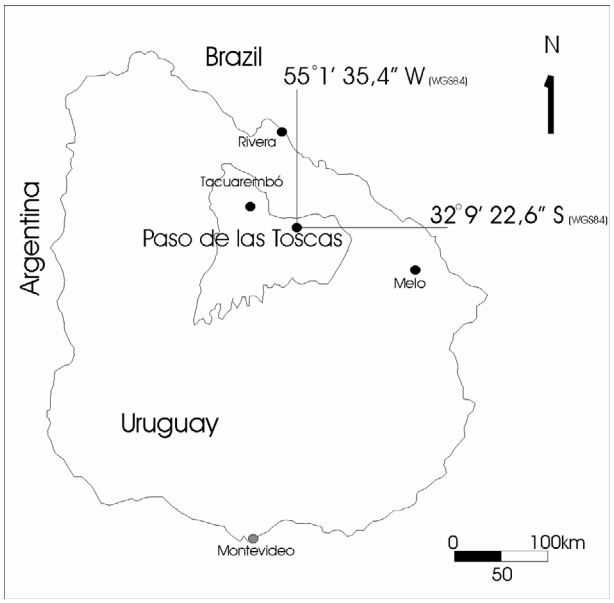

Figure 1.- Location map of the "Paso de las Toscas" borehole, P254, DINAMIGE

LITHOSTRATIGRAPHY

The San Gregorio Formation (Ferrando and Andreis, 1982) is composed by tillites, diamictites and shales with dropstones. It represents glacial and subglacial sedimentation (Bossi et al., 1998). The Tres Islas Formation (Ferrando & Andreis 1982) is not represented in this borehole.

The Melo Formation (Ferrando and Andreis, 1986) is subdivided into three members from base to top: Frayle Muerto, Mangrullo and Paso Aguiar (Bossi and Navarro, 1991). This Formation is composed by sandstones, siltstones, shales and occasional carbonates, with a concentration of pirobituminous shales in the Mangrullo Member, caracterized by *Mesosaurus* remains. This Formation was deposited in a wide, shallow basin in anoxic conditions, allegedly in a marine environment (Andreis and Ferrando, 1986). An U-Pb SHRIMP age of 279 ± 6 Ma (Artinskian) has been obtained by Basei et al. (2004) for ash beds in the Mangrullo Member.

The Yaguarí Formation is composed by sandstones and subordinated siltstones deposited in oxic conditions in a slowly progradating fluvial depositional system (Bossi et al., 1998). Ash beds occurring in this unit yielded an U-Pb SHRIMP age of 277 ± 8 Ma (late Artinskian, Basei et al., 2004).

These Formations are characterized by an important and diverse microfossil record, studied by numerous authors and compiled by Beri (2003). Fossils suggest an age ranging from Carboniferous/Permian to Lower or Upper Permian.

MATERIAL AND METHODS

Standard thin sections of carbonates were prepared, stained (Alizarin Red-S) and analyzed under a petrographic microscope Leica DM LP. Domains consisting of pure carbonates were selected. Approximately 1g of these domains was extracted from the corresponding rock specimen by microdrilling. C and O isotope ratios of the resulting samples were analyzed at the stable isotope laboratory (LABISE) at the Federal University of Pernambuco. CO_2 gas was extracted from powdered carbonates samples by reacting 10-20 mg of

sample with 100% orthosphosphoric acid, under high vacuum, at 25ºC for approximately 24 hours. The released CO_2 gas was analyzed in a SIRA II dual inlet, triple collector mass spectrometer, using the BSC reference gas (Borborema skarn calcite) calibrated against NBS – 18 (carbonatite), NBS – 19 (toilet seat limestone) and NBS – 20 (Solenhofen limestone), with a composition of $\delta^{18}O$ = -18.3 ‰ PDB and $\delta^{13}C$ = -8.6 PDB.

Palynological macerations were prepared at the Palynology laboratory of the Facultad de Ciencias (Montevideo) following standard techniques of HF and HCl digestion.

RESULTS

PETROGRAPHY

From the five samples analyzed, three of them are composed by calcite and two by dolomite. Sample 501 from the San Gregorio Formation is a diamictite with calcitic cement. Samples 207, 170, 155 and 100 consist of thin levels of carbonates interbedded between siltstones and bituminous shales.

