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## Carbon and oxygen isotope geochemistry of Ediacaran outer platform carbonates, Paraguay Belt, central Brazil

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### ABSTRACT

After the late Cryogenian glaciation the central region of Brazil was the site of extensive deposition of platform carbonates of the Araras Group. This group includes a basal cap carbonate sequence succeeded by transgressive, deep platform deposits of bituminous lime mudstone and shale. Facies and stratigraphic data combined with carbon and oxygen isotopic analyses of the most complete section of the transgressive deposits, exposed in the Guia syncline, were used to evaluate the depositional paleoenvironment and to test the correlation of these deposits along the belt and with other units worldwide. The studied succession consists of 150 m thick tabular beds of black to grey lime mudstone and shale with predominantly negative  $\delta^{13}\text{C}_{\text{PDB}}$  values around  $-2.5$  to  $-1\text{‰}$ . The  $\delta^{13}\text{C}_{\text{PDB}}$  profile of Guia syncline shows a clear correlation with the upper portion of Guia Formation in the Cáceres region, about 200 km to the southwest. The  $\delta^{13}\text{C}_{\text{PDB}}$  profile of the Araras Group is comparable with  $\delta^{13}\text{C}_{\text{PDB}}$  profiles of Ediacaran units of the southern Paraguay Belt, western Canada, and the Congo and Kalahari cratons. Moreover, facies distribution, stratigraphy and the carbon isotopic profile of the Araras Group match the middle Tsumeb Subgroup in Namibia, which reinforces the Ediacaran age assigned to the Araras Group.

**Key words:** carbon and oxygen isotopes, Ediacaran, Araras Group, Guia Formation, Amazon Craton, glaciation.

### INTRODUCTION

The transition zone between the southern margin of the Amazon Craton and the northern portion of the Paraguay Belt is an extensive thrust-and-fold belt formed during the final stages of Brasiliano-Pan-African orogenesis (ca. 540-500 Ma, Almeida 1984, Trompette 2000, Alvarenga et al. 2000), as a result of the convergence and collision of the Amazônia (West), São Francisco-Congo (East) and Paraná (South) blocks (Almeida 1984, Basei and Brito Neves 1992, Alkmim et al. 2001). It is inter-

preted as a foreland basin (cf. Trompette 1994) whose sedimentary deposits record a late Neoproterozoic depositional history including extensive glaciation, anomalous carbonate deposition, syn-sedimentary seismicity and isotopic excursions (Nogueira et al. 2003). The final extensional events allowed granite emplacement at about 500 Ma (Almeida and Mantovani 1975).

After a severe glaciation that finished at ca. 630 Ma this region was the site of extensive deposition of platform carbonates of the Araras Group, now exposed along the southern border of the Amazon Craton and at the northern Paraguay Belt (Fig. 1). A carbonate succession over 600 m thick overlies late Cryogenian glacio-

