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Redox variations and bioproductivity in the Ediacaran: Evidence from inorganic and organic geochemistry of the Corumbá Group, Brazil

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ABSTRACT

Stable isotope ratios combined with elemental compositions and molecular biomass data provide a powerful tool in Neoproterozoic palaeoenvironmental interpretations. Here, we report the results of an extensive organic and inorganic geochemical study performed in the Ediacaran sedimentary succession of the Corumbá Group (CG) from SW-Brazil, deposited in a shallow marine basin in southwestern Gondwana. This sedimentary succession and in particular the Tamengo Formation, a unit bearing metazoan fossils, has been investigated by means of stable isotopes from carbonates ($\delta^{13}C_{car}$ and $\delta^{18}O$) and associated organic matter ($\delta^{13}C_{ker}$ and $\delta^{15}N_{ker}$) together with hydrocarbon distribution and concentrations of major, trace and rare earth elements (REE). A short post-glacial $\delta^{13}C_{car}$ negative excursion, interpreted as a period of water mixing, is recorded in the cap carbonates overlying diamictites of the Puga Formation, related to Gaskiers or end-Cryogenian glaciation. The overlying Tamengo Formation by contrast, represents a return to redox-stratified conditions in the basin before the Precambrian-Cambrian boundary. Two distinct biogeochemical modes alternate during deposition of Tamengo sediments: 1) an eutrophic, redox-stratified basin well defined by carbonaceous marls from the middle part of the unit but also recorded upwards, at the transition between bioclastic limestones and calcisiltites. 2) An anoxic basin well characterized in the shallow facies, particularly by bioclastic limestones of the upper Tamengo Formation. A positive $\Delta^{13}C_{car-ker}$ ($\Delta^{13}C_{car-ker} = \delta^{13}C_{car} - \delta^{13}C_{ker}$) excursion of ~5‰ in the carbonaceous marls is explained by enhanced primary productivity in surface waters probably related to an increase of pCO_2, nutrient supply and possibly also changes of the primary producer communities. Abundant pyrite, a biomarker distribution characterized by the occurrence of gammacerane and a low Pr/Ph ratio (~0.7) are also remarkable signatures of these facies, most probably associated with a sulfate-reducing microbial consortium in an anoxic and sulfidic (euxinic) environment. However, low concentrations in redox-sensitive trace elements in these facies suggest a largely oxygenated water column, thus constraining the euxinic setting to the sediments and/or bottom waters. The shallow-water bioclastic limestones record higher concentrations of redox-sensitive elements and ΣREE as well as a positive Ce anomaly supporting reducing conditions. Oxygenated conditions and dominance of eukaryotic algae characterize the overlying Guaicurus Formation. Principal component analysis (PCA) was used to assess the major geochemical associations. The most significant component combines parameters involved in primary production, such as P concentrations and $\delta^{13}C_{ker}$ values. The bio-chemostratigraphic variations in this part of SW-Gondwana point to a stratified ocean with oxic surface waters, alternating periods of high and low bioproductivity and anaerobic conditions at the bottom waters, in the aftermath of younger Neoproterozoic glaciations and close to the Precambrian–Cambrian boundary.

1. Introduction

The Neoproterozoic is marked by the early evolution of animals and the most severe glaciations known in Earth history (Hoffman et al., 1998). These glaciations are characterized by diamictite horizons covered worldwide by successions of carbonates known as "cap carbonates" (Hoffman and Schrag, 2002). The abrupt lithological contact records a genuinely rapid change in depositional regime from icehouse to greenhouse conditions. The global isotopic signature of cap carbonates is strongly ^{13}C-depleted, approaching mantle carbon values (~−6‰; e.g., Hayes et al., 1999). Excursions in the isotopic difference between carbonate and associated kerogen ($\Delta^{13}C_{car-ker} = \delta^{13}C_{car} - \delta^{13}C_{ker}$) record changes in the extent of isotopic discrimination from fixation to burial of organic carbon (Hayes et al., 1999) and alternatively, it can reflect changes in the biomass composition. There is also evidence that $\Delta^{13}C_{car-ker}$ values have varied as a function of pCO_2 (Hayes et al.,

