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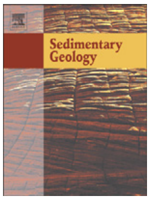

# Septarian carbonate concretions in the Permian Rio do Rasto Formation: Birth, growth and implications for the early diagenetic history of southwestern Gondwana succession

Luciano Alessandretti [a,*], Lucas Veríssimo Warren [b], Rômulo Machado [a],
Valdir Felipe Novello [a], Isaac Jamil Sayeg [a]

[a] *Instituto de Geociências, Universidade de São Paulo, Rua do Lago, 562, Cidade Universitária, São Paulo, SP CEP 05508-080, Brazil*
[b] *Instituto de Geociências e Ciências Exatas, Departamento de Geologia Aplicada, Universidade Estadual Paulista, Avenida 24-A, Bela Vista, Rio Claro, SP CEP 13506-900, Brazil*

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ABSTRACT

Between the Late Carboniferous and Early Triassic, the southwestern Gondwana supercontinent was characterized by the development of a huge intracratonic basin. A large confined epeiric sea and the accumulation of a transgressive–regressive sequence were formed by continuous subsidence related to tectonic effects caused by the Sanrafaelic Orogeny and the consequent generation of accommodation space. The Permian Rio do Rasto Formation documents the last progradational cycle related to the complete continentalization of this epeiric sea. The basal member of the Rio do Rasto Formation (Serrinha) is believed to have been deposited in a shallow epicontinental water body subjected to storms and influenced by episodic deltaic incursions. One of the most remarkable characteristics of the Serrinha Member is the presence of carbonate concretions hosted in mudstones and very fine sandstones. Here, we combine sedimentological and petrographic descriptions coupled with geochemical and stable carbon and oxygen isotopic data to elucidate the nature of these carbonate concretions. The non-deformed internal structure, decreasing proportion of carbonate cements relative to detrital grains toward the concretion edges, core-to-rim isotopic variations, and perhaps most importantly, the preservation of a well-developed cardhouse fabric support an early diagenetic origin for these structures at shallow burial depths of tens of meters. Stable isotope analyses of micritic calcite cements and calcites filling the septarian fractures reveal major negative excursions in both $\delta^{18}O$ and $\delta^{13}C$ values. Oxygen isotope ratios obtained for the micritic calcite cements vary between −12.1 and −2.6‰. The calcite filling septarian fractures also exhibit negative values of $\delta^{18}O$ (−14.2 to −13.8‰), with an average of −14‰. The $\delta^{13}C$ values of micritic calcite cements range from −5.0–0.2‰. The carbon isotopic data from the calcite-filling septarian fractures are also negative (−4.4 to −3.3‰). The $\delta^{18}O$ signatures suggest that the early diagenetic carbonate concretions precipitated in a shallow freshwater environment rather than in a marine setting. The $\delta^{13}C$ values suggest that the carbon isotopes were derived from a source with slightly depleted $^{13}C$, supporting at least a partial organogenic contribution with weak sulfate reduction rates typical of freshwater systems. Sedimentological analysis shows that the epicontinental water body in which the Serrinha Member was deposited was constantly supplied by rivers and meteoric waters, which suggests that an enormous freshwater basin with restricted marine connections to the Panthalassa Ocean once existed.

## 1. Introduction

Carbonate concretions are typical diagenetic features commonly found in fine-grained sedimentary rocks. These concretions provide substantial information about the progressive chemical evolution of interstitial pore waters and the cementation of mineral phases during the early burial of the sediments (Irwin et al., 1977; Hudson et al., 2001; Seilacher, 2001; McBride et al., 2003, Raiswell, 2002, Mozley and Davis, 2005; Woo and Khim, 2006; Dale et al., 2014). Although much of the geochemical (Irwin et al., 1977; Curtis et al., 1986; Wilkinson, 1993; Abdel-Wahab and McBride, 2001; Raiswell et al., 2002; Woo and Khim, 2006; Wanas, 2008; Mahboubi et al., 2010; Dale et al., 2014) and textural information (Astin, 1986; Selles-Martinez, 1996; Yemane and Kelts, 1996; Seilacher, 2001) has contributed to our increased knowledge about the genesis of these concretions, the nucleation and growth of these structures are still not fully understood. It is generally accepted that they were formed at burial depths of tens to hundreds of meters via carbonate and/or sulfate cementation as a consequence of geochemical changes in the pore waters (Irwin et al., 1977; Froelich et al., 1979; Curtis et al., 1986, Compton, 1988, Mozley

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[*] Corresponding author at: Programa de Pós-Graduação em Recursos Minerais e Hidrogeologia Instituto de Geociências - Universidade de São Paulo.
*E-mail address:* luciano.geoufrgs@gmail.com (L. Alessandretti).

