



Calcium Carbonate Dissolution Triggered by High Productivity During the Last Glacial–Interglacial Interval in the Deep Western South Atlantic

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Studies reconstructing surface paleoproductivity and benthic environmental conditions allow us to measure the effectiveness of the biological pump, an important mechanism in the global climate system. In order to assess surface productivity changes and their effect on the seafloor, we studied the sediment core SAT-048A, spanning 43–5 ka, recovered from the continental slope (1,542 m water depth) of the southernmost Brazilian continental margin, deep western South Atlantic. We assessed the sea surface productivity, the organic matter flux to the seafloor, and calcite dissolution effects, based on micropaleontological (benthic and planktonic foraminifers, ostracods), geochemical (benthic $\delta^{13}\text{C}$ isotopes), and sedimentological data (carbonate and bulk sand content). Superimposed on the induced changes related to the last glacial–interglacial transition, the reconstruction indicates a significant and positive correlation between the paleoproductivity proxies and the summer insolation. From the reconstructed data, it was possible to identify high (low) surface productivity, high (low) organic matter flux to the seafloor, and high (low) dissolution rates of planktonic Foraminifera tests during the glacial (postglacial). Furthermore, within the glacial, enhanced productivity was associated with higher insolation values, explained by increased northeasterly summer winds that promoted meandering and upwelling of the nutrient-rich South Atlantic Central Water. Statistical analyses support the idea that productivity is the main cause for seafloor calcium carbonate dissolution, as opposed to changes in the Atlantic Meridional Overturning Circulation (at least for the 25–4 ka period). Further efforts must be invested in the comprehension and quantification of the total organic matter and biogenic carbonate burial during time intervals with an enhanced biological pump, aiming to better understand their individual roles.

Keywords: planktonic Foraminifera, stable isotopes, Atlantic meridional overturning circulation, upper circumpolar deep water, North Atlantic deep water

INTRODUCTION

The oceanic biological pump is a primary mechanism to exchange CO₂ between the atmosphere and the oceans, and is therefore critically important for the acidity of the sea water and associated carbonate dissolution (Riebesell, 2004). An intensified biological pump in the oceans leads to an increase of exported biogenic carbon and carbonate burial in the sediments (Brummer and van Eijden, 1992). Since planktonic Foraminifera are important contributors to the pelagic calcium carbonate flux (Milliman et al., 1999; Schiebel, 2002; Kučera, 2007) they represent an important component of the global climate system through their role in the oceanic carbon and carbonate pump. The connection between strong changes in the oceanic biological pump and calcite dissolution is difficult to study in modern oceans, as sample areas with sufficient differences in bioproductivity also differ in several other environmental factors, thus confounding the results. In contrast, Pleistocene climate scenarios offer the possibility to investigate a relatively stable ecosystem under intensely changing bioproductivity scenarios.

The Late Quaternary climate is characterized by orbit-related glacial–interglacial fluctuations (EPICA Community Members, 2004; Jouzel et al., 2007) associated with CO₂ variations (Petit et al., 1999; Shakun et al., 2012). Nevertheless, the orbital forcing alone is not strong enough to induce the observed temperature changes and, thus, feedback mechanisms in the Earth's climate system are expected to have amplified (or reduced) the primary signal (Lorius et al., 1990; Shackleton, 2000). The oceanic carbonate pump system is critically influenced by changes in bioproductivity. High biological surface productivity can boost population densities and biomass of benthic communities, increasing the respiration processes and leading to the remineralization of higher percentages of organic matter (OM), resulting in the release of CO₂ and a reduction of the biogenic carbon burial (Cronin et al., 1999; Hales, 2003). Besides, higher CO₂ release at the seafloor can lead to increased dissolution of biogenic carbonate, (e.g., planktonic Foraminifera tests; Schiebel, 2002). Therefore, an enhanced biological pump can have an unexpected effect, both decreasing the OM burial and dissolving biogenic carbonates, inhibiting higher quantities of C to be stored in the seafloor sediments (e.g., Zamelczyk et al., 2012; Naik et al., 2014).

Supra-lysocline pelagic carbonate dissolution has been described from the western South Atlantic in the past, being related to changes in bottom water masses (Petró et al., 2018a; Petró and Burone, 2018; Petró et al., 2021). Nevertheless, the relation between calcium carbonate dissolution and sea surface productivity has not yet been approached in the studied area. In this paper, we 1) reconstruct past changes in primary and export productivity during the last glacial–interglacial interval, 2) determine mechanisms that triggered calcium carbonate dissolution, and 3) investigate the role of productivity changes on carbonate corrosion from a core retrieved above the lysocline.

Oceanographic Setting

The studied sediment core was recovered off Santa Marta Cape in the western South Atlantic (Figure 1A,B). The proximal portion