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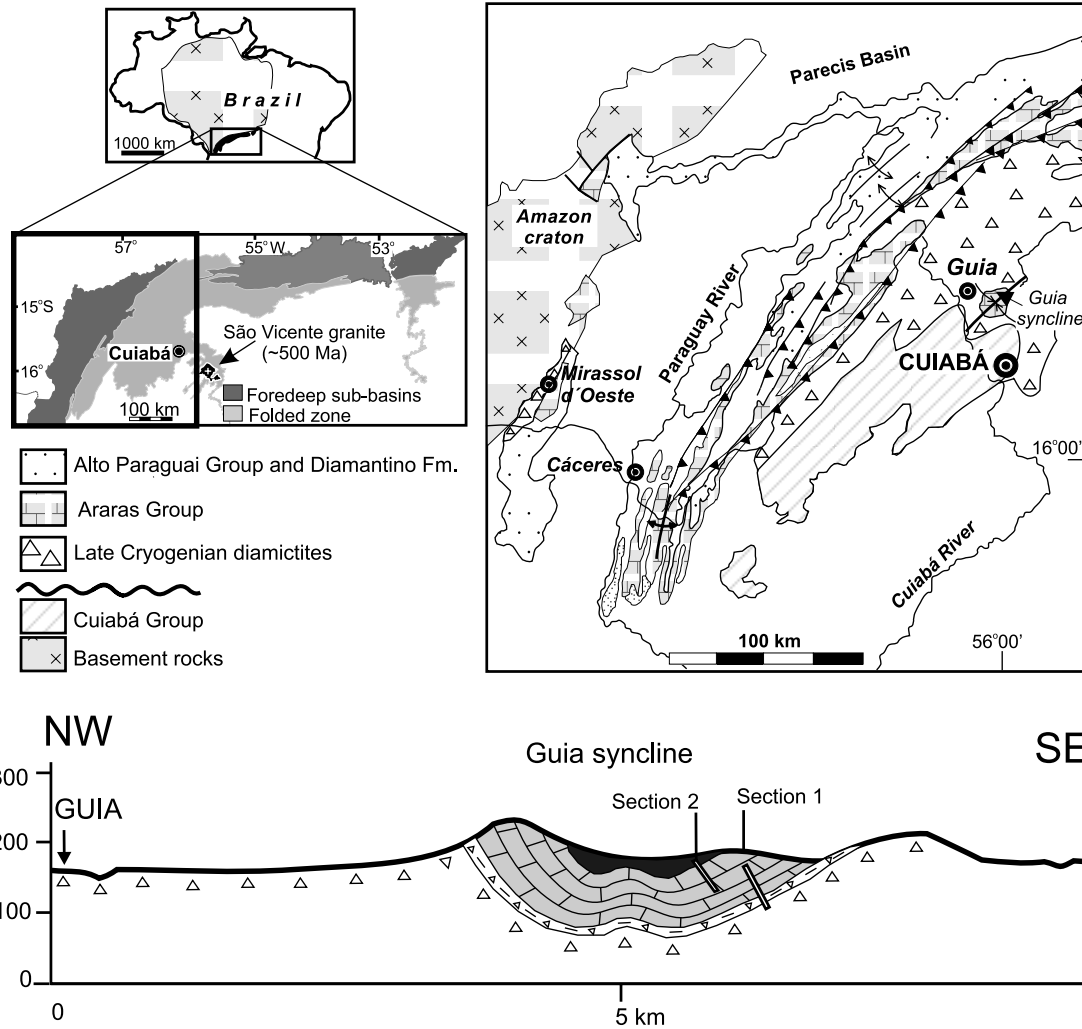


Fig. 1 – Geologic map of Paraguay Belt with location of the Guia region and detailed geologic section of Guia syncline (after Almeida 1964) with location of studied profiles.

genic diamictites and includes the first well-documented cap carbonate sequence in South America (Nogueira et al. 2003). Paleomagnetic data indicate a low paleolatitude ( $22+6/-5^\circ$ ) for the Amazon block, right after deposition of the diamictite (Trindade et al. 2003). The post-glacial cap carbonate was succeeded by an impressive transgression recorded by a thick accumulation of bituminous lime mudstone and shale, discontinuously distributed for more than 400 km in the region, and considered as deep platform deposits (Nogueira et al. 2003). The most complete section of these deposits occurs in the Nossa Senhora da Guia mine, preserved in an asymmetric syncline with NE-SW-oriented axis, located 30 km

northwest of Cuiabá (Fig. 1). Facies and stratigraphic data combined with carbon and oxygen analysis were used to evaluate the depositional paleoenvironment and to test the correlation of these deposits along the belt and with other units worldwide.

**STRATIGRAPHY AND AGE**

Three major lithostratigraphic units may be distinguished in the region (Fig. 2), from base to top: the Puga Formation (diamictite, siltstone with dropstones); the Araras Group (dolostone, limestone, sandstone); and Alto Paraguay Group (sandstone, mudstone and calca-