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1992). Many researchers consider the existence of an unusually large dissolved organic carbon (DOC) reservoir in the Ediacaran ocean, and oxidation of the DOC as a plausible cause of $\delta^{13}C_{car}$ fluctuations (Rothman et al., 2003; Fike et al., 2006; McFadden et al., 2008). The extreme isotopic shifts in both carbonate and organic carbon at and before the Precambrian–Cambrian boundary suggest periods of major chemical changes in the ocean–atmosphere system (e.g., Och and Shields-Zhou, 2012). These biogeochemical changes are crucial events accompanying the transition from a microbial-dominated ocean to the early stages of metazoan radiation. In addition, other events revealing a great dynamism of the Neoproterozoic Earth such as supercontinental break-up and rising oxygen levels could probably have triggered the extraordinary biotic evolution at the end of the era (e.g., Knoll, 2005; Gaucher et al., 2009a).

In recent years, several studies of Precambrian sedimentary successions focused on the understanding of the biotic events and their relationship to chemical changes in the ocean–atmosphere–lithosphere system. These studies concentrate particularly on major and trace element concentrations (Schroder and Grotzinger, 2007), stable isotope ratios (Kaufman and Knoll, 1995; Hayes et al., 1999; Walter et al., 2000; Shields and Stille, 2001; Rothman et al., 2003; Bartley and Kah, 2004; Kaufman et al., 2007; McFadden et al., 2008; Shen et al., 2008; Frei et al., 2009, 2011, 2013) and hydrocarbon biomarkers (Summons et al., 1999; Arouri et al., 2000; Li et al., 2003; Greenwood et al., 2004; Brocks et al., 2005; Olcott et al., 2005; Grosjean et al., 2009). Studies integrating all three approaches are sparse (e.g., Bagnoud-Velásquez et al., 2013). Localized environmental and biological signals can be discerned and resolution enhanced by combining isotopic and molecular information.

This paper reports the results of an extensive geochemical investigation of the Ediacaran Corumbá Group in SW-Brazil (Fig. 1), encompassing major, trace and rare earth element (REE) concentrations, hydrocarbon distribution, and stable isotope ratios of carbonates ($\delta^{13}C_{car}$ and $\delta^{18}O$) and associated kerogen ($\delta^{13}C_{ker}$ and $\delta^{15}N_{ker}$). Correlating the variations of the $\Delta^{13}C_{car-ker}$ values, the concentrations of some redox sensitive elements, ΣREE and the Ce/Ce* ratios, new insights about changes in atmospheric ρCO_2, biomass productivity and local palaeoenvironmental conditions could be gained. The distribution of hydrocarbon biomarkers gives insight into the microbial diversity present in the Ediacaran oceans.

The sedimentology, stratigraphy, paleontology and some chemostratigraphic data of this unit were previously reported (Gaucher et al., 2003; Boggiani et al., 2010). A correlation of the Corumbá Group with the Arroyo del Soldado Group from Uruguay was proposed by Gaucher et al. (2003) suggesting that they were deposited on an extensive marine shelf, developed on a large area at the eastern margin of the Rio de la Plata Craton. The new biogeochemical data combined with the previous sedimentological and paleontological observations of the studied sections of the Corumbá Group allow tracing changes in ocean chemistry during a period close to the Precambrian–Cambrian boundary in this part of SW-Gondwana.

2. Geological setting

The main geological features of the Corumbá area in the wetland Pantanal region of Mato Grosso do Sul, SW-Brazil are determined by the evolution of Gondwana (Fig. 1). The Gondwana supercontinent was formed by the reassembly of cratonic blocks that previously rifted off Rodinia around 530 Ma, at the end of the Pan-African–Brasiliano orogeny (Li et al., 2008; Gaucher et al., 2009b). Pan-African–Brasiliano orogenic belts mark the sutures between these cratons, one of them being the Paraguay Belt. In this context, the Corumbá area is located in the Rio Apa Block, which may be part of the Amazon Craton (Fig. 1), and was separated from Laurentia (~550 Ma) by the opening of the Iapetus Ocean (Grunow et al., 1996; Trompette, 2000; Gaucher et al., 2009b). The arrangement between the Paraguay Belt and Tucavaca aulacogen was explained as the result of the opening and later closure of a triple junction, in which the Corumbá basin could have evolved in a rift-to-drift context (Alvarenga et al., 2000), also associated to the siliciclastic and overlying iron and manganese deposits of the Jacadigo Group (Piacentini et al., 2013).