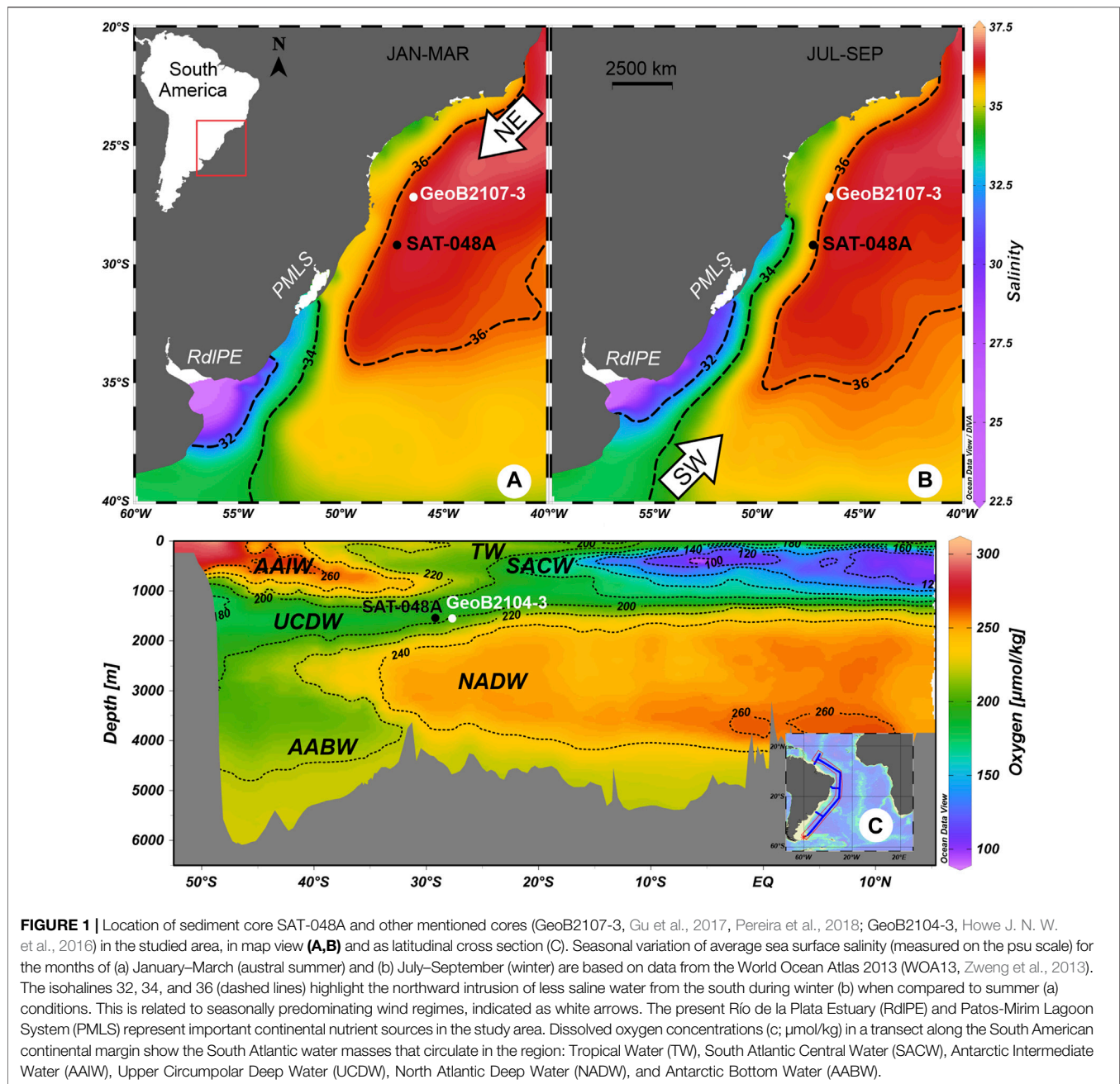
of the continental shelf of the Pelotas Basin represents a submerged coastal plain (Martins, 1984) that was exposed during the last Pleistocene regression (Marine Isotope Stage 2) and dissected by drainage networks from fluvial systems (Weschenfelder et al., 2014), which contributed to larger nutrient inputs from continental outflows compared to the Holocene.

Surface circulation in the shelf portion of the study area is dominated by the northward flowing Brazil Coastal Current, which carries the Coastal Water (CW), a mixture of oceanic and continental drainage waters. Offshore, the Brazil Current (BC) transports the warm (temperature, $T > 20^{\circ}\text{C}$) and salty (salinity, $S > 36$) Tropical Water (TW) southwards within the surface layer. The BC flows along the South American margin slope until it converges with the Malvinas Current (MC), a northward flowing surface current carrying the cold ($T < 15^{\circ}\text{C}$) and fresher ($S < 34.2$) Subantarctic Water, forming the Brazil/Malvinas Confluence (BMC) close to 38°S (Gordon and Greengrove, 1986). The BMC forms a large meander, which separates southward of the continental margin (Peterson and Stramma, 1991; Piola and Matano, 2017), and varies seasonally and interannually, moving to the north in austral autumn and winter, and to the south in spring and summer. This variation influences the nutrient distribution along the continental shelf of the Argentinian, Uruguayan, and south Brazilian coasts (Gonzalez-Silvera et al., 2006). Presently, two main continental sources of nutrients and freshwater for the area are the Río de la Plata Estuary (RdLPE) and the Patos-Mirim Lagoon System (PMLS). Although the configuration of continental drainage certainly changed under the varying sea-level conditions of the late Quaternary, they both represent sources of continental drainage and, thus, nutrients to the study area.

The water masses that circulate in the subsurface (Figure 1C) immediately below the TW are: the South Atlantic Central Water (SACW), the Antarctic Intermediate Water (AAIW), the Upper Circumpolar Deep Water (UCDW), the North Atlantic Deep Water (NADW), and the Antarctic Bottom Water (AABW) (Reid et al., 1976; Campos et al., 1995; Hogg et al., 1996; Stramma and England, 1999). The NADW promotes the preservation of carbonate, due to its oversaturation with carbonate ion (CO_3^{2-}) when compared to the overlying UCDW and the underlying AABW. Both, the UCDW and AABW, are undersaturated in CO_3^{2-} and, therefore, may lead to the dissolution of carbonate (Frenz et al., 2003). Indeed, Frenz and Henrich (2007) have shown that the depth of the interface between the NADW and the AABW defines the lysocline, below which carbonate dissolution occurs.

MATERIALS AND METHODS

The piston core SAT-048A was collected by *FUGRO Brasil-Serviços Submarinos e Levantamentos Ltda* for the *Agência Nacional do Petróleo (ANP, Brazilian National Agency of Petroleum, Natural Gas and Biofuels)* at $29^{\circ}11' \text{S}$ and $47^{\circ}15' \text{W}$ at 1,542 m water depth (Figure 1). The core, with a total recovery of 315 cm, was sampled at intervals of about 6 cm, for a total of 54



samples. The core was missing the top 20 cm and the 196–217 cm interval. Each sample was washed over a 63 μm sieve and oven dried at temperatures below 60°C. The taxonomical identification of the planktonic Foraminifera species, from subsamples of at least 300 specimens larger than 150 μm split with a microsplitter, followed Bé (1967), Bé et al. (1977), Bolli and Saunders (1989), Hemleben et al. (1989), Kemle-von Mücke and Hemleben (1999), Schiel and Hemleben (2017), and Morard et al. (2019).

We used a revised version of the Frozza et al. (2020) age model, based on the *rbacon* package (Blaauw and Christen, 2011; version 2.4.2) for the R software (R Core Team, 2019). The age model (**Supplementary Material**) used the ten AMS radiocarbon dates

presented by Frozza et al. (2020), carried out on monospecific samples of planktonic Foraminifera, and the Laschamp geomagnetic excursion (J. Savian, personal communication, June 5, 2020) as an additional control point.

Past sea surface temperatures (SST) at 100 m water depth ($\text{SST}_{100\text{m}}$) were estimated using the modern analogue technique (MAT; Hutson, 1980) in the software PAST (version 4.05; Hammer et al., 2001). The paleo- $\text{SST}_{100\text{m}}$ were calibrated with a dataset composed of: 1) relative abundances of planktonic Foraminifera of surface sediments from the South Atlantic Ocean extracted from the ForCenS database (Siccha and Kučera, 2017) as training data and 2) modern mean annual

temperature estimates for 100 m below sea level, obtained from the World Ocean Atlas 2013 (Locarnini et al., 2013) and extracted with the software Ocean Data View (Schlitzer, 2020). For the weighting parameter, we used the inverse dissimilarity based on the squared Chord dissimilarity index with a threshold of 0.28 and five analogues.