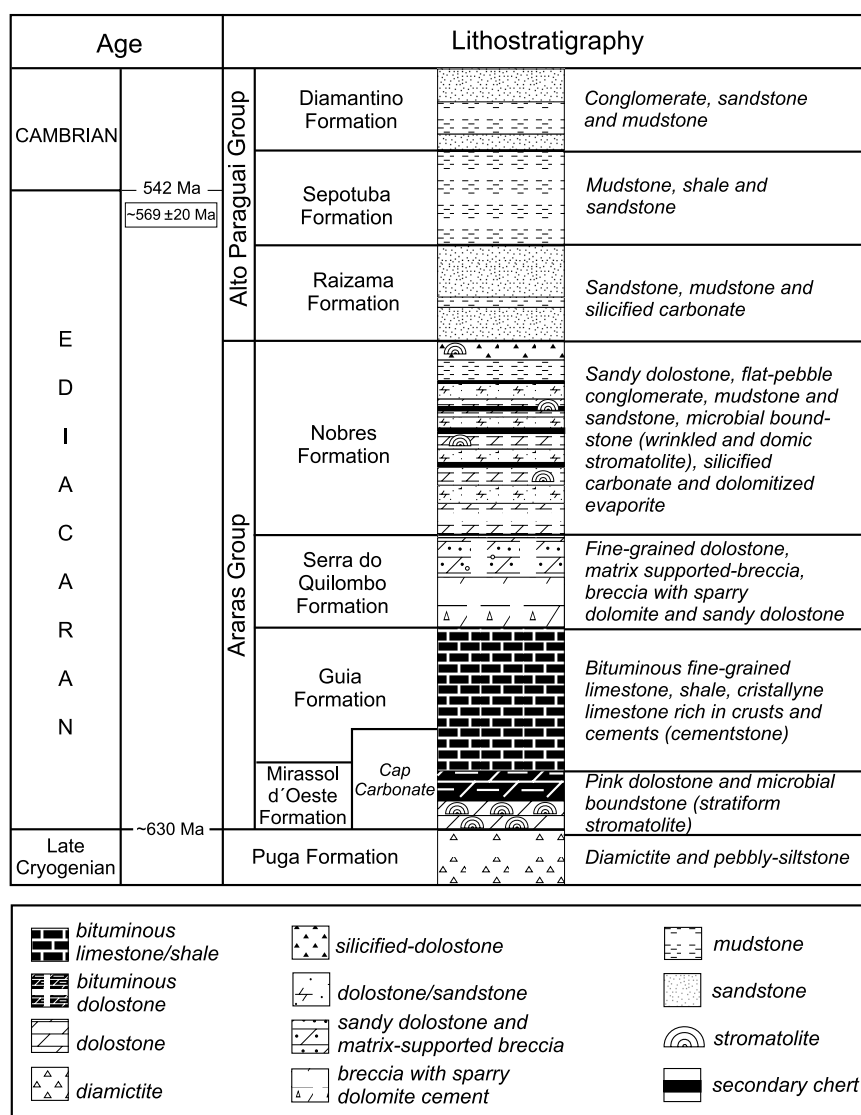


Fig. 2 – Stratigraphic units of northern Paraguay Belt (after Nogueira et al. 2007, modified). The inferred ages based in correlation with Marinoan glaciation and Rb/Sr age for Sepotuba Formation are debatable.

renite). The laterally extensive Araras Group is interpreted as platform carbonate deposits, as suggested by its homogeneous, predominantly deep-water lithofacies exposed on the craton and in the Paraguay Belt. The stratigraphic succession of the Araras Group includes megacycles, cycles and event beds distributed in most of 600 m (composite section) with distinct isotopic signatures (Nogueira et al. 2007). In particular, the cap carbonate sequence (Hoffman and Schrag 2002) is characterized by the presence of the Puga cap carbonate, predominance

of deep-water deposits,  $\text{CaCO}_3$ -oversaturation events, and  $\delta^{13}\text{C}$  with predominantly negative values (Nogueira et al. 2003).

The carbonate rocks of the Araras Group have not yet been dated radiometrically, nor have tuffs or volcanic rocks been identified. Reported Rb-Sr ages for mudrocks of the overlying Alto Paraguai Group ( $569 \pm 20$  Ma, Cordani et al. 1978, Bonhomme et al. 1982; and  $660 \pm 60$  Ma, Cordani et al. 1985) are open to debate. The Rb-Sr age of the São Vicente Granite ( $483 \pm 8$  Ma,

