New age constraints on Aptian evaporites and carbonates from the South Atlantic: Implications for Oceanic Anoxic Event 1a

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4International Atomic Energy Agency CO-1 standard gave a standard deviation (σ) of ±0.07‰ for δ13C and ±0.12‰ for δ18O. We also compiled δ13C and total organic carbon (TOC) values from cuttings from supraevaporite Petrobras well X, Santos Basin (Quintaes, 2006), and subevaporite Petrobras well CP-5, Campos Basin (Dias, 1998), to generate composite carbonate carbon isotope and TOC curves (Santos-Campos composite), where original samples were not available for further analyses. All results, detailed methods, quality control, and compilation of data are provided in the GSA Data Repository1.

INTRODUCTION

Oceanic anoxic events (OAEs) are time intervals when oxygen depletion characterized much of the middle and/or deeper waters of the world’s oceans. As a result, an unusual amount of organic matter was preserved in marine sediments worldwide (Jenkyns, 2010). OAE 1a is typically identified by an organic-rich sedimentary record and/or characteristic carbon isotope signature (δ13C) in carbonate or organic matter: phenomena recorded in geographically widespread localities (Menegatti et al., 1998; Bottini et al., 2015). Possible causative mechanisms include accelerated input of nutrients from basalt-seawater interaction, massive CO2 release from extrusion of the Ontong Java Plateau, and/or dissociation of methane hydrate (Méhay et al., 2004; Huber and Leckie, 2011). We analyzed 195 core samples (from depth interval 2437–2689 m) for carbon and oxygen isotopes (δ13C and δ18O) on bulk carbonate. Data are reported in parts per thousand (‰) relative to the Vienna PeeDee belemnite standard. The International Atomic Energy Agency CO-1 standard gave a standard deviation (σ) of ±0.07‰ for δ13C and ±0.12‰ for δ18O. We also compiled δ13C and total organic carbon (TOC) values from cuttings from supraevaporite Petrobras well X, Santos Basin (Quintaes, 2006), and subevaporite Petrobras well CP-5, Campos Basin (Dias, 1998), to generate composite carbonate carbon isotope and TOC curves (Santos-Campos composite), where original samples were not available for further analyses. All results, detailed methods, quality control, and compilation of data are provided in the GSA Data Repository1.

METHODS

Petrobras well CB-3 is located in the offshore Campos Basin (22°44’S, 40°40’E) (Fig. 1) and terminated an unknown distance above the evaporites (Fig. 2). We prepared and analyzed 171 core samples (from depth interval 2484–2689 m) for foraminiferal biostratigraphy in the Research Center of Petrobras (Rio de Janeiro, Brazil), using concepts from Premoli Silva and Verga (2004) and Huber and Leckie (2011). We analyzed 195 core samples (from depth interval 2437–2689 m) for carbon and oxygen isotopes (δ13C and δ18O) on bulk carbonate. Data are reported in parts per thousand (‰) relative to the Vienna PeeDee belemnite standard. The International Atomic Energy Agency CO-1 standard gave a standard deviation (σ) of ±0.07‰ for δ13C and ±0.12‰ for δ18O. We also compiled δ13C and total organic carbon (TOC) values from cuttings from supraevaporite Petrobras well X, Santos Basin (Quintaes, 2006), and subevaporite Petrobras well CP-5, Campos Basin (Dias, 1998), to generate composite carbonate carbon isotope and TOC curves (Santos-Campos composite), where original samples were not available for further analyses. All results, detailed methods, quality control, and compilation of data are provided in the GSA Data Repository1.