Sea surface paleo-productivity was assessed from the relative abundances of the species *Globigerinita glutinata* (Conan and Brummer, 2000; Souto et al., 2011) and the ratio between *Globigerina bulloides* and *Globigerinoides ruber* (*albus* and *ruber*) (*G.bull*:*G.rub*; Conan et al., 2002; Toledo et al., 2008). The OM flux to the seafloor, as a response to sea surface productivity, was estimated based on the benthic:planktonic Foraminifera ratio (B:P; Berger and Diester-Haass, 1988; Loubere, 1991; Gooday, 2002). While this parameter was applied on different size fractions in the past, with no clearly defined standard, it was shown that small size fraction differences do not impact analyses considerably (Schönfeld 2012; Weinkauf, 2018). As long as data for benthic and planktonic communities, as in our case, were extracted from the same sieve size fraction. The resulting B:P ratios will be comparable, indeed, being used in the literature (e.g., de Almeida et al., 2022). The ostracod valves abundances (number of valves in the >150 μm fraction per gram of sediment), and the $\delta^{13}\text{C}$ record of *Uvigerina* spp. ($\delta^{13}\text{C}_{Uvi}$; Mackensen, 2008) were also used to infer the OM flux to the seafloor. Part of these data (relative abundances of *G. bulloides* and *G. ruber*, $\delta^{13}\text{C}_{Uvi}$) were previously published by Frozza et al. (2020). For the $\delta^{13}\text{C}_{Uvi}$ measurements, approximately seven specimens of the benthic foraminiferal genus *Uvigerina* were selected from the 250 μm sediment fraction from each sample. The geochemical analyses were performed with a Thermo Scientific MAT-253 mass spectrometer, coupled to a Kiel IV carbonate device, by the Laboratory of Stable Isotopes of the University of California–Santa Cruz (SIL-UCSC). All results are expressed in δ -notation relative to the Vienna Pee-Dee Belemnite (VPDB) standard.

Dissolution effect proxies for this core were published by Suárez-Ibarra et al. (2021) and were based on the 1) the planktonic Foraminifera fragmentation intensity, which follows Berger (1970)'s fragments and broken shells counting, 2) the bulk sand fraction (%; Berger et al., 1982; Gonzales et al., 2017), 3) the number of whole planktonic Foraminifera tests per Gram of sediment (PF/g, Le and Shackleton, 1992), and 4) the relative CaCO_3 content of the sediment. Bulk sand contents were determined using a laser diffraction particle size analyzer Horiba Partica-LA-950 at the Climate Studies Center Centro de Estudo de Geologia Costeira e Oceânica (CECO) of the Universidade Federal do Rio Grande do Sul (UFRGS). The calcium carbonate content for the samples was determined by weight loss after reaction with 10% hydrochloric acid (HCl) at the Calcareous Microfossils Laboratory of the UFRGS.

All statistical analyses were conducted in the software PAST (version 4.05; Hammer et al., 2001). An overall relation between productivity and dissolution proxies was quantified using Spearman rank-order correlation. To objectively define phases of changing conditions through the analyzed time interval, a principal component analysis (PCA) on the correlation matrix

including all the correlatable paleo-productivity proxies (PCA_P) and all dissolution proxies (PCA_D), respectively, was carried out. Using the first principal component of PCA_P (PC1_P), we objectively defined the borders between the three phases using a piecewise ordinary least-squares regression (OLS; Weinkauf et al., 2013): 1) We subdivided the PC1_P vs age date into three subsets. The age-borders for each subset varied over a range of reasonable values (25.11–31.46 ka for the phase 1–Phase 2 border, 18.274–15.515 ka for the phase 2–Phase 3 border); 2) for each possible combination of phase borders, we calculated three independent OLS regression lines and their associated R^2 -value; 3) we calculated the overall fit of the solution as the product of the three individual R^2 -values; 4) the best phase border solution was the one that showed the highest overall R^2 -value. The relationship between summer insolation and paleo-productivity, represented by the score of PC1_P , was analyzed using a reduced major axis regression. To study the interaction between productivity (PC1_P), bottom water intensity (reconstructed by the $^{231}\text{Pa}/^{230}\text{Th}$ ratio; McManus et al., 2004; Böhm et al., 2015), and dissolution (PC1_D), a multiple linear regression was carried out.

RESULTS

Sediments from core SAT-048A represent hemipelagic muds rich in carbonate. The average grain size of the samples is slightly sandy mud, and in general, ranges from slightly clayey mud to muddy sand in some cases. The recovered sediments correspond to the latest Pleistocene and early/middle Holocene muds of the Imbé formation. The age model (**Supplementary Material**) indicates sample ages ranging from 43 to 5 ka.

Planktonic Foraminifera species indicate two contrasting temporal distribution patterns: 1) species with higher abundances during the Late Pleistocene that decreased in abundance towards the Holocene, *Globigerinita glutinata* (**Figure 2C**), *Globigerina bulloides*, *Globoconella inflata*, and *Neogloboquadrina incompta* (**Supplementary Material**); 2) species with lower abundance values during the Late Pleistocene and higher abundances in the Holocene, *Globigerinoides ruber albus* and *G. ruber ruber*, *Trilobatus sacculifer*, *Globorotalia menardii*, *Globigerinella calida*, *Orbulina universa*, *Globorotalia tumida*, and *Globigerinoides conglobatus* (**Supplementary Material**).

The performance of the MAT (shown in the **Supplementary Material**) was generally very good, with an R^2 of 0.993. The annual mean paleo-SST_{100m} estimates for core SAT-048A are shown in **Figure 2E** (residuals shown in **Supplementary Material**). The annual mean reconstructions show lower values from the bottom of the core until 37 ka (on average 16°C), although the lowest value occurred at 25 ka (15.2°C). For the 37–15 ka period, the observed temperature variation was larger and fluctuated faster than during the rest of the record, spanning from 15 to 19°C. A warming trend is indicated to have occurred before the Last Glacial Maximum (LGM) at 25 ka, with values between 19 and 23°C and the warmest SST_{100m} value (22.5°C) observed at 7 ka.