Carbonates analyzed in thin sections are composed by sparitic calcite in samples 207 and 170 and dolomite in Samples 155 and 100, but a mixture of finely intergown dolomite and calite commonly occurs in all the samples. Carbonates are associated with fine- grained quartz, pyrite framboids, phyllosilicates and small, angular quartz clasts. Possible shards, especially in sample 207, suggest a pyroclastic input during deposition of some carbonate levels. The sparitic texture of the carbonates, with floating phyllosilicates and quartz indicate that they where possibily deposited during early diagenesis, before significant compaction could take place.

CARBON AND OXYGEN ISOTOPES

The results of the isotopic analyses are shown in Table 1 and are plotted in Figure 2 with litological and palynological data.

Sample	Prof. (m)	$\delta^{13}C_{PDB}$	$\delta^{18}O_{PDB}$
100	63	1.12	-0.52
155	100	-8.41	-9.95
170	108	-13.65	-14.67
207	127	-11.96	-13.13
501	333	-4.37	-11.99

Table 1.- Carbon and oxygen isotopic data

The carbonates analyzed are moderately to strongly depleted in ^{13}C, especially those of the Mangrullo Member of the Melo Formation (up to –14 ‰ V-PDB). Similar values were reported by De Giovani et al (1974) from the Iratí Formation of Brazil, which is correlative of the Melo Formation. Even though they report both unusually heavy and light $\delta^{13}C$ values, we only found light values.

In the Paso de las Toscas borehole, the most negative $\delta^{13}C$ values occur in thin levels of carbonates interbedded with bituminous shales in the Mangrullo Member of the Melo Formation. This is in accordance with the the data presented by De Giovani et al. (1974) for the Iratí Formation in the southern Paraná Basin. Both the underlying San Gregorio Formation and the overlying Yaguarí Formation display less negative and positive $\delta^{13}C$ values, respectively. Thus, maximum ^{13}C-depletion occurs in the Melo Formation (Mangrullo Member), concomitantly with the highest organic carbon contents and peak anoxic conditions (Bossi and Navarro, 1991).

PALYNOLOGY

The preliminar analysis of the palinoflora observed in samples 207, 170, 155, and 100 shows an assemblage assignable to *Striatoabieites anaverrucosus – Staurosaccites cordubensis* Biozone (Beri et al. 2004) indicating an Upper Permian age (Figure 2). The sample 501 (333,5m) was sterile, but sample 509 extracted at 340,5m shows an assemblage that could indicate an older age that the one assigned to *Cristatisporites inconstans – Vittatina subsaccata* by Beri et al. (2003) as lower Permian (Figure 2).

The paleoenvironment suggested by this microfossil assemblage for the Mangrullo Member is a shallow embayment with brackish waters and a strong influence of continental runoff (Beri and Pecoits, 2001; Beri, 2003).

DISCUSSION

We envisage that two mechanisms may be responsible for the extreme $\delta^{13}C$ depletion in the Melo Formation, namely: (1) oxidation of organic matter leading to production of CO_2 enriched in ^{12}C which was later incorporated in the carbonates during early diagenesis (Murata et al. 1969; De Giovani et al., 1974); and (2) deposition in a fresh water environment (Keith and Weber, 1964). Carbonates from samples 207, 170 and 155 present $\delta^{13}C$ between -8 and -14 ‰ V-PDB. Thus, deposition in an open marine environment can be ruled out. However, marine microfossils such as acritarchs and ostracods of the genera *Estheria* and *Liocaris* occasionally occur in the Mangrullo Member, evidencing the influence of marine waters in this unit (Da Silva, in Bossi and Navarro, 1991; Beri and Pecoits, 2001). This facts, together with the petrography of carbonates, clearly supports the idea that they precipitated during early diagenesis from formation water enriched in ^{12}C by the nonequilibrium oxidation of organic matter, as suggested by De Giovani et al. (1974) for the correlative Iratí Formation. To account for the oxygen necessary for the oxidation of organic matter, and the occurrence of sporadic levels of marine microfossils, we envisage periodical marine transgressions onto a large, fresh-water or brackish, stagnant basin. The similarity of our results with those reported by De Giovani et al. (1974) for the Brazilian part of the basin suggests that these oscillating conditions affected an area in excess of 1.000.000 km^2.