GEOLOGICAL SETTING OF THE SANTOS AND CAMPOS BASINS

The Santos and Campos Basins formed during the opening of the central segment of the South Atlantic Ocean in the Early Cretaceous (Davison, 2007; Chaboureau et al., 2013). The stratigraphic record, based on offshore wells, is divided into three main supersequences, rift, postrift, and drift, as described by Moreira et al. (2007) and Winter et al. (2007). Above the basement, the rift supersequence comprises volcanic rocks, continental siliciclastics, and...
interbedded lacustrine coquinas and organic-rich shales (Coqueiros and Itapema Formations; Fig. 2); in distal settings, the overlying postrift supersequence comprises interbedded microbial carbonates and shales (Macabu and Barra Velha Formations; Fig. 2). The evaporites terminate the postrift supersequence and comprise cycles of predominantly anhydrite and halite, locally with more soluble salts such as carnallite, sylvite, and tachyhydrite (Retiro and Ariri Formations; Fig. 2). Halite and anhydrite from the Espírito Santo Basin, north of the Campos Basin (Fig. 1), have Br contents and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios that indicate derivation from marine waters (Dias, 1998). The anhydrite probably formed from dewatering of gypsum during burial and shows textures typical of precipitation in subaqueous settings, such as thin laminations and twinned crystals, as well as nodules of probable sabkha facies (Dias, 1998). Above the evaporites, in distal settings, the early drift supersequence is represented by shallow-marine platform carbonates (Quissamã and Guarujá Formations; Fig. 2) containing planktonic foraminiferal species that are not age-diagnostic (e.g., Favusella ex grege washitensis; Azevedo et al., 1987). Following platform drowning, deeper water sediments accumulated (Outeiro and Itanhaém Formations; Fig. 2), in which Aptian and younger calcareous nannofossils (e.g., Nannoconus truittii) and planktonic...
foraminifera are present (e.g., Globigerinelloides ferroelensis; Ticinella raynaudi; Azevedo et al., 1987; this study).

RESULTS AND STRATIGRAPHIC CORRELATION WITH REFERENCE SECTIONS

An assemblage of 11 planktonic foraminifera (Hedbergella aptiana, H. gorbachkiae, H. infracretacea, H. sigali, H. luterbacheri, H. tuschepsensis, H. kuznetsovae, H. occulta, G. ferroelensis, G. barri, and Favussella ex gr. washitensis) was identified from 2484 to 2508 m from Petrobras well CB-3. This assemblage indicates the upper Aptian from the G. ferroelensis to the G. algerianus zones (cf. Premoli Silva and Verga, 2004; Ogg et al., 2012) (Fig. 2; Fig. DR1 in the Data Repository). Samples below 2508 m, deposited in relatively shallow water, contain a low-diversity assemblage with relatively long-ranging species of benthic (e.g., Lenticulina ex gr. nodosa) and planktonic foraminifera (ex. Favussella ex gr. washitensis), and are interpreted as early-middle Aptian or older.

The carbon isotope profile from Petrobras well CB-3 shows a defined pattern (Fig. 2): a stratigraphically lower section (2689–2517 m) showing relatively high δ13C values (3.60‰–4.97‰) and a stratigraphically higher section (2517–2437 m) that shows a trend of decreasing δ13C values from bottom (3.0‰–3.3‰) to top (1.2‰–1.6‰), interrupted by a positive excursion with values >4‰. Relatively high δ13C values, as in the interval 2689–2517 m, characterize part of the so-called C7/Ap7 isotopic segment (latest early Aptian–earliest late Aptian interval), with the highest δ13C values of the Aptian stage (e.g., Menegatti et al., 1998; Bottini et al., 2015) (purple band in Fig. 2). Although no biostatigraphic constraints are available stratigraphically above 2484 m, the trend of decreasing δ13C values and positive excursion, as in the interval 2517–2450 m, are similar to the C8–C10/Ap8–Ap15 segments of the late Aptian (cf. Bradlow et al., 1999; Bottini et al., 2015) (yellow band in Fig. 2). Deeper water sediments stratigraphically above 2450 m do not have biostatigraphic constraints and do not show diagnostic δ13C patterns. They are here interpreted as latest late Aptian or younger in age.