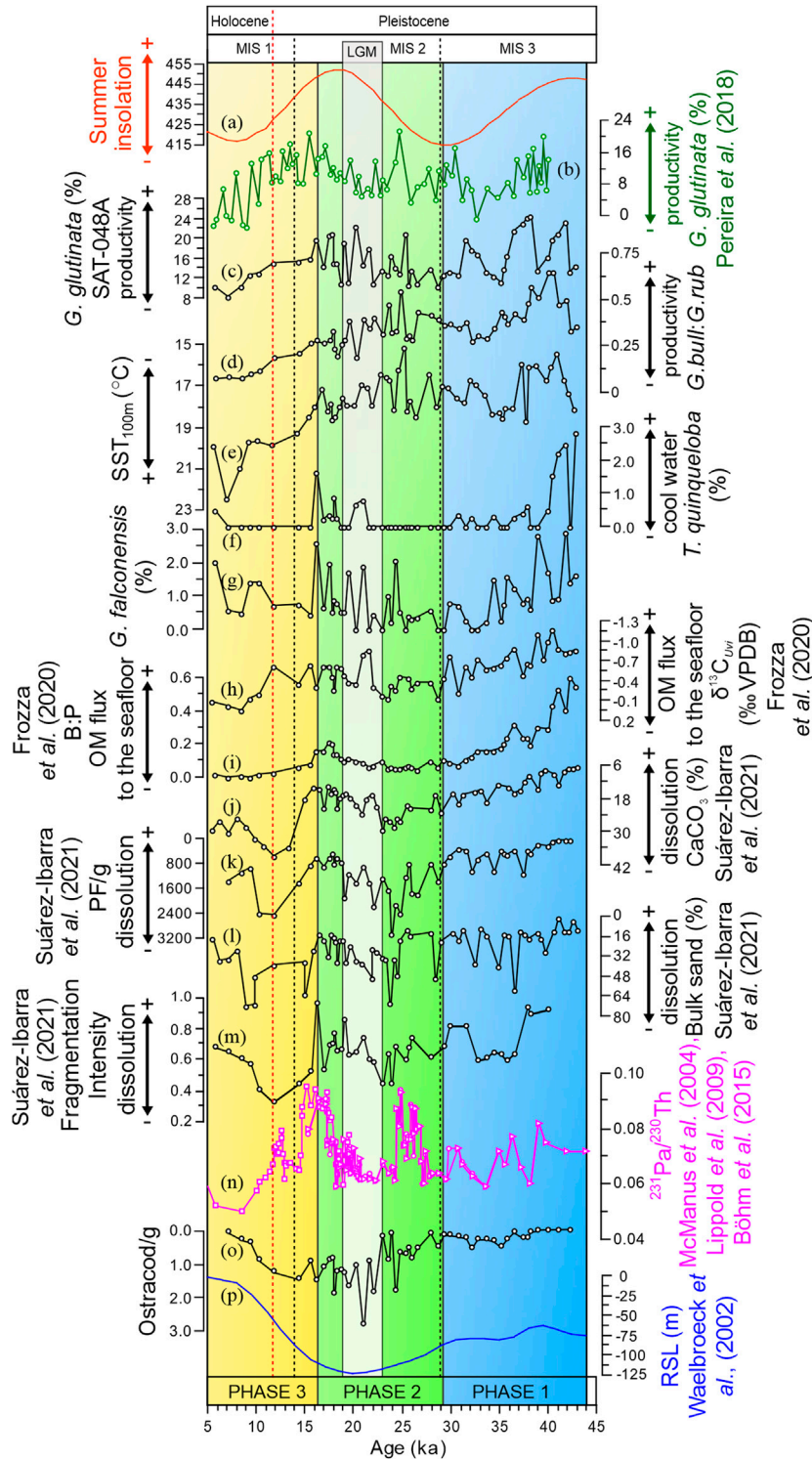


FIGURE 2 | Fluctuations in summer insolation, paleoenvironmental proxies for surface productivity, organic matter (OM) flux to the seafloor, CaCO_3 dissolution, Atlantic Meridional Overturning Circulation (AMOC) speed, and relative sea level. **(A)** Austral summer (February) insolation at 31°S (Laskar et al., 2004) **(B–C)** relative abundance of *G. glutinata* in cores GeoB2107-3 (b; Pereira et al., 2018) and SAT-048A (c; this study); **(D)** *G. bulloides*/*G. ruber* ratio (*G.bull:G.rub*); **(E)** $\text{SST}_{100\text{m}}$ ($^\circ\text{C}$) **(F–G)** relative abundance of *T. quinqueloba* (f) and *G. falconensis* (g); **(H)** $\delta^{13}\text{C}_{\text{org}}$ (‰); **(I)** Benthic/Planktonic Foraminifera ratio (B:P) **(J)** CaCO_3 content of the sediment **(K)** number of planktonic Foraminifera tests per gram of sediment (PF/g) **(L)** sand bulk content (%) **(M)** fragmentation intensity **(N)** $^{231}\text{Pa}/^{230}\text{Th}$ values from McManus et al. (2004; squares), Lippold et al. (2009; circles), and Böhm et al. (2015; triangles) **(O)** Ostracods per gram of sediment (valves/g) **(P)** relative sea level (RSL; Waelbroeck et al., 2002). Note the inverted y-axes in (f), (g), and (i–k) to aid visualization. Proxies printed in black belong to sediment core SAT-048A. The three phases indicated in the plot are based on a principal component analysis of all productivity values, as shown in **Figure 3**.

All reconstructed paleoenvironmental proxies are shown in **Figure 2**. Paleo-productivity shows highest values in the 43–32/34 ka interval (superimposed on a decreasing trend), when reconstructed from *G. glutinata* abundances (**Figure 2C**) and the *G. bull*:*G. rub* ratios (**Figure 2D**), respectively. A relative plateau is witnessed for both proxies from 32/34 to 25 ka. The following time interval (25–17 ka) is characterized by an increasing trend. From 17 to 5 ka, *G. glutinata* and the *G. bull*:*G. rub* ratio show a decreasing trend with some of the lowest values of the entire record. The abundance of ostracods valves (**Figure 2**) is low during the 43–27 ka interval, then increases until 10 ka, and decreases afterward.

We ran a Spearman rank-order correlation to test the relationship between different productivity and dissolution proxies (**Table 1**). When the correlation was significant at the $\alpha = 0.05$ -level, the correlation coefficients ρ were categorized as either weak ($|\rho| = 0-0.33$), medium ($|\rho| = 0.34-0.66$), or strong ($|\rho| = 0.67-1$). The paleo-productivity proxies *G. bull*/*G. rub* and *G. glutinata* (%) are not significantly correlated ($p = 0.556$), nevertheless, the correlations between productivity and OM flux proxies are all significant, ranging from medium to strong correlations. All the dissolution proxies are significantly correlated, also ranging from medium to strong. The correlation between productivity, OM flux and dissolution proxies are all significant, ranging from weak to strong relations, except for the FI vs *G. glutinata* (%) and the bulk sand (%) vs *G. glutinata* (%) proxies. The OM flux proxy Ostracod valves only showed a medium correlation with the *G. bull*/*G. rub* proxy and was also weakly–moderately correlated to three dissolution proxies.