Almeida and Mantovani 1975), an anorogenic granite intruding the Cuiabá Group (a lateral equivalent of the studied units of the Araras Group), provides a minimum age for the sedimentary succession of the Paraguay Belt. The age of the Araras Group has been inferred in part on the basis of lithostratigraphic correlation with carbonate rocks of the Corumbá Group, which crop out about 500 km south of the study area. Nevertheless, this correlation is speculative because facies, sedimentary environments, chemostratigraphy of carbonates and fossils are different (P.C. Boggiani, unpublished data, Gaucher et al. 2003, Alvarenga et al. 2004, Figueiredo et al. 2006). Although lithologically similar, diamictites assigned to the Puga Formation in its type area (southern Paraguay Belt) and in the northern part of the belt may be different stratigraphic units with different ages. Recent descriptions of more than one glacial horizon both in the Corumbá Group (Boggiani et al. 2004) and in the northern Paraguay Belt (Serra Azul Formation, Figueiredo et al. 2004, 2006, Alvarenga et al. 2007) make lithostratigraphic correlations more complex. The Corumbá Group is notable for the occurrence of *Cloudina*, an index fossil of the latest Neoproterozoic, and considered contemporaneous with the Ediacara biota (Germs 1972, Grant 1990, M.F. Zaine, unpublished thesis, Zaine and Fairchild 1985, 1992, Gaucher et al. 2003). The Araras and Corumbá groups overlain glacial deposits.

Reported  $\delta^{13}\text{C}_{\text{PDB}}$  values for the Araras Group (Nogueira et al. 2007) from Cáceres and Mirassol d'Oeste regions (Fig. 1), interpreted as representative of the original seawater ( $\delta^{18}\text{O}_{\text{PDB}} > -10\text{‰}$ , Jacobsen and Kaufman 1999), exhibit a trend from strongly negative values around  $-9\text{‰}$  at the base to positive values at the top of the succession (Fig. 3). The cap dolostone succession is composed of moderately deep platform deposits (Mirassol d'Oeste Formation) overlain by limestone rich in crusts and cements with  $\delta^{13}\text{C}_{\text{PDB}}$  values around  $-5$  to  $-4\text{‰}$  (lower Guia Formation). The anoxic, deep-platform limestone succession (upper Guia Formation) overlying the cap carbonate succession shows almost constant  $\delta^{13}\text{C}_{\text{PDB}}$  values around  $-2.5$  to  $-1\text{‰}$  (Fig. 3). Up section, a switch to positive values ( $+0.1$  to  $+0.3\text{‰}$ ) occurs in dolomites deposited in shallow-platform and peritidal environments (Serra do Quilombo and Nobres formations).

#### SAMPLING AND ANALYTICAL METHODS

Sampling for C- and O-isotope analyses were performed on 38 fine-grained limestone samples, collected along 150 m of two stratigraphic sections of the Guia Formation, organized in a composite stratigraphic profile representative of the proposed stacking for the Araras Group (Fig. 3). As the carbonate succession of this area was affected by low-grade metamorphism, homogeneous samples with little diagenetic or metamorphic alteration were selected, although some dolomitized samples were also analyzed. Fractured, mineral-filled and weathered zones were avoided. Samples were micro-drilled with a 1 mm drill.

Carbon isotope analyses were performed at the Stable Isotope Laboratory (LABISE) of the Department of Geology, Federal University of Pernambuco, Brazil.  $\text{CO}_2$  gas was extracted from powdered carbonate in a high vacuum line after reaction with 100% phosphoric acid at  $25^\circ\text{C}$  for one day (three days were allowed when dolomite was present). The  $\text{CO}_2$  was analyzed in a double inlet triple collector SIRA II mass spectrometer following cryogenic cleaning. The results are reported in conventional notation in per mil ( $\text{‰}$ ) relative to the VPDB (Vienna – PDB or Pee Dee Belemnite) standard. VPDB is a scale recognized by the National Institute for Standards and Technology (NIST) of USA that is used for reporting relative abundances of  $^{13}\text{C}$  or  $^{18}\text{O}$  via the delta notation. The uncertainties of isotope measurements were 0.1% for carbon and 0.2% for oxygen, based on multiple analyses of an internal laboratory standard (BSC, Borborema skarn calcite).