The Santos–Campos composite (Fig. 2) does not have any biostatigraphic constraints based on planktonic marine fossils, and this correlation with the Tethyan reference section is based on δ13C values. The basal interval (0–173 m) lacks diagnostic features on the δ13C curve and it is stratigraphically below an important regional unconformity identified in seismic lines and other oil wells in southern Brazilian basins called the pre-Alagoas unconformity (Dias, 1998; Fig. 2). Therefore, it cannot be correlated with the Tethyan reference curve. The stratigraphically higher subevaporite interval 186–501 m, with δ13C generally in excess of 1.2‰, is tentatively correlated with upper Barremian B5–B8 segments and lower Aptian Ap1–Ap2 segments (green band in Fig. 2; Wissler et al., 2003; Bottini et al., 2015); the subevaporite interval 501–573 m, with δ13C generally <1.2‰, is tentatively correlated with the C3/Ap3 segment that characterizes the base of the OAE 1a interval worldwide (cf. Menegatti et al., 1998; Bottini et al., 2015) (blue band in Fig. 2). However, the correlations of the interval 186–573 m are tentative, especially the lower values found in the interval 501–573 m, because of deposition in continental environments (e.g., Sabato Cereda and Green, 2017) and/or diagenetic overprints.

Above the evaporites, the interval 2600–2756 m shows a general trend of increasing δ13C values typical of the C6/ Ap6 segments and TOC values as high as 1.4‰ (cf. Menegatti et al., 1998; Bottini et al., 2015) (blue band in Fig. 2), geochemical characteristics that likely constrain this interval to the latter part of OAE 1a. The highest δ13C values (3.14‰–4.77‰) from the Santos–Campos composite (2756–2906 m) are diagnostic of the Aptian immediately post-OAE 1a sediments of the C7/ Ap7 segment (cf. Menegatti et al., 1998; Bottini et al., 2015) (purple band in Fig. 2). The interval 2906–2948 m (basal part of yellow band in Fig. 2) shows a trend of decreasing δ13C values that may record the lower part of the C8–Ap8 segment (cf. Bradlow et al., 1999; Bottini et al., 2015). The Campos–Santos composite does not show the lower δ13C values and subsequent increasing trend of δ13C values (C8–C9/ Ap8–Ap16 segments; Bradlow et al., 1999; Bottini et al., 2015) present in the Tethyan reference curve (Fig. 2; time scale of Ogg et al., 2012). It is significant that the Ap8–Ap11 segments are apparently extremely condensed or possibly missing. The broad positive excursion in the interval 2948–3803 m has been observed in upper Aptian sediments worldwide (C10/ Ap13–Ap15 segments; Bradlow et al., 1999; Bottini et al., 2015) (yellow band in Fig. 2). Because we lack biostatigraphic analyses of the shallow- and deep-water carbonates above 3803 m, they are interpreted as latest late Aptian or younger in age.

STRATIGRAPHY OF SOUTH ATLANTIC EVAPORITES

The evidence suggests that the top of the evaporites correlates with the upper part of the OAE 1a interval and that most of the postevaporite shallow-water carbonates are Aptian in age; this constitutes a major stratigraphic revision of southern Brazilian basins. Deposition of the South Atlantic evaporites is estimated to have lasted 400–600 k.y., based on cyclostratigraphy, and the reconstructed depositional rate of ~5 mm yr⁻¹ is similar to modern evaporite depositional rates from Lake Assal, Africa (10 mm yr⁻¹), MacLeod Basin evaporites, western Australia (4–100 mm yr⁻¹), and Messinian evaporites of the Mediterranean (6.6 mm yr⁻¹) (Dias, 1998; Davison et al., 2012; and references therein). Therefore, it is likely that the formation of South Atlantic evaporite body was shorter than the duration of OAE 1a (~1.1 m.y.; cf. Malinverno et al., 2010) and formed during the OAE 1a interval, although we cannot confidently exclude the possibility that the onset of deposition was as early as Barremian.