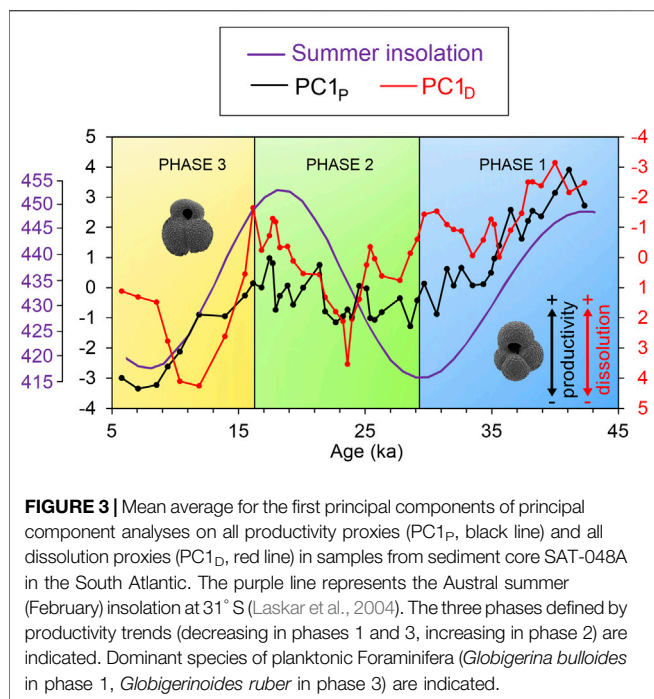
These results indicate that all these proxies are also influenced by other environmental parameters, not just productivity and

dissolution, respectively. Therefore, not any single proxy is suitable to provide an unbiased picture of the past environment. We, thus, aimed to develop synthetic productivity and dissolution proxies by combining all information in a PCA, which on its first axis amplifies the direction of largest variation in both parameters. PCAs were run both for productivity/OM flux (*G. bull*/*G. rub*, *G. glutinata* (%), $\delta^{13}\text{C}_{Uvi}$, and B:P; PCA_P) and dissolution proxies (CaCO₃, FI, PF/g, and bulk sand (%), PCA_D) on the data centered at zero and scaled to unit variance (**Supplementary Material**). The first principal component of the productivity/OM flux analysis (PC1_P) explains 62.14% of the variance in the data, while the first principal component for the dissolution proxies (PC1_D) captures 74.88% of data variance. The trends of PC1_P and PC1_D are shown in **Figure 3**, where the borders between three phases are based on the best solution of a set of piecewise OLS regressions with combinations of 70 feasible phase border scenarios. The loadings of the components on the principal component axes and the individual R^2 -values from the piecewise regressions on which the phase borders are based are shown in the **Supplementary Material**. The optimal phase borders were determined by the R^2 -product of 0.251 as follows: phase 1 (42.32–29.12 ka), where PC1_P values decreased, indicating a reduction in productivity; phase 2 (28.56–16.15 ka), with stable to slightly increasing paleo-productivities; and phase 3 (15.51–5.77 ka), where productivity decreased again during the Holocene.

A reduced major axis regression between summer insolation and PC1_P (**Supplementary Material**) yielded a significant ($p < 0.001$) correlation value of 0.476. A multiple linear regression between the independent variable PC1_P and bottom water velocity ($^{231}\text{Pa}/^{230}\text{Th}$) and PC1_D as dependent variable was carried out and results are shown in **Table 2**. Only PC1_P is

TABLE 1 | Correlation coefficient (ρ) and statistical significance (p) for productivity and dissolution indices in sediment core SAT-048A from the western South Atlantic. *G. glutinata* (%): Relative abundance of *Globigerinita glutinata*; $\delta^{13}\text{C}_{Uvi}$: VPDB $\delta^{13}\text{C}$ -values of shells of the benthic foraminifer genus *Uvigerina*; B:P: Ratio between benthic and planktonic Foraminifera; CaCO₃ (%): Relative CaCO₃ content of the sediment; FI: Planktonic foraminifera fragmentation intensity; PF/g: Number of Planktonic foraminiferal tests per gram of sediment; bulk sand (%): Relative sand content of the sediment; Ostracod valves: Number of Ostracod valves per Gram of sediment. Significant p -values (at $\alpha = 0.05$) are highlighted in bold; for these, the correlation coefficient was marked as weak (italics), medium (bold), or strong (bold-italics).

		G.bull/ G.rub	G. glutinata (%)	$\delta^{13}\text{C}_{Uvi}$	B:P	CaCO ₃ (%)	FI	PF/g	Sand bulk (%)
<i>G. glutinata</i> (%)	ρ	0.086	—	—	—	—	—	—	—
	p	0.556	—	—	—	—	—	—	—
$\delta^{13}\text{C}_{Uvi}$	ρ	-0.441	-0.508	—	—	—	—	—	—
	p	0.002	<0.001	—	—	—	—	—	—
B:P	ρ	0.458	0.511	-0.795	—	—	—	—	—
	p	0.001	<0.001	<0.001	—	—	—	—	—
CaCO ₃ (%)	ρ	-0.518	-0.430	0.777	-0.914	—	—	—	—
	p	<0.001	0.002	<0.001	<0.001	—	—	—	—
FI	ρ	0.329	0.287	-0.304	0.452	-0.567	—	—	—
	p	0.024	0.05	0.038	0.001	<0.001	—	—	—
PF/g	ρ	-0.371	-0.302	0.703	-0.811	0.831	-0.53	—	—
	p	0.009	0.035	<0.001	<0.001	<0.001	<0.001	—	—
Sand bulk (%)	ρ	-0.389	-0.204	0.473	-0.579	0.629	-0.606	0.576	—
	p	0.006	0.16	0.001	<0.001	<0.001	<0.001	<0.001	—
Ostracod valves	ρ	-0.354	0.129	0.187	-0.229	0.24	-0.334	0.479	0.304
	p	0.015	0.387	0.207	0.121	0.104	0.022	0.001	0.038



significantly influencing dissolution, and explains around 51% of the observed dissolution signal.