At several localities, the Corumbá Group rests on diamictites of the Puga Formation, probably glaciogenic in origin (Alvarenga and Trompette, 1992; Piacentini et al., 2007; Alvarenga et al., 2011; Freitas et al., 2011). In the northern Paraguay Belt, another carbonate unit known as Araras Group overlies the Puga Formation (Nogueira et al., 2007; Alvarenga et al., 2008). The Puga Formation in its type area in the southern Paraguay Belt is probably not correlated with the Puga Formation in the northern Paraguay Belt. The latter has been assigned to the end-Cryogenian glacial event (Marinoan) on the basis of C and Sr chemostratigraphy (Nogueira et al., 2007; Alvarenga et al., 2008, 2011) and a Pb–Pb isochron age for the cap carbonate of 633 ± 25 Ma (Alvarenga et al., 2009). The Puga formation in the southern Paraguay Belt with a possible cap carbonate (Boggiani et al., 2003), is overlain by the Corumbá Group which bears a late Ediacaran acritarch assemblage, the late Ediacaran index-fossil *Cloudina*, C and Sr isotopic curves similar to other late Ediacaran units and volcanic zircons at the top dated by ion microprobe U–Pb method at 545–543 Ma (Gaucher et al., 2003; Babinski et al., 2008; Alvarenga et al., 2009; Boggiani et al., 2010). This allows the possibility of a younger age for these diamictites regarding those of the North. The stratigraphy of the Araras Group is significantly different (Alvarenga et al., 2009, 2011) and cannot be directly correlated to the Corumbá Group.

The stratigraphy and related palaeoenvironments of the Corumbá Group are presented in Fig. 2, and rock outcrops shown in Fig. 3A–E. The Corumbá Group includes a wide spectrum of environments embracing open marine (mostly fine siliciclastics), moderately deep shelf (mixed siliciclastics and carbonates) and adjacent shallow-platform sedimentation (carbonates and fine siliciclastics). These palaeoenvironments characterize a shallow sea and are represented by the Cerradinho, Bocaina, Tamengo and Guaicurus formations, the whole sequence having a composite thickness of nearly 600 m (Gaucher et al., 2003). The Corumbá Group conformably overlies the Puga Formation, which consists of diamictite with pebbles accounting for 10 to 30% of the rock volume, thin sandstones intercalations and minor banded iron formation and ferruginous matrix diamictite (BIF; Piacentini et al., 2007; Babinski et al., 2013). The Cerradinho Formation, at the base of the Corumbá Group, consists of a deepening-upward sequence including arkose, quartz-arenite and greenish to reddish siltstones (Fig. 3D). This unit was probably deposited in a fault-bounded basin and represents distal alluvial plain environments probably occurring at waning stage of rifting and concomitant glaciation (Gaucher et al., 2003). The Bocaina Formation is characterized by light colored stromatolitic and oncoidal dolostones and phosphorite horizons at the top, which were deposited in a shallow marine to intertidal environment in a post-rift context (Freitas et al., 2011). Tubestone stromatolites, typical of cap carbonates, occur at some localities (Fig. 3C; Boggiani et al., 2010). These carbonates may be correlated to the red limestones occurring as cap carbonates in the Morro do Puga hill based on a similar carbon isotope signature (~−5‰; Boggiani et al., 2003, 2010). The contact between the Bocaina and Cerradinho formations is not observable and could correspond to a lateral facies variation (Fig. 3C, D). The dolostones are covered by the Tamengo Formation, which is mainly composed of calcisiltites (mudstones sensu Dunham, 1962), carbonaceous marls (micrite), dark organic-rich limestones and oolitic calcarenites (Fig. 3E; Gaucher et al., 2003). Levels very rich in euhedral and framboidal pyrite occur in the organic-rich marls of the middle of Tamengo Formation (Fig. 3F). Polymictic, carbonatic breccias were observed at the base of this unit at the Laginha Mine, where despite the presence of low- to high-angle reverse faults and duplex structures, it is possible to reconstruct the original stratigraphy. The carbonatic breccia at the base of Tamengo Formation represents an expressive lowering of the sea level, followed by a transgressive event on a passive continental margin. The sedimentation represents marine