The current view is that the South Atlantic evaporites were deposited between 116 and 111 Ma in the late Aptian–earliest Albian interval (Davison, 2007; Chaboureau et al., 2013; Gomes et al., 2016; time scale of Ogg et al., 2012), ~4–13 m.y. after OAE 1a (cf. Bottini et al., 2012). This interpretation is based on the stratigraphic relationships between the evaporites and supposedly extrusive rocks with Ar–Ar ages of 117 Ma (cited in Moreira et al., 2007) and 113±2–0.1 Ma (cited in Dias et al., 1994). However, no details are available as to whether the dated samples are from pristine or altered rocks, and detailed analytical methodologies are not reported. In addition, this evidence alone is at odds with the presence of lower Aptian ammonites (Dyfrenovia justinae) described by Bengtson et al. (2007) from supraevaporite sediments in the Sergipe–Alagoas Basin (Fig. 1) and the record of lower Aptian planktonic foraminifera (presence of Leopoldina cabri) in supraevaporite sediments from the African side, offshore Angola (Davison, 2007). These associations suggest that evaporite deposition took place, at least locally, before or during the early Aptian. It is significant that the new stratigraphic correlation for the evaporites from the Campos and Santos Basins with OAE 1a corresponds closely with the well-dated ages of those from the African margin and Sergipe–Alagoas Basin, onshore northeastern Brazil, suggesting a similar age for these sediments across the entire central segment of the South Atlantic Ocean.

Important evidence for the age of the evaporites is offered by sulfur isotope values (δ34S) between −17‰ and −22‰, obtained from anhydrite of the Santos Basin (blue rectangle in Fig. 2; Santos Neto et al., 2013), that can be compared to δ34S values from barite and carbonate-associated sulfate in sediments worldwide (red data in Fig. 2). The values from the Santos Basin evaporites are higher than the range of δ34S values postdating OAE 1a (14‰–17‰) and lower than the highest values recorded in the latest late Barremian (24‰–25‰; Fig. 2). Therefore, they likely constrain evaporite deposition to the interval latest late Barremian–early Aptian, including OAE 1a.

The decrease in δ34S values recorded worldwide (Fig. 2) coincides with the characteristic pattern in δ13C profiles during OAE 1a, i.e., a negative excursion followed by the onset of a positive excursion (e.g., Gomes et al., 2016).
Formation of the Ontong Java Plateau probably released massive amounts of CO2 and SO2 during basalt-seawater interaction, both relatively $^{34}$S and $^{13}$C depleted, which could explain low $\delta^{34}$S and $\delta^{13}$C values at the onset of OAE 1a (e.g., Paytan et al., 2004; Méhay et al., 2009). However, it cannot explain the decoupling between $\delta^{34}$S and $\delta^{13}$C profiles, whereby the positive excursion in $\delta^{13}$C occurs with relatively low $\delta^{34}$S values during and after OAE 1a. This pattern is in marked contrast with positive excursions in both $\delta^{13}$C and $\delta^{34}$S profiles of the Toarcian and Cenomanian–Turonian OAEs, when enhanced burial of organic matter and pyrite preferentially sequestered $^{14}$C and $^{34}$S, respectively (Gill et al., 2011; Gomes et al., 2016). Geochemical models indicate that burying a huge volume of gypsum and/or anhydrite in the South Atlantic would have led to a reduction of the global concentration of sulfate, limiting pyrite burial and enhancing organic-matter preservation, which could explain this behavior of $\delta^{34}$S and $\delta^{13}$C profiles during and after OAE 1a (Wortmann and Chernyakovsky, 2007).

In summary, our new stratigraphic revision suggests that deposition of the South Atlantic evaporites, after the release of CO2 and SO2 during the formation of the Ontong Java Plateau, may have removed massive amounts of sulfate from the world ocean, decreasing global pyrite burial, increasing average marine organic-matter preservation worldwide, and leading to relatively elevated $\delta^{13}$C values and lower $\delta^{34}$S values in sediments deposited during and after the end of OAE 1a.

ACKNOWLEDGMENTS

We acknowledge Petrobras (Brazil) for support and permission to publish this research. We thank the reviewers for their helpful comments on the manuscript.

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Manuscript received 12 December 2016 Revised manuscript received 10 February 2017 Manuscript accepted 13 February 2017

Printed in USA