DISCUSSION

Radiocarbon Reversals

The occurrence of reversals in planktonic Foraminifera radiocarbon dates are not rare in the studies of the south Brazilian continental margin (SBCM, e.g., Sortor and Lund, 2011; Hoffman and Lund, 2012; Portilho-Ramos et al., 2019), being related either to: 1) morphological features of the sea bottom that remobilize sediments (such as turbidity or contour currents), or to 2) post-depositional chemical processes that affect the ¹⁴C concentrations. The age model of core SAT-048A here presented (Supplementary Figure S3) indicates three intervals where samples yielded mean older ages (Supplementary Table S3). Nevertheless, the only significant difference is shown in the sample at 183.5 cm depth (31.1 ka before calibration), between 217 and 149 cm (27.8–22.7 ka), an interval constituted by hemipelagic mud

rich in carbonate. According to Kowsmann et al. (2014), features of geological instability for the SBCM usually occurred between 28 and 15 ka, during relative low sea levels. Nevertheless, reversals of AMS ¹⁴C planktonic Foraminifera dates from core SAT-048A are not associated to abrupt changes on the grain size record (Supplementary Figure S4). Moreover, the action of contour currents in the proximities of the study area (Viana, 2001; Duarte and Viana, 2007; Hernández-Molina et al., 2016) could, have gradually remobilized older particles (such as planktonic Foraminifera shells), masking the ¹⁴C ages and increasing the temporal mixing.

Regarding the chemical processes, Rodrigues et al. (2020) reported older radiocarbon dates likely due to the upward migration of ¹⁴C-depleted methane fluids from gas chimneys, as already reported for the south portion of the SBCM (Portilho-Ramos et al., 2018; Ketzer et al., 2020), which can precipitate in shell interstitial pores (Wycech et al., 2016), producing an alteration in the radiocarbon dates. Given the above, we tried to diminish the impact of radiocarbon reversals by using 1) a high number of correlation points (10 radiocarbon dates and one geomagnetic correlation point) and, 2) the *rbacon* package for software R, which implements Bayesian statistics that calculate mean ages for age model constructions, and has the capacity to deal with ¹⁴C reversals.

Sea Surface Productivity

Three phases were defined from the PC1_P trends (Figure 3). Phases 3 and 1 fall into time intervals with decreasing summer insolation values, while phase 2 is characterized by increasing summer insolation. The correlation between PC1_P and summer insolation values is supported by the significant ($p < 0.001$) values of a reduced major axis regression ($r = 0.476$). This is supported by mechanisms, reported in the literature, that drove the paleo-productivity changes in the western South Atlantic. Portilho-Ramos et al. (2019) explained the high glacial productivity by a combination of short – but highly productive – austral summer upwelling periods and prolonged winter conditions favorable to the intrusion of RdIPE.

The short summer upwelling periods resulted from the enhanced northeasterly (NE) winds blowing along the shore during intervals with high summer insolation, both directly, by pushing surface waters offshore due to the Ekman transport (Chen et al., 2019), and indirectly by strengthening the BC meandering and, therefore, enhancing shelf break upwelling (Portilho-Ramos et al., 2015; Pereira et al., 2018). This interpretation is supported by the observed changes in the relative abundances of: 1) *Globigerinita glutinata* (Conan and Brummer, 2000; Souto et al., 2011), a species that feeds on

TABLE 2 | Results from a multiple linear regression between summarized paleo-productivity (PC1_P; first axis of a principal component analysis including all correlatable productivity proxies) and bottom water velocity ²³¹Pa/²³⁰Th and summarized dissolution (first axis of a principal component analysis including all dissolution proxies) as dependent variable for sediment core SAT-048A from the South Atlantic. p -values significant at $\alpha = 0.05$ are indicated in bold.

	Coefficient	Standard error	t	p	R^2	r
Constant	0.286	1.425	0.201	0.842	—	—
PC1 _P	-0.781	0.122	-6.402	<0.001	0.519	0.720
²³¹ Pa/ ²³⁰ Th	-4.141	20.458	-0.202	0.840	0.091	0.302

diatoms (Schiebel and Hemleben, 2017) and therefore benefits from the glacial silicic acid-rich SACW intrusions in the area (Portilho-Ramos et al., 2019) (**Figure 2B,C**); 2) *Turborotalita quinqueloba*, which is associated with stronger intrusions of cooler SACW into the photic zone (Souto, et al., 2011; Lessa et al., 2014, 2016) (**Figure 2F**); and 3) *Globigerina falconensis*, which is associated with eutrophic conditions (Sousa et al., 2014) (**Figure 2G**). Additionally, a reconstructed SST_{100m} cooler than 20°C (Campos et al., 2000; Silveira et al., 2000; Castelão et al., 2004) along with a *G. bull:G.rub* ratio higher than 0.25 (Lessa et al., 2014) for the Pleistocene portion of the record indicates a constant presence of the SACW in the subsurface during the short austral upwelling of the late glacial.

Prolonged winter conditions involved prevalent southwesterly (SW) winds year-round which carried outflows from the Río de La Plata (RdLPE) (Pimenta et al., 2005; Piola et al., 2005) and other continental sources (Camaquã, Jaguarão, and Jacuí rivers)—presently converging in the PMLS—closer to the study area (Piola et al., 2000; Nagai et al., 2014). Strengthened SW winds would also displace the BMC to a location closer to the area (Gonzalez-Silvera et al., 2006), which is supported by the higher relative abundances of *Globoconella inflata* and *Neogloboquadrina incompta* (**Supplementary Material**). The abundances of these two species can be interpreted as an indicator for a BMC closer to the study area (Boltovskoy et al., 1996), induced by the enhanced SW winds during the late last glacial.

Several authors suggest that during low relative sea levels (glacial times), periods of higher nutrient availability and increased terrigenous sediment input were favored due to the more offshore position of the BC and the exposure of the continental shelf (Mahiques et al., 2007; Gu et al., 2017; Pereira et al., 2018; Portilho-Ramos et al., 2019). Moreover, the Río de la Plata (Lantzsch et al., 2014) and Jacuí and Camaquã river paleo-drainages (Weschenfelder et al., 2014) were closer to the study area during this interval (higher influence of the PMLS). Higher Fe/Ca values (Heil, 2006), higher relative abundances of eutrophic dinoflagellate cysts species (Gu et al., 2017), and high terrestrial palynomorph proportions (Bottezini et al., 2022), are all evidence of the greater influence of continental outflow in the study area under lower relative sea levels during the late last glacial (which approximately corresponds to our phases 1 and 2). Medium paleo-productivity estimates during the LGM (relative sea level approximately 120 m lower; **Figure 3**) stand in contrast to the higher sea levels during phase 1 (relative sea level approximately 75 m below, Waelbroeck et al., 2002), where higher (terrestrial-related) fertilization was expected due the lower eustatic sea level. This suggests a different influence for the continental terrigenous fertilization for mid-depth cores retrieved from the continental slope. In contrast, for the Holocene, the higher relative sea level and onshore displacement of the BC, as well as the absence of the SACW, inhibited the photic zone fertilization, leading to oligotrophic conditions (Mahiques et al., 2007), witnessed in the phase 3.