#### RESULTS

##### THE OUTER PLATFORM DEPOSITS IN THE GUIA SYNCLINE

The sedimentary succession in the Guia syncline consists of tabular beds of black to grey lime mudstone and shale 150 m in thickness (Fig. 4). Silt and fine sand are disseminated in the limestones and pyrite crystals are found locally. These rocks are disposed in compositionally uniform and laterally extensive beds for dozens of meters in the Nossa Senhora da Guia mine, but certainly extends for more than 200 km to the southwest, reaching the region of Cáceres (Figs. 1, 2). The main sedimentary structure in these rocks is the even parallel lamination

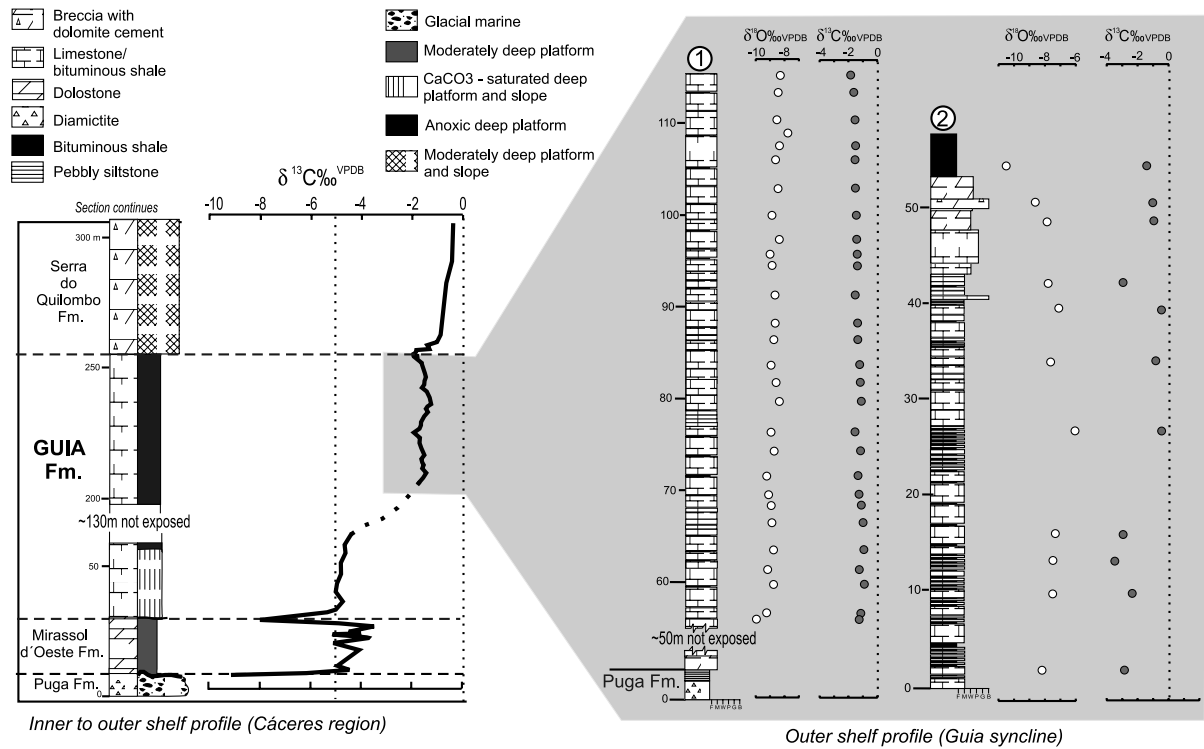


Fig. 3 – Isotopic correlation of outer shelf platform deposits of Cáceres and Guia regions. The  $\delta^{13}\text{C}_{\text{PDB}}$  profiles are perfectly comparable and the measured sections in the Guia syncline can be correlated to the top of Guia Formation.

but cross-lamination occurs locally associated with thin beds of intraclastic packstone. This succession overlies a diamictite with abundant silty-matrix or graded-pebbly siltstone. The first meters of limestone above the diamictite are dolomitized and exhibit a pinkish color. A level of intensely dolomitized breccia with clasts of fine limestone occurs at the top of section 2 (Fig. 5).

The deep platform setting is indicated by the predominance of low energy carbonate facies (laminated lime mudstone) and suspension deposits (shale). Their distribution in monotonous, laterally extensive beds for more than 200 km, suggest deposition into an ample deep platform (Pfeil and Read 1980, Coniglio and James 1990). The dark color of lime mudstone associated with bituminous and pyritous shale indicate anoxic conditions responsible for the accumulation and preservation of organic matter. Weak to moderate currents caused ripple migration. Locally brecciated limestone beds were accumulated within the slope setting (Coniglio and Dix 1992).

The position of the Guia syncline, more than

200 km far from the craton, suggests that the studied succession represents the most distal part of Araras carbonate platform.