The $\delta^{13}C$ value of sample 501 from the San Gregorio Formation (-4.4 ‰ V-PDB) probably represents early diagenetic conditions in a largely marine basin, as suggested by radiolarians occurring in that unit (Braun et al., 2003). Negative carbon isotopic excursions are known to be associated with Neoproterozoic glaciations (Hoffman and Schrag, 2002). The extent of the glacial perturbation of the Carboniferous carbon cycle is not fully understood yet, and needs to be tested.

Sample 100 from the top of Melo Formation near the boundary to the Yaguarí Formation yielded $\delta^{13}C$ of +1.1 ‰ V-PDB, which is consistent with reported values for Lower Permian marine carbonates elsewhere. It falls well within the field of marine carbonates in the diagramme of Keith and Weber (1964). A marine environment for these rocks has been suggested by Elizalde (in Bossi and Navarro, 1991) on the basis of clay mineral and cement composition.

The oxygen isotopic behaviour is dificult to analyze. In primary carbonates it could indicate marine or fresh water conditions and even paleotemperature, but in this case study, interpretation is more complex. However, the isotopic composition of water involved in the precipitation of the analyzed carbonates probably exerted an important control, as suggested by the trends observed in Fig. 3.

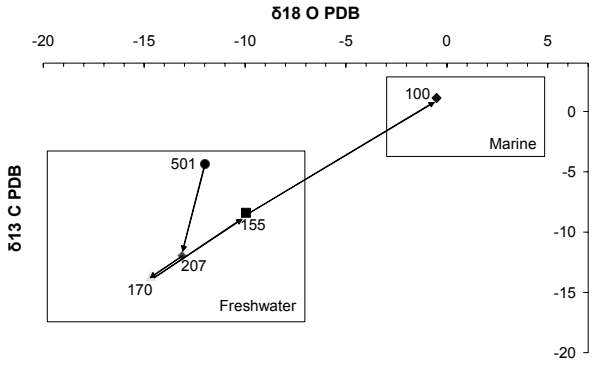

Figure 3.- Relationship between carbon and oxygen isotopic compositions in analyzed carbonates. Note the tendency toward marine ratios in the uppermost Melo Formation. Compositional fields according to Keith and Weber (1964).

CONCLUSIONS

According to petrographic and isotopic analyses samples 501, 207, 170 and 155 are early diagenetic precipitates, whereas sample 100 could represent a primary carbonate.

Extreme ^{13}C depletion in samples 207, 170 and 155 are probably the product of organic matter oxidation during early diagenesis. Negative $\delta^{13}C$ values for the San Gregorio Formation are likely the product of diagenetic alteration, but an influence of glaciation, as in Neoproterozoic cap carbonates, cannot be ruled out yet. Finally, $\delta^{13}C$ values for the Melo-Yaguarí transition probably reflect Lower Permian seawater composition.

A tendency from marine environments in the San Gregorio Formation, to more restricted, brackish environments in the Melo Formation is both indicated by fossils and isotopes. Maximum restriction and anoxic conditions occur in the Mangrullo Member of the Melo Formation. Cyclic marine transgressions affected this largely stagnant, brackish water body, providing oxygen and more saline waters. This conditions affected a large area of the Paraná Basin, from the state of São Paulo in the north (De Giovani et al., 1974) to Uruguay in the south. Final transgression of the Permian sea occurred at the transition between the Melo and Yaguarí formations, as indicated by isotopic composition of carbonates, fossils and sedimentary facies.

ACKNOWLEDGMENTS

To Ing. Jorge Spoturno for facilitate the study of the samples of the borehole at DINAMIGE. To CSIC I*D for partial financial support.

REFERENCES

Basei, M.A.S., Rocha Campos, A.C., Nutman, A.P., 2004. Idade e proveniência de zircões de rochas neopaleozóicas do Brasil: resultados preliminares. In: Simpósio 40 Anos de Geocronologia no Brasil, Boletim de Resumos, p. 9 (São Paulo).