Organic Matter Flux to the Seafloor and Carbonate Dissolution

Orbital to suborbital climate cycles can influence the abundance of deep-sea benthic communities (Cronin et al., 1999). Since abundance fluctuations of benthic Foraminifera and ostracods are related to variations in particulate organic carbon fluxes to the seafloor (Smith et al., 1997; Rex et al., 2006; Rex and Etter, 2010), their use as surface paleo-productivity indicators is widespread (Nees et al., 1999; Herguera, 2000; Rasmussen et al., 2002; Gooday, 2003; Yasuhara et al., 2012). The surface productivity fluctuations, indicated by the *G. glutinata* abundance and *G. bull:G.rub*, are significantly correlated to those of the OM flux recorded by the B:P ratio and the $\delta^{13}C_{Uvi}$ (**Table 1**). This effective OM export from the surface to the seafloor revealed a high benthic–pelagic coupling (Toledo et al., 2007). The B:P changes are accompanied by a similar trend in inverse $\delta^{13}C_{Uvi}$ (**Figure 2H,I**), which are expected to decrease when higher OM fluxes, rich in ^{12}C due to the preferential incorporation of the light isotope during photosynthesis (Wefer et al., 1999), reach the seabed (Ravello and Hillaire-Marcel, 2007). Nevertheless, the abundance of ostracod valves (**Figure 2**) was only significantly correlated with *G. bull:G. rub* ratio values. Intriguingly, ostracod valves showed a hump-shaped relation with productivity (Yasuhara et al., 2012), where values increased under moderate OM supply and declined under very low and very high productive conditions. This is because under high-productivity scenarios, oxygen levels at the sea floor tend to decrease and deep-sea ostracods, which are mostly epifaunal (Jöst et al., 2017), would not respond well to such an environment. On the other hand, ostracods valves had a significant ($p > 0.001$) strong correlation ($\rho = -0.701$) with paleo-bathymetric variations, where abundances decreased exponentially with water depth increase (Rex et al., 2006; Rex and Etter, 2010).

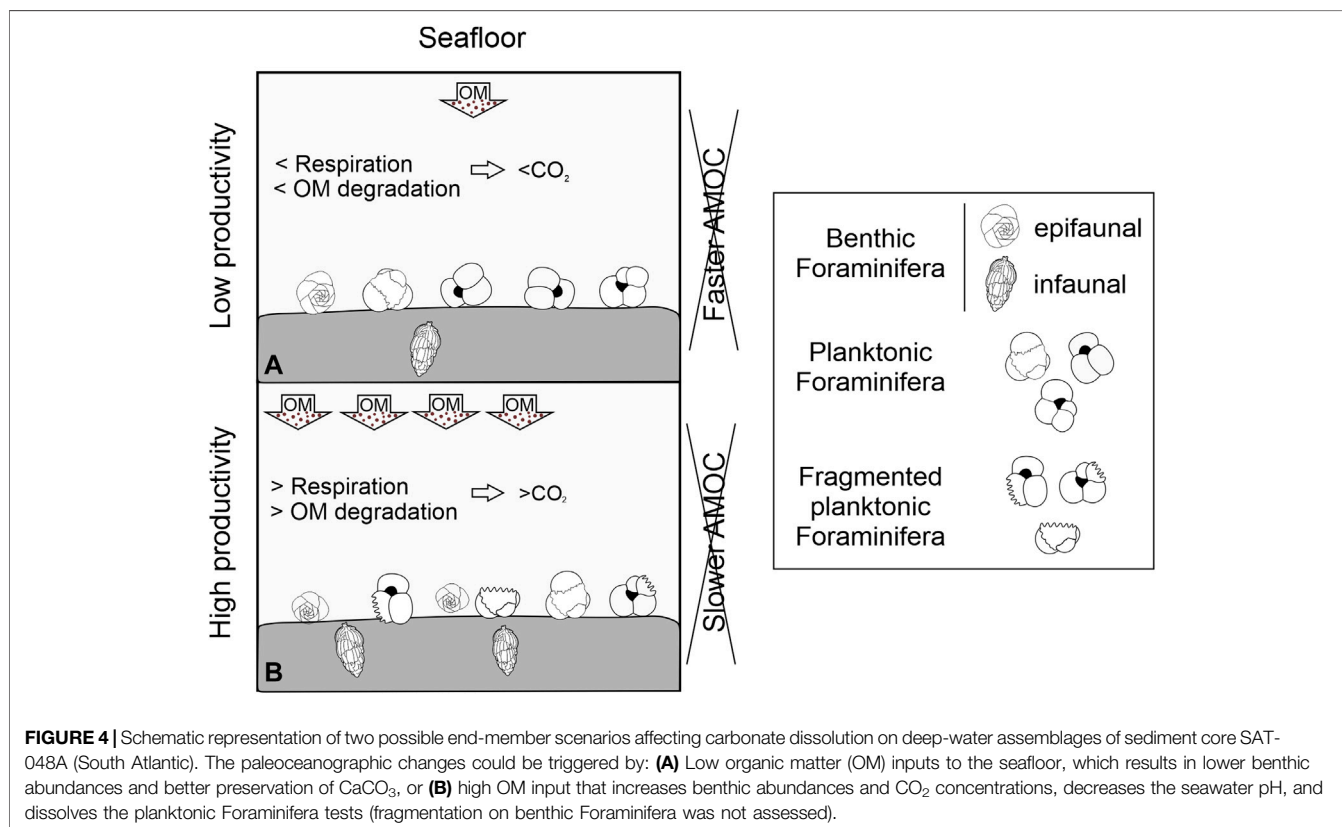
Dissolution indicators suggest higher calcium carbonate dissolution during the beginning of Phases 1 and the transition of phases 2 and 3 (**Figure 2, 3**), related to the OM flux. Enhanced dissolution could theoretically be triggered by two different processes: 1) increase in CO₂ concentrations (decreasing the water pH) due to the remineralization of OM at the seafloor (Jahnke et al., 1997; Schiebel, 2002) or 2) changes in the bottom water mass configuration related to AMOC dynamics (speed or geometry). Although the B:P ratios are also used as a dissolution indicator (Berger and Diester-Haass, 1988; Conan et al., 2002), Kučera (2007) states that this is only applicable for abyssal depths. We also have evidence from regional studies (Petró et al., 2018b) that benthic foraminifera are more prone to dissolution in this setting than planktonic foraminifers. This means that our observed B:P ratios are, in the worst case, an underestimate of the real situation because dissolution would attenuate it.