#### C AND O ISOTOPES

The  $\delta^{13}\text{C}_{\text{PDB}}$  values for the carbonate succession of the Guia syncline (Fig. 3) are interpreted as reflecting original seawater composition ( $\delta^{18}\text{O}_{\text{PDB}} > -10\text{‰}$ ), which is corroborated by available Mn/Sr < 2 values (Alvarenga et al. 2004). In section 1  $\delta^{13}\text{C}_{\text{PDB}}$  values are uniform, ranging from  $-1$  to  $-2.5\text{‰}$ . These negative values indicate that the low metamorphic overprint did not affect the original  $\delta^{13}\text{C}_{\text{PDB}}$  values (Fig. 3). Contrarily, in section 2 (Fig. 3) dolomitization may have modified slightly the  $\delta^{13}\text{C}_{\text{PDB}}$  values that reach  $-4\text{‰}$ , as indicated by  $\delta^{18}\text{O}_{\text{PDB}}$  values lower than  $-10\text{‰}$ . Strontium isotopic ratios up to 0.71151 in dolostones of the upper part of section 2 were related to low-grade metamorphism (Alvarenga et al. 2004).



Fig. 4 – Tabular beds of black to grey lime mudstone and shale, Nossa Senhora da Guia Mine, Guia syncline.

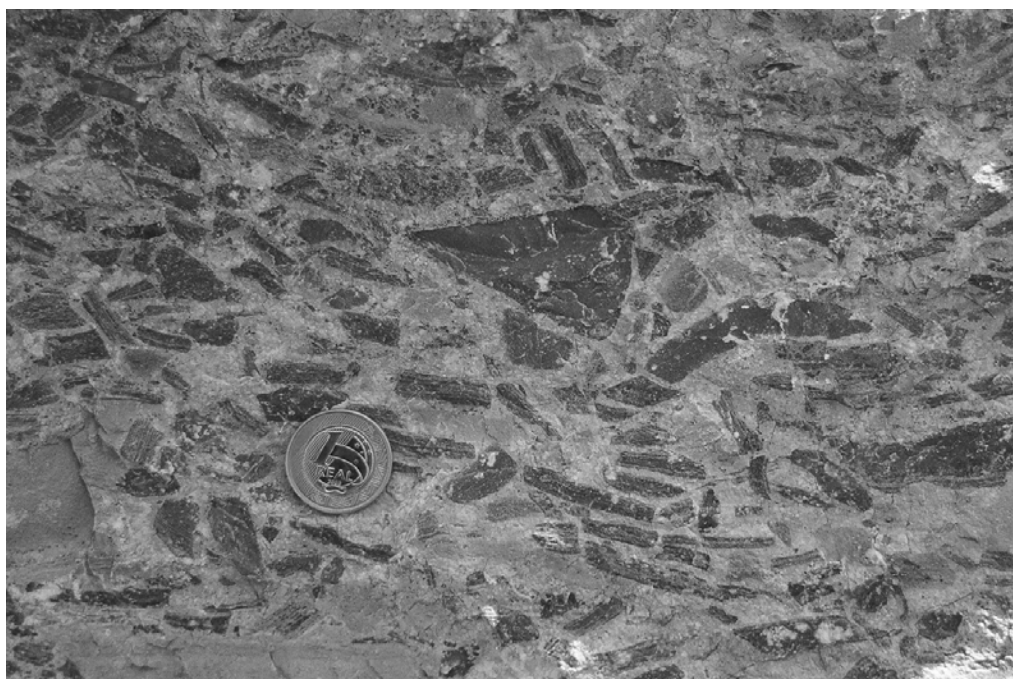


Fig. 5 – Dolomitized breccia with clasts of fine limestone at the top of the section, Nossa Senhora da Guia Mine, Guia syncline.

## DISCUSSION

### STRATIGRAPHIC IMPLICATIONS

The isolated occurrence of bituminous limestone and shales in the Guia syncline has been previously positioned as a unit of the Cuiabá Group (Alvarenga et al. 2004), but our data points to a correlation of facies, paleoenvironmental significance and C and O isotopic values between the Cáceres and Guia regions (Fig. 3). The  $\delta^{13}\text{C}_{\text{PDB}}$  profile at the Guia syncline shows a clear correlation with the upper portion of Guia Formation of Cáceres region, indicating that the succession in the Guia syncline belongs to the Araras Group (Figs. 2 and 3). The present-day distribution of this limestone within a syncline is related to relief evolution forming an isolated testimony.