Beri, Á., 2003. Revisión del conocimiento paleontológico del Paleozoico Tardío del Uruguay. Revista del Museo Argentino de Ciencias Naturales. 5 (2): 163-168.

Beri, A., Pecoits, E., 2001. Palinología y sedimentología de la Formación Melo (Pérmico) en la cañada "El Barón", departamento de Cerro Largo, Uruguay. Ameghiniana, v. 38, pp. 419-428.

Beri, A., Gutierrez, P., Cernuschi, F. & Balarino L., 2004 Palinoestratigrafía del Pérmico de la Cuenca Paraná, Uruguay. XI Reuniao de Paleobotanicos e Palinólogos. Gramado, RS, Brasil. Resúmenes p 29

Bossi, J., Navarro, R., 1991 Geología del Uruguay. 2 tomos. Departamento de Publicaciones de la Universidad de la República. Montevideo. Uruguay.

Bossi, J.; Ferrando, L. A.; Montaña, J.; Campal. N.; Morales, H.; Gancio,F.; Schipilov, A.; Piñeyro, D.; Sprechmann, P., 1998. Carta Geológica del Uruguay. E 1/500.000 Memoria Explicativa. Geoeditores. Montevideo, Uruguay.

Braun, A., Sprechmann, P., Gaucher, C., 2003. Stratigraphic age of phosphorite-nodules from the San Gregorio Formation of Uruguay. Neues Jahrbuch für Geologie und Paläontologie, Monatshefte, v. 2003, pp. 739-748.

De Giovanni, W. F., Salati, E., Marini, O. J., Friedman, I., 1974. Unusual Isotopic Composition of Carbonates from the Irati Formation, Brazil. Geological Society of America Bulletin, v.85, p.41-44, 3 figs.

Ferrando, L.A., Andreis, R.R. 1982 Correlación entre las columnas estratigráficas paleozoicas de Uruguay y Rio Grande del Sur, Brasil. (Resumen). Proyecto Nº 42 IUGS-UNESCO. Boletín Nº 5: 34-35. Montevideo. Uruguay.

Ferrando, L. A. Y Andreis, R.R. 1986 Nueva estratigrafía en el Gondwana de Uruguay. Actas I Congreso Latinoamericano de Hidrocarburos. ARPEL. I: 295-323. Buenos Aires, Argentina.