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and Burns, 1993; Dong et al., 2013). The degradation of organic matter by sulfate-reducing bacteria is related to carbonate precipitation and growth of carbonate nodules in organic-rich sediments. The interstitial pore waters in such environments lead to an increase in the carbonate alkalinity and lower the sulfate ion concentration to near zero (Compton, 1988). The concretions have been found in sediments and sedimentary rocks over a wide range of depositional environments, including marine (Abdel-Wahab and McBride, 2001; Woo and Khim, 2006; Wanas, 2008) and non-marine environments (Yemane and Kelts, 1996; Wanas, 2008; Hoareau et al., 2009). Furthermore, these depositional environments have ages ranging from the Precambrian (Goldberg et al., 2006; Dong et al., 2013) through the entire Phanerozoic (Vochten and Geys, 1974; Pirrie and Marshall, 1991; Rabassa, 2006; Woo and Khim, 2006; Wanas, 2008). The concretions are typically sub-spherical to spherical but frequently take on a variety of other shapes including disks, ellipses, continuous or discontinuous bands, grape-like aggregates, coalescent bodies and complex shapes (McBride et al., 1995; Selles-Martinez, 1996; Seilacher, 2001).

The concretions are often cut by one or more generations of fractures also known as septarian cracks/fractures. These fractures are completely or partially filled by carbonate cements and secondary minerals such as silica, phosphates and sulfates. They typically range in shape: sub-vertical lenses, concentric sheets, radial or crosscutting fractures. The processes involved in the formation of septarian cracking have been explained by the following: (i) shrinkage (brittle fracturing) induced by the dehydration of clay minerals or organic matter (Raiswell, 1971); (ii) compaction and overpressure of pore waters (Astin, 1986); (iii) gas generation due to bacterial decay of organic compounds (Irwin et al., 1977); and (iv) syn-depositional earthquake-induced ground motion (Pratt, 2001). Due to the post-depositional origin of the concretions, they have been used as key features for understanding the diagenetic evolution of the sedimentary rocks (Irwin et al., 1977).

The Rio do Rasto Formation is sub-divided into the lower Serrinha and upper Morro Pelado members, and their depositional environments range from offshore settings affected by storms to deltaic and aeolian systems (Warren et al., 2008). Because typical marine fossils (such as echinoderms, bryozoans and brachiopods) are lacking and sedimentological evidence refutes the action of astronomic tides (e.g., tidal bundles, mud/sand pairs, asymmetry in paleocurrents), all of the Permian succession of the Passa Dois Group is considered to have been deposited in a confined interior sea of uncertain salinity (Lavina, 1991).

The presence of Permian-aged carbonate concretions in the Paraná Basin (Fig. 1), particularly in the Rio do Rasto Formation, has been acknowledged for many years, although few studies have been published. On the basis of sedimentological and paleontological evidence (Schneider et al., 1974; Gama Jr., 1979; Rohn, 1994; Warren et al., 2008; Holz et al., 2010), it is impossible to definitively determine if these concretions were formed in a freshwater lacustrine or a marine depositional environment.

In this work, we combine field, petrographic and stable $\delta^{18}$O and $\delta^{13}$C isotopic data to elucidate the diagenetic fluid history and the genesis of the carbonate concretions and their septarian fractures in the Late Permian Serrinha Member. Despite the importance for lithification, the origin and growth pattern of these structures during early diagenesis can reveal important environmental information about the immediate stages after the sedimentary deposition.