Another observation concerns the relationship between pink dolostone and diamictite observed in the Guia syncline. This relationship is very similar to that observed in cap dolostones, but is still open to debate mainly because the dolomite is secondary (dolomitized limestone). Moreover, although no single cap carbonate develops the full set of anomalous sedimentary structures observed worldwide above glacial diamictites, this pink dolostone does not exhibit any of them. Thus, no evidence is available to support the interpretation that the lower part of the section of the Guia syncline is a cap carbonate.

It is difficult to estimate the elapsed time of erosion that represents the transgressive boundary between pebbly siltstone and the limestone, but it is possible to consider that the Guia Formation represents a long-term transgression deposit, not influenced by late Cryogenian glaciation.

### REGIONAL AND GLOBAL CORRELATIONS

The  $\delta^{13}\text{C}_{\text{PDB}}$  profile for more than 600 m of the Araras Group, with negative values around 0‰, is comparable with  $\delta^{13}\text{C}_{\text{PDB}}$  profiles of post-late Cryogenian units of the Kalahari and Congo cratons, western Canada and southern Paraguay Belt (Nogueira et al. 2007). It is worth mentioning the similarities between the stratigraphy and the carbon isotopic profile of the Araras Group in Amazonia and the middle Tsumeb Subgroup in northern Namibia (Halverson et al. 2005). The similarity of facies associations with this Namibian succession is the

base for tentatively correlate the Araras Group carbonate rocks to the post-Ghaub time-interval.

## CONCLUSIONS

- (1) The carbonate succession in the Guia syncline is represented by limestone and shale deposited in an outer platform setting;
- (2) the clear comparison of facies, paleoenvironment and carbon isotopes with the Guia Formation of the Araras Group in Cáceres region indicate that the studied section in the Guia syncline belongs to the upper part of the Guia Formation;
- (3) evidence that the pinkish dolostone beds overlying glaciogenic pebbly siltstone in the Guia syncline comprise a cap carbonate has yet to be found;
- (4) the Guia Formation represents a first-order transgressive deposit postdating the late Cryogenian glaciation;
- (5) the composite  $\delta^{13}\text{C}_{\text{PDB}}$  profile of the Araras Group shows the same pattern of other post-Ghaub units worldwide; the similarity of facies associations with the Namibia succession lead us to assign the Araras Group carbonate rocks to the post-Ghaub (Ediacaran) time-interval.

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## RESUMO

Após a glaciação do final do Criogeniano, a região central do Brasil foi palco de extensa deposição de carbonatos plataformais do Grupo Araras. Este grupo inclui na sua base uma seqüência de capa carbonática sucedida por depósitos transgressivos de calcilutitos betuminosos e folhelhos de plataforma

profunda. Dados de fácies e estratigráficos combinados com análises isotópicas de carbono e oxigênio da seção mais completa desses depósitos transgressivos, expostos no sinclinal da Guia, foram empregados para avaliar o paleambiente deposicional e para testar a correlação desses depósitos ao longo da faixa e também com outras unidades de outros continentes. A sucessão estudada consiste de 150 m de espessura de camadas tabulares de calcilitos e folhelhos cinza a pretos com valores de  $\delta^{13}\text{C}_{\text{PDB}}$  negativos, entre  $-2,5$  e  $-1\text{‰}$ . O perfil de  $\delta^{13}\text{C}_{\text{PDB}}$  do sinclinal da Guia mostra clara correlação com a porção superior da Formação Guia da região de Cáceres, 200 km a sudoeste. O perfil de  $\delta^{13}\text{C}_{\text{PDB}}$  do Grupo Araras é comparável aos perfis de  $\delta^{13}\text{C}_{\text{PDB}}$  de outras unidades ediacaranas da parte sul da Faixa Paraguai, oeste do Canadá, e crátons do Congo e do Kalahari. Além disso, a distribuição de fácies, estratigrafia e o perfil isotópico do Grupo Araras são equiparáveis à porção média do Subgrupo Tsumeb na Namíbia, o que reforça a atribuição de idade Ediacarana para o Grupo Araras.

**Palavras-chave:** isótopos de carbono e oxigênio, Ediacarano, Grupo Araras, Formação Guia, Cráton Amazônico, glaciação.

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