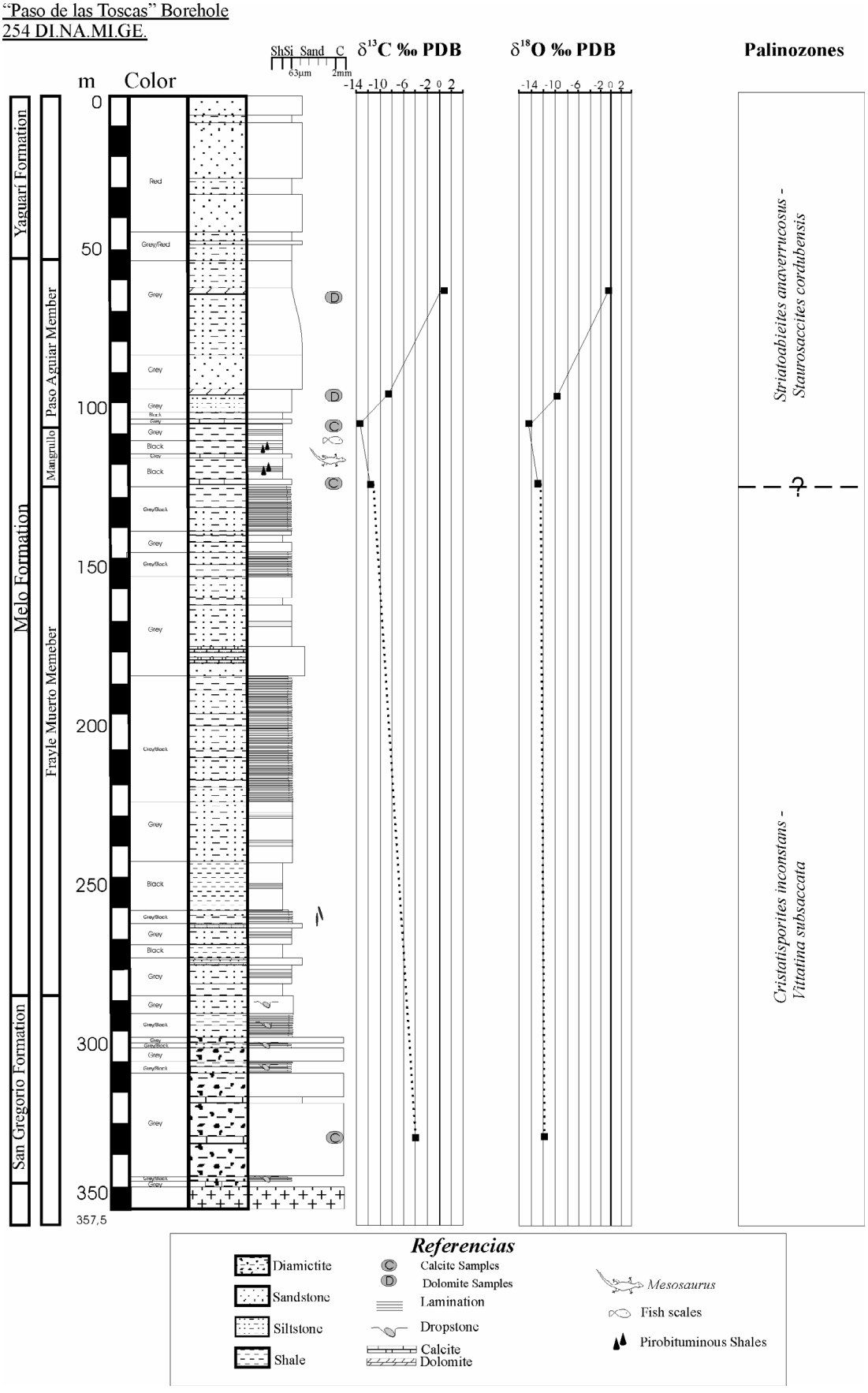

Figure 2.- Stratigraphic column of the "Paso de las Toscas" borehole, P254, DI.NA.MI.GE, showing C and O isotopic composition and palinozones.

Hoffman, P.F., Schrag, D.P. 2002. The snowball Earth hypothesis: testing the limits of global change. Terra Nova, 14, 129-155.

Keith, M.L., Weber, J.N. 1964. Carbon and oxygen isotopic composition of selected limestone and fossils. Geochimica et Cosmochimica Acta, v. 28, pp. 1787-1816.

Murata, K. F. ; Friedman, I., and madsen, B. M., 1969, Isotopic composition of diagenetic carbonates in marine Miocene formations of California and Oregon: U.S: Geologial Survey. Prof. Paper 614-B, p. B1-B24.

RESUMEN

Esta contribución presenta los primeros datos isotópicos de cinco muestras, una de la Formación San Gregorio y cuatro de la Formación Melo extraídas de la perforación Paso de las Toscas (DINAMIGE) junto a un análisis palinológico preliminar de la misma.

El análisis preliminar de la palinoflora observada en las muestras indica una edad entre Pérmico inferior y superior.

Los valores más negativos de $\delta^{13}C$ ocurren en finos niveles de carbonato interestratificados entre esquistos bituminosos del Miembro Mangrullo de la Formación Melo. Tanto la infrayacente Formación San Gregorio como la suprayacente Formación Yaguarí muestran valores de $\delta^{13}C$ menos negativos y positivos respectivamente.

De acuerdo con el análisis isotópico y petrográfico las muestras 501, 207, 170 y 155 son precipitados diagenéticos tempranos, mientras que la muestra 100 puede representar carbonatos primarios.

El empobrecimiento extremo en ^{13}C en las muestras 207, 170 y 155 es probablemente el producto de la oxidación de la materia orgánica durante la diagénesis temprana. Tanto los fósiles como los isótopos indican una tendencia desde ambientes marinos en la Formación San Gregorio a ambientes salobres más restrictos en la Formación Melo.