## 2. Regional geological context

The Paraná Basin is an enormous intracratonic basin that was located in the southwestern portion of the Gondwana supercontinent during the Phanerozoic eon (Milani, 1997). Its origin and evolution has been associated with several subsidence cycles, presumably caused by litospheric flexure related to different orogeny cycles that occurred at the marginal portions of southwestern Gondwana (Milani and Ramos, 1998). This portion of the supercontinent was subjected to the successive amalgamation of several allochthonous terrains that collided against the Gondwana proto-Pacific margin (Ramos, 1984, 1986, 2008; Gohrbandt, 1992; Milani and Ramos, 1998). Ramos (1986) divided the orogenic phases into three major tectono-sedimentary cycles: the Pampean (Neoproterozoic to Early Cambrian), the Famatinian (Ordovician to Devonian) and the Gondwanic (Carboniferous to Triassic). The sedimentary successions that were deposited during the major tectonic subsidence cycles consist of, from the base to the top, the following supersequences: Rio Ivaí (Ordovician–Silurian), Paraná (Devonian), Gondwana I (Carboniferous–Eotriassic), Gondwana II (Meso-Neotriassic), Gondwana III and Bauru (Neocretacic). The first three supersequences represent successions deposited under the influence of transgressive–regressive cycles related to fluctuations of the relative sea level during Paleozoic times. The remaining supersequences (Gondwana II, Gondwana III and Bauru) include continental sedimentary successions associated with the breakup of the Gondwana supercontinent, and the Cretaceous volcanic eruptions related to the Large Igneous Province of the Serra Geral Formation. Each of these supersequences encompasses a time interval of tens of millions of years and is temporally delimited by regional disconformities.

The deposition of the second-order supersequence “Gondwana I” (Pennsylvanian–Eotriassic) is related to a flexural subsidence cycle associated with the subduction of the Panthalassa oceanic lithosphere under the South Gondwana plate, and the subsequent docking of the Patagonia terrane (Ramos, 2008). Due to the lithospheric thickening and the rise of mountain chains along the southwestern Gondwana margin, large-scale marine incursions became restricted in the subsiding basin area, resulting in the formation of a large and confined body of shallow water (Milani, 1997). Between the Late Permian and the Early Triassic, this newly formed basin occupied a vast area and was characterized by the accumulation of a transgressive-regressive succession.

Lithostratigraphically, the Gondwana I supersequence is composed of the Itararé, Guatá and Passa Dois groups. The Itararé Group forms the basal part of the supersequence and consists of diamictites and other glacial-related rocks deposited during the Late Carboniferous and Early Permian on the southern hemispherical Gondwana supercontinent. After the end of the Paleozoic glaciation, a new sedimentary state was established in southern Gondwana in response to drastic climate changes and consequent sea level rise (Limarino et al., 2013), as documented in the chrono-correlated sedimentary units in South America (Fig. 11), South Africa, Namibia, Tanzania, Antarctica, India and Australia (Veevers and Powell, 1987). At the end of the Paleozoic, warm, semi-arid conditions existed in southern Gondwana, which were synchronous with an important progradational cycle. Low subsidence rates associated with a high sediment influx provided the conditions for the deposition of a second-order progradational succession. The deltaic, fluvial, lacustrine and eolian rocks of the Rio do Rasto and Piramboia formations are representative of this marine regression that culminates with the definitive continentalization of the basin during the Permian–Triassic transition (Lavina, 1991; Warren et al., 2008).

### 2.1. The Rio do Rasto Formation

The Rio do Rasto Formation (Fig. 2) outcrops along the eastern border of the Paraná Basin, mainly in the Paraná, Santa Catarina and Rio Grande do Sul states. The unit is delimited at the base and at the top by transitional contacts with the Teresina and Piramboia formations, respectively (Milani, 1997; Warren et al., 2008). Lithologically, it is characterized by an alternating 250–300-m-thick succession of sandstones, siltstones and mudstones, supposedly deposited during the Late Permian–Early Eotriassic (Schneider et al., 1974; Lavina, 1991; Warren et al., 2008). The Rio do Rasto Formation represents the upper portion of the Permo-Triassic transgressive–regressive cycle in the Paraná Basin. During this period, the limited or absent marine connection of the Paraná Basin with the Panthalassa Ocean was likely related to orogeny at the Gondwana continental margin, which led to the formation of a large