In the SBCM basins, the $\delta^{13}C_{Uvi}$ values have been used to infer oscillations of OM input (Toledo et al., 2007; Dias et al., 2018; Rodrigues et al., 2018; Frozza et al., 2020). Nevertheless, $\delta^{13}C_{Uvi}$ values are influenced by several factors, such as

accumulation rates of organic carbon, regional changes of water masses, the global carbon cycle, photosynthesis respiration processes, temperature, and pH (Ravelo and Hillaire-Marcel, 2007; Hesse et al., 2014). Calcite dissolution has, in contrast, no influence on the foraminiferal $\delta^{13}\text{C}$ (Petró et al., 2018b). Lund et al. (2015) suggested that lower values of benthic $\delta^{13}\text{C}$ during glacial times are associated with a weak AMOC. Nevertheless, the fluctuations of $\delta^{13}\text{C}_{Uvi}$ and the carbonate preservation could be the result of the interplay between the OM flux and water masses changes.

Based on ϵNd in planktonic Foraminifera at mid-depths in the western South Atlantic, Howe et al. (2016, 2018) showed variations of water masses at intermediate depths of 1,000–1,200 m (cores GeoB2107-3 and KNR159-3-36GGC) during the Holocene, and at 2,200 m (core GL-1090) since Heinrich Stadial 1. After the Heinrich Stadial 1, core GL-1090s ϵNd values decreased, becoming less radiogenic and more related to modern upper NADW values, while cores GeoB2107-3's and KNR159-3-36GGC's ϵNd values increased after about 10 ka, becoming more radiogenic and showing more affinity with modern AAIW. Sediment core GeoB2104-3 (1,500 m) is located between these aforementioned cores, at the same depth as sediment core SAT-048A on which the present study is based, at its ϵNd values remained stable during the 25–4 ka interval (Howe J. N. W. et al., 2016). This indicates that SAT048A's $\delta^{13}\text{C}_{Uvi}$ fluctuations were produced by the OM bottom flux rather than water masses reconfigurations—at least throughout the studied time interval.

In addition, the $^{231}\text{Pa}/^{230}\text{Th}$ ratio (Figure 2N) has been used to track the intensity of the AMOC (McManus et al., 2004; Lippold et al., 2009; Böhm et al., 2015), where lower values indicate a strengthened AMOC. During periods of high $^{231}\text{Pa}/^{230}\text{Th}$ values and indicating AMOC slowdown (like Heinrich Stadials), a higher concentration of respired CO_2 is accumulated in seafloor water masses. As proposed by Howe JN. et al. (2016), this is a possible explanation for the intervals of increased calcium carbonate dissolution. Nevertheless, the results from the multiple linear regression (Table 2) point to paleo-productivity as the main factor to influence dissolution. The multiple linear regression designates the sea surface productivity and OM flux to the seafloor as the principal agents of the calcium carbonate dissolution (Figure 4), at least for the 25–4 ka interval, which is related to changes in the summer insolation. This is true, even including the decoupling between productivity and dissolution visible in our data during the last ca. 5 kyrs (Figure 3). We hypothesize that the increasing dissolution at constantly low productivity, high AMOC rates (Figure 2N) and stable water mass configuration during this last segment of the record is related to the rising temperatures in this period, which increased the Mg/Ca values of the biogenic carbonate. Since higher Mg content facilitates dissolution of calcite, shells produced during this time would be more prone to dissolution, so that other environmental parameters were no longer the major factors that affected calcite dissolution. Future studies should investigate possible changes in bottom water mass configuration through ϵNd isotopes for the entire



studied section to 1) increase our understanding of productivity-related carbon dissolution at the sea floor and 2) quantify the impact of changes of the biological pump on the total organic carbon and biogenic carbonates burial. This will considerably aid the understanding of the glacial inorganic carbon sequestration.

CONCLUSION

Planktonic Foraminifera assemblages from sediment core SAT-048A, along with geochemical analyses and sedimentological data, enabled us to reconstruct the surface and bottom water conditions that occurred during the last 43 kyrs in the western South Atlantic, and to contextualize the related production-dissolution processes in the area. The Pleistocene–Holocene transition was characterized by a shift from a glacial eutrophic environment to more oligotrophic post-glacial conditions, as suggested by the *G. bulli*:*G. rub* ratio and the SST_{100m}, where intrusions of the nutrient-rich SACW were inhibited and the RdlPE and local river discharges (nowadays PMLS) were placed further away from the core site. The orbital-scale fluctuations of the upwelling dynamics (indicated by the relative abundances of *G. glutinata* and *T. quinqueloba*), modulated by insolation and NE wind changes, directly influenced the surface productivity and the OM fluxes to the seafloor (as shown by the B:P ratio and $\delta^{13}C_{Uvi}$). Imposed on the mechanisms behind the glacial–interglacial changes, stronger NE winds, generated by higher summer insolation, fertilized the photic zone, strengthened the BC, increased meandering, and enhanced intrusion of cooler and nutrient-richer waters into the subsurface layers. The enhanced upwelling conditions were also registered at the sea floor, where the bacterial decomposition of OM and the respiration of higher abundances of benthic communities increased the CO₂ concentration, which created more acidic conditions that caused different levels of carbonate dissolution, evidenced in the fragmentation of the planktonic Foraminifera tests. While changes in the bottom water masses could hypothetically cause the calcium carbonate dissolution, ϵNd analyses in a nearby sediment core at the same depth suggest no changes in the bottom water mass influence for the 25–4 ka interval, pointing to sea surface productivity and the intensity of the AMOC as possible causes of the carbonate dissolution. A multiple linear regression between summarized productivity and $^{231}Pa/^{230}Th$ (proxy for AMOC intensity), indicates that productivity is the main controlling factor of calcium carbonate dissolution. The continental influence (i.e., terrigenous input) must be better assessed in future studies, since, in contrast to expectations, no increased productivity was registered during the lowest relative sea level (LGM), when terrestrial input should have been highest. The dissolution of planktonic Foraminifera tests, induced by an enhanced biological pump (evidenced in the high glacial surface productivity and the high OM fluxes to the sea floor), must call the attention to future research, since a strong biological pump

influences biogenic carbonate burial and CO₂ sequestration and burial at the seafloor.

DATA AVAILABILITY STATEMENT

The original contributions presented in the study are included in the article/**Supplementary Material**, further inquiries can be directed to the corresponding author.

AUTHOR CONTRIBUTIONS

JYSI and MAGP conceptualized the study; JYSI curated the data; JYSI conducted the formal analyses; MAGP and MFGW acquired funding; JYSI, CFF and PLP investigated the samples; JYSI, CFF, MFGW, MAGP developed the methods; MAGP provided the resources; MFGW and MAGP supervised the project; MFGW and MAGP validated the results; JYSI visualized the results; JYSI wrote the original draft; JYSI, CFF, PLP, SMP, MFGW, and MAGP reviewed and edited the manuscript.

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SUPPLEMENTARY MATERIAL

The Supplementary Material for this article can be found online at: <https://www.frontiersin.org/articles/10.3389/feart.2022.830984/full#supplementary-material>

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